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Corrosion of Solid-Fuel Boilers in Biopellet Combustion.

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ABSTRACT

This paper summarizes experimental results for combustion of biopellets in an experimental burner. The pellets from agricultural wastes are known for high concentration of alkali metals and chlorine and low concentration of sulfur, which results in ash sedimentation and boiler surface corrosion. These issues depend both on fuel characteristics and the design of the burner used for biofuel combustion. It is possible to reduce the low-temperature corrosion by modifying the burner design. The purpose of this paper is to assess how the characteristics of pelleted biofuel affect the corrosion degree in the flues of the innovative range of energy-efficient heating systems to obtain heat energy from timber processing wastes and agricultural feedstock showing high ash content, the primary element of which is a burner operating with any type of pelleted biofuel.

Keywords: ash content, pelleted biofuel, burner, corrosion.

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INTRODUCTION

The energy strategy of the Russian Federation proclaims the principle of replaceability of exhaust resources as one of the most important in terms of ensuring the energetic safety [1]. For the last 25 years, multiple studies and projects have been implemented globally to manufacture units to generate heat energy from household and industrial wastes. The wastes produced as a result of timber processing, processing of agricultural products and food industry can be converted into high quality fuel feedstock. Renewable energy sources the most important of which is the energy accumulated in plants may play a significant role in solving energetic issues [2]. In biofuel combustion, the emissions of sulfur oxides, nitrogen oxides, volatile ash are significantly reduced, and the emissions of carbon dioxide are assumed to be zero, since the plants absorb the same amount of carbon dioxide during the growth as the amount of oxygen emitted [3].

According to Rosstat, it is estimated that for the needs of private households and subsidiary farming, 800,000 to 1,000,000 off-line individual heat generators are used – heating boilers that utilize various types of fuel for their operation. As a rule, a heat generator consists of a combustion chamber with a heat exchanger, a burner and a centrifugal or axial fan. Depending on the type of the burner used, the fuel for the heating boiler can be natural gas, diesel fuel, biogas, oil, coal, turf, timber, fuel pellets and other types of natural and artificial flammables [4].

Pelleted biofuel is produced from timber processing wastes (softwood, wood chips, sawdust and bark) and agricultural wastes (hay, straw, sunflower husk, reed, corn wastes). Using pelleted biofuel allows utilizing various types of wastes; obtaining environmentally friendly high-calorific fuel; providing the production with the status of low-waste and environmentally friendly; reducing the costs for fuel transportation and storage as compared to timber wastes (lump and soft) or fire wood; increasing the production culture and getting additional profit from selling pelleted biofuel [5].

Currently, there are solid-fuel boilers that ensure convenient and affordable heating with primary wastes of timber processing used as feedstock (sawdust). However, as compared to food wastes, raw wood is more popular and more expensive product, since it is used in related productions, for example, in the production of wood-filled composites. So, those studies take relevance that are intended to investigate the properties of boilers equipped with burners capable of efficiently burning the fuel feedstock of other waste types: sunflower husk, buckwheat husk, straw, etc.

A significant reserve in the fuel and energy balance of many Russian regions is various types of biofuels that are the primary energy resources capable of ensuring high saving of resources and energy independence of factories, or even whole regions in certain cases [2]. The development of highly effective furnaces and burners used to burn pelleted biofuel made of timber processing and agricultural wastes with high ash content allows significantly decreasing the environmental effect of power engineering facilities.

As a rule, biopellets contain a high level of alkali metals, potassium, in particular, high chlorine content and low sulfur concentration, which results in ash sedimentation and heat exchanger corrosion during combustion. The fuel produced from agricultural wastes shows a 12.5 higher ash content than in the fuel from timber wastes. The ash softening and liquefaction temperature is 1000 to 1100 °C unlike timber wastes where the ash becomes powder at 1100 °C. Non-organic substances contained in agricultural wastes exceed those contained in timber wastes. For example, sunflower husk pellets contain 7.7 times more potassium (K) than in wood pellets [7]. In this connection, there is an issue associated with the effect of the pellets' chemical composition on the walls of furnaces. This is an issue of corrosion during biopellet combustion.

The corrosion intensity of heating surfaces depends on such factors as:

- steel grade,
- metal temperature,
- properties of ash sediments on heating surfaces,
- properties of combustion gases,
- time factors

This article will not describe such factors as the steel grade and time factor, but instead it covers the effect of other factors on the corrosion during biopellet combustion.

The tasks put forward by this article were solved by theoretical analysis and experimental study of biopellet combustion in the burner.

State-of-the-art

When studying the combustion process optimization, the elemental composition and fuel characteristics must be known. If we know these parameters, we can increase the fuel combustion efficiency, reduce the amount of ash formed and probability of corrosion which is especially relevant in biopellet combustion.

