UDC 662.6 DOI https://doi.org/10.32782/2663-5941/2023.3.2/08

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EFFECT OF CATALYTIC FUEL ADDITIVE ON THE EFFICIENCY OF A GAS STEAM BOILER

Reducing the negative impact of thermal power industry on the environment and climate can be achieved by increasing the efficiency of fuel use in the production of heat and electricity. This not only saves fuel, but also reduces emissions of pollutants and carbon dioxide as the main greenhouse gas. One of the ways to increase the boiler efficiency is the use of fuel additives that contribute to the intensification of the fuel combustion process. The REDUXCO catalytic fuel is used to increase the efficiency of the natural gas steam boiler, which accelerates the process of chain combustion of carbon monoxide and other gases. Industrial tests of a steam gas boiler with a steam productivity of 420 t/h were conducted at the Kaunas CHPP (Lithuania) to verify the feasibility of using the REDUXCO fuel additive to increase the efficiency of the boiler. The gross efficiency of the boiler was determined by a direct balance by measuring the amount of energy produced, transferred to steam, and the energy of burned natural gas. The introduction of a catalytic fuel additive into the primary air led to an increase in the gross efficiency of the gas boiler from 93.4% to 94.88%. An increase in boiler efficiency by 1.48% corresponds to a relative decrease in carbon dioxide emissions by 1.56%. A decrease in the temperature of flue gas at the outlet from 143 °C to 137 °C during 7 days of industrial experiments testified to the intensification of fuel combustion in the burner zone and the cleaning of the heating surfaces from soot particles in the furnace and convective pass. Intensification of burning natural gas in furnace chamber when using a fuel additive did not lead to an increase in the emission of nitrogen oxides. This is a consequence of reducing excess air in the furnace The emission of carbon monoxide when supplying a catalytic additive to the fuel remained at a low level of about 10 ppm.

Key words: fuel additive, steam boiler, natural gas, efficiency, emission reduction.

Introduction. The issues of combating climate change are global in all areas of human activity. The Paris Agreement and the materials of the last Conference of the Parties to the UN Framework Convention on Climate Change testified to the desire of most countries in the world to reduce emissions of anthropogenic greenhouse gases [1, 2]. The thermal power industry, which uses hundreds of millions of tons of coal and billions of cubic meters of natural gas to generate electricity and heat, is traditionally one of the largest emitters of carbon dioxide, the emissions of which are predominant among the emissions of other greenhouse gases defined by the Kyoto Protocol to the UN Framework Convention on Climate Change [1, 3, 4]. Reduction of carbon dioxide emissions in thermal energy can be achieved by increasing the efficiency of using traditional carbon fuels [5] or burning carbon-free fuels in boilers, for example, hydrogen, ammonia or their mixture [6, 7].

Combustion of any organic fuel containing carbon leads to emissions of carbon dioxide, which is formed by an exothermic reaction:

$$C + O_2 \leftrightarrow CO_2 - 394 \text{ kJ/mol}$$
 (1)

Natural gas is a low-carbon fuel. The carbon dioxide emission coefficient kCO_2 for natural gas is 56.1 kg/GJ of fuel energy [4]. For coal, the carbon dioxide emission factor exceeds 100 kg/GJ.

If you divide the coefficient of carbon dioxide emission kCO_2 by the gross efficiency of the boiler η_{br} , you can get the value of the specific emission of carbon dioxide per unit of energy produced (kg/GJ or kg/Gcal). It will decrease as the efficiency of the boiler increases. With a gross efficiency value of 93%, the specific emission of carbon dioxide will be 60.32 kg/GJ, and with $\eta_{br} = 95\%$ is 59.05 kg/GJ.

The relative decrease in carbon dioxide emissions after the implementation of the measure, which increases the efficiency of the boiler, is described by the dependence [5]

$$\Delta C = 1 - \eta_1 / \eta_2 \tag{2}$$

where η_1 is the effectiveness before the implementation of the measure, %

 η_2 is efficiency after implementation of the measure, %.

A similar formula describes the relative decrease in fuel consumption after the implementation of the measure, which increases the efficiency of the boiler [5]:

$$\Delta e = 1 - \eta_1 / \eta_2 \tag{3}$$

The gross efficiency of the boiler η_{br} according to the direct method is determined as the ratio of the amount of heat received in the boiler by the working medium (water, steam), Q_1 , kJ/s, to the amount of heat introduced into the boiler, Q_{in} , kJ/s

$$\eta_{br} = 100 \times Q_1 / Q_{in}, \%$$
 (4)

The amount of heat received by the working body (water and steam) in a steam boiler without intermediate overheating can be determined by the formula

$$Q_1 = D_{se} \cdot (i_{se} - i_w) + D_{pr} \cdot (i' - i_w)$$
(5)

where D_{se} is the consumption of hot steam in the boiler, kg/s;

i_{se} is enthalpy of hot steam, kJ/kg;

 i_w is enthalpy of feed water, kJ/kg;

 D_{pr} is water consumption for purging, kg/s;

i' – enthalpy of purge (boiling) water, kJ/kg;

The specific amount of heat introduced into the boiler during the combustion of fuel with a flow rate of *B*, m³/s (for gas fuel), Q_{in}/B , kJ/m³, consists of the lower heat of combustion for the working state of the fuel Q_i^r , kJ/m³, the specific physical heat of the fuel Q_{fl} , kJ/m³, and specific physical heat of the input air Q_{air} , kJ/m³:

 $Q_{in}/B = Q_i^r + Q_{fl} + Q_{air} = Q_i^r + c_{fl} \times T_{fl} + \varepsilon_{ex} \times V^0 \times c_{air} \times T_{ca}$ (6) where c_{fl} is the heat capacity of gas fuel, kJ/(m³×K); T_{fl} is fuel temperature, K;

 ε_{ex} is air equivalent ratio;

 V^0 is stoichiometric air consumption for gas combustion, m³/m³;

 c_{air} is heat capacity of air, kJ/(m³×K);

 T_{ca} is the temperature of cold air, K.

As a rule, $Q_i^r >> (Q_{fl} + Q_{air})$, so they are often limited to the first term in formula (6).

Over many years of operation of the boilers, a few measures to increase the use of fuel were developed and implemented: special burners, optimization of air supply conditions to the boiler fuel, cleaning of heating surfaces, elimination of parasitic air suctions, etc.

One of the ways to increase boiler efficiency is the use of special fuel additives. These additives can improve the efficiency and intensity of fuel combustion. This attracted the attention of many researchers to develop additives [8-11]. Most often, fuel additives were developed for solid fuel boilers, as it contributes to the reduction of significant heat losses due to the presence of unburned carbon in the waste.

When entering the combustion zone, fuel additives are heated to high temperatures, as a result of which molecular bonds in them are broken with the formation of chemically active atoms and radicals, which contribute to the intensification of the fuel combustion process [8]. This process is accompanied by numerous explosions and the release of additional energy, which can be visually determined by the increase in the brightness of the fireball (the Lenard effect). The water contained in the additive is intensively decomposed into atomic (radical) hydrogen (H), oxygen (O) and hydroxyl (OH), increasing the reactivity of the fuel and intensifying the process of its combustion.

When using organic fuel additives, the flame temperature increases in the initial part of the combustion chamber and decreases at the exit from it. This indicates that the air mixture takes less time and, accordingly, burns faster. Organic fuel additives were sprayed onto dried coal powder, evenly distributed on a flat surface in a layer 3–5 mm thick. Organic fuel additives Omstar-DX1 and Open Flame are mixtures of light ethers. The use of Omstar-DX1 and Open Flame additives with a concentration of up to 5 cm³/kg of coal leads to a somewhat more efficient burning of Ekibastuz low-grade coal and contributes to the reduction of emissions of carbon oxides CO and nitrogen oxide NO, an increase in the concentration of fuel [9].

In the article [10], samples of fuel additives – modifiers made using salts: CuSO₄·2H₂O, NaCl, NH₄Cl, $MgSO_4$ ·7H₂O, CaCl₂ and urea were investigated. The modifier for burning fine coal is an aqueous solution containing 25% of active substances. For greater dosing accuracy, modifiers were used in the form of aqueous solutions, which are easier to apply by spraying on the fuel before feeding it to the boiler. The concentration of the active components of the modifier was selected so that the consumption of the aqueous solution was within 2-3 Liters per Mg of coal. The tests were carried out in a laboratory boiler with a thermal capacity of 12 kW, equipped with a grate retort furnace. Higher boiler efficiency and reduced emissions of pollutants were observed. In the pulverized coal combustion tests using the above modifier, the flue gas levels of carbon monoxide CO, nitrogen oxides NOx, and carbon dioxide SO₂ were reduced by approximately 9%, 12%, and 10%, respectively, compared to the combustion test without the modifier. In this case, the efficiency of the boiler increased from 65% in the test without the modifier to 76% in the test with the modifier.

In the article [11], the additive used was a 20% aqueous solution of four different

compounds. It contained manganese II acetate tetrahydrate, isopropanol, glacial acetic acid, and N,N-dimethylethanolamine. The first component was used to increase the oxidizing capacity of the fuel, so it should act as a catalyst and reduce heat loss of unburned fuel. Isopropanol was used to prevent ice caps from forming in dosing lines, while N,N-dimethylethanolamine was found to prevent corrosion. In turn, for experimental purposes, glacial acetic acid was added as a component that should remove deposits from the surfaces of the boilers. Studies using the STA (simultaneous thermal analysis) technique, which allows simultaneous measurements of TG (thermogravimetric) mass changes and DSC (differential scanning calorimetry) thermal effects, showed that combustion with and without the additive was the same, but there were a few notable differences. First of all, the additive affects the ignition temperature of fuel T_i , which becomes lower by about 10 K. In studies on an industrial water heating boiler WR-10, the use of the additive at a rate of 0.1 l/kg of coal led to a reduction in flue gas heat loss and heat loss due to the presence of unburnt carbon by about 2%. Boiler efficiency increased from 86.05% to 88.15%. The increase in efficiency not only contributes to fuel economy, it also reduces CO₂ emissions per unit of energy by 5%.

To determine the effect of the REDUXCO fuel additive on the efficiency of a steam boiler on natural gas, industrial comparative experiments were conducted in the amount necessary to determine the gross efficiency of the boiler according to the direct balance, heat loads, heat losses during the combustion of natural gas, the formation of emissions of pollutants and their comparison during operation without and with the addition of REDUXCO, respectively.

Methods and materials. The REDUXCO fuel additive is an aqueous solution of the reaction product of acetic acid and acetylferrocene and butan-1-ol and 2-methylpropan-1-ol and propan-1-ol and propan-2-ol. It is registered in the European Chemicals Agency REACH ECHA [12]. chemical formula: $C_5H_5FeC_5H_4COC_xH_n$. This additive is a source of formation of free radicals in a gaseous environment when it evaporates in a high-temperature environment. The use of REDUXCO catalytic additive contributes to lower activation energy of chemical reactions [13]. As a result, chain radical reactions of gasphase oxidation of CO and hydrocarbons occur at a higher rate. In Figure 1 shows a scheme of chain high-temperature oxidation (combustion) of carbon monoxide [14]. The positive effect of this combustion additive due to chain radical reactions in a gas medium on increasing the efficiency of the water boiler is described in [15].

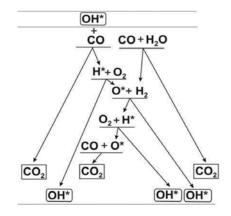


Fig. 1. The chain mechanism of carbon oxide combustion

The experimental research of the use of REDUXCO fuel additive were carried out at Kaunas Combined Heat and Power Plant (CHPP), Lithuania, on steam boiler No. 3 types of E-420-13.8-560 GMN (BKZ-420-140 GMN-4). The boiler is designed for operation on natural gas or fuel oil with steam turbines at high steam parameters. Experiments were carried out with constant consumption of natural gas per boiler.

The E-420-13,8-560 HMN boiler (Figure 2) is a vertical water-tube, single-drum with natural circulation, single-body, U-shaped layout in a gastight version of a closed layout and designed for high steam parameters, intended for operation under pressure. Table 1 shows the main design characteristics of the E-420-13.8-560 GMN.

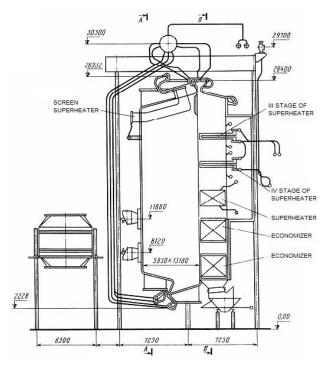


Fig. 2. Longitudinal section of boiler E-420-13.8-560 GMN (BKZ-420-140 NGM-4)

The prismatic furnace chamber of the open type, with dimensions in plan along the pipe axes of $5.93 \times 13.18 \text{ m}^2$, has a volume of 1427 m³. The fuel chamber and the convective shaft are shielded with membrane panels made of smooth pipes Ø 60×6 mm (steel 20 and 15KGM) with welded strips (steel 20) and pipe pitch 80 mm.

Main Specifications of E-420-15	-300 GIVILY DUILEI			
Rated steam capacity, t/h	420			
Type of fuel	natural gas, fuel oil			
Steam pressure at the outlet of the superheater, MPa (kgf/cm ²)	13.8 (140)			
Temperature, °C:				
superheated steam	560			
feed water	230			
flue gas	109/147*			
Efficiency (gross), at rated load, %:				
calculated	94.8/93.4*			
warranty	94/93*			
Fuel consumption, t/h:				
natural (for NG – m ³ /h), t/h	30.2×10 ³ /28.5*			
coal equivalent (LHV = 29.3 MJ/kg)	38.2			
Aerodynamic resistance of the tract on the side, mm of the w.c.:				
flue gas	318.6			
air	76.4			
Heat output, Gcal/h	250			
Temperature in the air heater, °C:				
air:				
inlet	30/70*			
outlet	235/272*			
flue gas:				
inlet	293/336*			
outlet	109/147*			
Thermal stress of the furnace cross-section, kcal/(m ² ×h)	1.66×10 ⁶			
Thermal stress of the furnace volume, $kcal/(m^{3} \times h)$	183×10 ³			
Furnace volume, m ³	1427			
Cell dimensions along the column axes, m:	24×36			
Height to the top of the spinal beam, m	32.4			
* In the numerator, data for natural g denominator – for fuel oil	gas combustion, in the			

	Table 1
Main Specifications of E-420-13.8-560 GMN	Boiler

The down part of the furnace is created by front and rear screens, has an inclination of 15° to the horizontal. The front screen from above forms an inclined ceiling of the firebox; the rear screen turns into a three-row festoon.

The blocks of the furnace chamber and the convective gas duct are suspended on rods to the ceiling of the boiler frame and freely expand downwards. The furnace is equipped with eight combined gas and oil burners located in two tiers (four in each tier).

The drum of the boiler is of welded construction, has an internal diameter of 1600 mm with a wall thickness of 112 mm (steel 16GNMA).

The steam path of the superheater consists of two independent streams. The temperature of superheated steam is regulated by injecting its own condensate and recirculating flue gas to the air path of the burners.

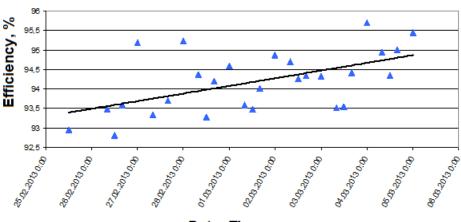
The boiler is equipped with the necessary fittings, devices for sampling, as well as control and measuring devices. The processes of feeding the boiler, regulating the temperature of superheated steam and burning fuel are automated.

For air heating, the boiler is equipped with two rotating regenerative air heaters with a rotor diameter of 5.4 m.

The boiler is equipped with an operational control system, the data of which is output to a computer and can be processed both graphically and tabularly. Subsequently, these data were used to calculate the efficiency of the boiler unit (determination of gross efficiency) according to the direct balance. A TESTO-350 portable gas analyser was used to assess the environmental characteristics of flue gas $(O_2, CO_2, CO, NOx \text{ content})$.

Research results and their discussion. The boiler tests began on February 25, 2013 at 12:00. On the first day of testing, the REDUXCO fuel additive was not used. This day of operation without the supplement was taken for comparison. Supply of the REDUXCO additive to the boiler with a specific consumption of 40 ml of solution per 1000 m³ of natural gas [13] began on February 26, 2013 at 12:00. It was accompanied by a decrease in air consumption for gas combustion throughout the period of REDUXCO additive injection (excess air in furnace $\alpha \leq 1.02$). In Fig. 3 shows the values of the gross efficiency of the boiler according to the direct balance of the boiler during the experiments. Each test day was divided into 4 periods: 1st period – 00:00-08:00, 2nd period - 08:00-12:00, 3rd period - 12:00-16:00, 4-and period - 16:00-23:59. It can be seen from the figure that the operation of the boiler unit was characterized by significant instability at different times of the day. The highest efficiency value was reached at night from 0:00 to 8:00, the lowest value was from 12:00 to 16:00. During the study, after the addition of the fuel additive, there was a monotonous increase in the efficiency of the boiler unit by an average of 0.3% per day, and by the end of the tests, it increased by 1.48% – from 93.4% to 94.88%.

In Fig. 4 shows the calculation data of the average daily efficiency of the boiler unit. Each test day was divided into 4 periods: 1st period -00:00-08:00, 2nd period -08:00-12:00, 3rd period -12:00-16:00, 4- and



Date, Time

Fig. 3. Change in the efficiency of the 420 t/h steam boiler No. 3 of the Kaunas CHPP during the research period

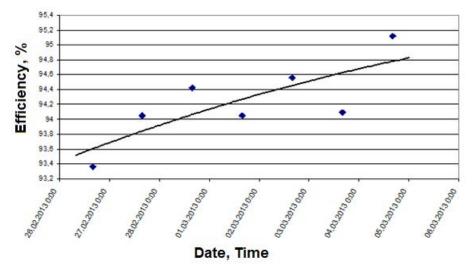


Fig. 4. Change in the average daily value of the efficiency gross of a boiler with 420 t/h steam capacity

period – 16:00-23:59. From Fig. 3 and Fig. 4, it can be seen that the operation of the boiler was characterized by significant instability at different times of the day. The highest efficiency value was reached at night from 0:00 to 8:00, the lowest – from 12:00 to 16:00. During the tests, after the addition of the fuel additive, a monotonous increase in the average daily value of the boiler efficiency was noted by approximately 0.3%, and by the end of the experiments, it increased by 1.48% – from 93.4% to 94.88% (Fig. 4).

The measurements of the exit flue gas temperature at the boiler outlet showed a gradual decrease in the exhaust gas temperature from 143°C to 137°C (Fig. 5). The reason for the decrease in the existing temperature of the flue gas is the intensification of the combustion process in the furnace and the improvement of heat transfer from the flue gases to the heating surfaces due to the cleaning of their surfaces. One day after the addition of the additive, the flue gas temperature decreased to 139.8°C (Table 2), which is evidence of the concentration of natural gas combustion in the fuel itself. A further decrease in flue gas temperature is caused by the completion of a long process of high-temperature oxidation of low-reactivity soot deposits by a radical mechanism in a convective pass [16, 17].

Table 2 shows the average values of measurements of environmental parameters of flue gases during the research. Measurements of the NOx content in the flue gas showed values from 205 to 198 mg/Nm³. The supply of REDUXCO fuel additive practically did not affect the values of nitrogen oxides emissions.

But the reduced outlet temperature of flue gas is still much higher than the design temperature for burning natural gas -109 °C. The use of a catalytic additive localized the burning of the gas torch in the zone of the

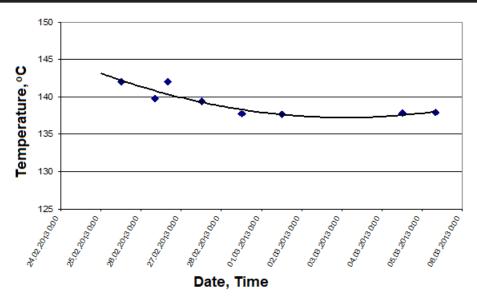


Fig. 5. Change in the outlet temperature of flue gas

Table 2

Parameter	Date					
	25.02.13	26.02.13	27.02.13	28.02.13	01.03.13	04.03.13
Content O ₂ , %	5.41	5.64	5.32	5.36	5.37	5.39
CO ₂ , %	10.11	9.95	10.17	10.13	10,12	10.12
CO, mg/Nm ³	5.7	0.5	6.0	6.0	10.6	9.25
NOx, mg/Nm ³	208.3	226.25	200.6	200.6	198.6	204.8
Temperature of flue gas, °C	143.0	139.8	139.4	137.7	137.6	137.8

burners, which made it possible to reduce the excess air in the fuel below the design value since there is no high-temperature corrosion when burning natural gas.

The use of REDUXCO catalytic fuel additive made it possible not only to increase boiler efficiency by 1.48%, but also to reduce carbon dioxide emissions by 1.56%:

 $\Delta C = 1 - \eta_1 / \eta_2 = 1 - 93.4 / 94.88 = 0.0156 = 1.56\%$

Another positive effect of the use of fuel additive is the achievement of the design efficiency of the gross operation of a boiler on natural gas -94.8% (table 1).

Conclusions. According to the results of the tests of boiler unit E-420-13.8-560 at Kaunas CHPP in order to compare the technical, economic and ecological characteristics of the boiler unit without and with the use of REDUXCO fuel additive, the following main effects were:

1. When using a catalytic combustion additive for 7 days, there was a gradual increase in boiler efficiency gross by 1.48%, which was determined by direct measurements. This made it possible to achieve the design efficiency of the gas-fired boiler.

D

2. The use of REDUXCO fuel additive resulted in a reduction of carbon dioxide emissions by 1.56%.

3. During the entire test period, a gradual decrease in the temperature of the flue gases from 143°C to 137°C was observed, which is associated with intensification of combustion in the furnace and cleaning of the heating surfaces in the convective pass.

4. Increasing the intensity of burning natural gas in fuel when using a fuel additive did not lead to an increase in the emission of nitrogen oxides. This is a consequence of reducing air excess in the furnace.

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Вольчин І.А., Провалов О.Ю., Мокрецький В.О. ВПЛИВ КАТАЛІТИЧНОЇ ПАЛИВНОЇ ДОБАВКИ НА ЕФЕКТИВНІСТЬ ГАЗОВОГО ПАРОВОГО КОТЛА

Зниження негативного впливу теплоенергетики на навколишнє середовище та клімат можна досягти за рахунок підвищення ефективності використання палива при виробництві теплової та електричної енергії. Це не тільки економить паливо, але й зменшує викиди забруднюючих речовин і вуглекислого газу як основного парникового газу. Одним із способів зростання ККД котла є використання паливних добавок, які сприяють інтенсифікації процесу згоряння палива. Для підвищення ефективності парового котла на природному газі використано каталітичну паливну REDUXCO, яка прискорює процес ланцюгового згоряння оксиду вуглецю та інших газів. На Каунаській ТЕЦ (Литва) проведено промислові випробування парового газового котла паропродуктивністю 420 m/год з метою перевірки доцільності використання паливної добавки REDUXCO для підвищення ККД котла. Загальний ККД котла визначався прямим балансом шляхом вимірювання кількості виробленої енергії, переданої в пару, та енергії спаленого природного газу. Введення каталітичної паливної добавки в первинне повітря призвело до збільшення ККД брутто газового котла з 93,4% до 94,88%. Збільшення ККД котла на 1,48% відповідає відносному зменшенню викидів вуглекислого газу на 1,56%. Зниження температури димових газів на виході зі $143^{\circ}\mathrm{C}$ до 137°С за 7 діб промислових дослідів засвідчило інтенсифікацію спалювання палива в зоні пальника та очищення поверхонь нагріву від частинок сажі в камері паливні та конвективній шахті. Інтенсифікація спалювання природного газу в паливні при використанні паливної добавки не призвела до збільшення емісії оксидів азоту. Це є наслідком зниження надлишку повітря в паливні. Викид оксиду вуглецю при подачі каталітичної присадки до палива залишився на низькому рівні близько 10 ррт.

Ключові слова: паливна добавка, паровий котел, природний газ, ефективність, зниження викидів.