The elemental composition is one of the most important characteristics of fuel that shows the mass content of individual elements in the respective fuel mass. The following relations are obtained from determining each fuel mass [8]:

$$C^r + H^r + N^r + O^r + S_p^r + S_o^r + A^r + W_t^r = 100\% \quad (1)$$

$$C^a + H^a + N^a + O^a + S_p^a + S_o^a + A^a + W^a = 100\% \quad (2)$$

$$C^d + H^d + N^d + O^d + S_p^d + S_o^d + A^d = 100\% \quad (3)$$

$$C^{daf} + H^{daf} + N^{daf} + O^{daf} + S_p^{daf} + S_o^{daf} = 100\% \quad (4)$$

where C, H, N, O = weight parts of carbon, hydrogen, nitrogen and oxygen in the respective fuel mass, %; S_p, S_o = weight parts of pyritic and organic sulfur in the respective fuel mass, %; A = ash content of fuel in %; W = fuel humidity in % [8].

The fuel characteristics are indicated with respective indexes:

- r = fuel as-received basis, e.g., the fuel going to the consumer;
- a = analytical fuel weight, e.g., the air dry fuel used in the laboratory for testing;
- d = dry fuel mass, e.g., the fuel containing no moisture;
- daf = dry, no-ash (flammable) fuel mass, e.g., the fuel mass minus total moisture and ash [9].

STUDIES

To achieve the task, a series of tests have been conducted to burn fuel pellets and dry pine firewood in the experimental burner (Table 1). The bed burning technology is used in the experimental burner. The fuel is supplied from a fuel hopper by using a screw mechanism and then forwarded to the furnace. The pellets in the burner are combusted in the air flow created by the burner fan. The combustion air is supplied by special nozzles through the gaps between grate elements. To achieve the combustion intensity in the combustion space, the air is additionally supplied in the form of overfire jets through the nozzles located in the rear wall. Pellets supplied to the combustion area are intensively converted into burning char and burn out to form a flame jet, the temperature of which may reach 1200 °C. A flow of hot gases is directed into the convective part of the boiler, to flue tubes, transfers its heat to the heat-carrying medium in the system and then is forwarded to the exhaust duct. The ash remained from fuel pellets fall from the combustion area to the ash-bin where it is evacuated by using a motorized screw to the heat storage vessel as in case of large burners.

The grate temperature, the temperature inside the combustion chamber and in the flue (combustion gases) were measured during the entire experiment. Gas emissions (O_2, CO, CO_2, NO_x) were measured with Testo 350 analyzer. All concentrations of combustion gases were calculated in equal conditions – 10% O_2 . Corrosion mass measurement (HCl and SO_2) was defined by absorbing some part of the combustion gas flow in the hydric dioxide solution (0.3%). Thereafter, the solution was analyzed for chlorine and sulphate content by means of ionic chromatography under the standard methodology of GOST R 54215-2010. Humidity, ash content and concentration of volatile substances can be determined under GOST R 54184-2010, GOST R 54185-2010, and GOST R 54211-2010.

Table 1. Physical and chemical parameters of pellets used for experimental burner tests.

| | Sunflower husk pellets | Timber processing waste pellets (1 class) | Hay pellets | Pine firewood |
|---------------------------|------------------------|---|-------------|---------------|
| Diameter, mm | 6 | 6 | 6 | - |
| Length, mm | 10-50 | 10-30 | 10-50 | - |
| Humidity, % | 7.7 | 7.3 | 6.8 | 6-8 |
| Ash content, % | 5.4 | 2 | 5.7 | 1 |
| Density, t/m ³ | 1.1 | 0.6 | 0.65 | - |
| Heat conductivity, MJ/kg | 18.46 | 16.9 | 16.0 | 17.5 |
| Elemental analysis | | | | |
| Carbon (C) % | 50.0 | 48.5 | 47.3 | 52.51 |
| Hydrogen (H) % | 6.0 | 6.9 | 5.8 | 6.19 |
| Oxygen (O) % | 38.5 | 39.8 | 40.43 | 40.53 |
| Nitrogen (N) % | 5.5 | 0.19 | 0.66 | 0.14 |
| Sulfur (S) % | 0.10 | 0.10 | 0.10 | 0.03 |

In burner tests (Figure 1), three various types of pellets were combusted: timber pellets, straw pellets, sunflower husk pellets and dry pinewood (Table 1).



Figure 1. Testing unit for experiential burner tests.

There is water in fuel combustion products that can condense in the flue when the temperature of combustion gases falls down. The temperature for water steam contained in combustion gases to condense into water is called the dew point. Each amount of water steam in combustion gases shows its own dew point, e.g., its specific temperature. The mineral composition of solid fuels contains alkali compounds that greatly neutralize sulfur oxides SO_3 , so the final content of SO_3 in exhaust gases and the dew point depend on fuel ash content A^p . Usually, in this case, the temperature is determined:

$$t_p = t_{con} + 202(S^n)^{0.33} / 1.23^{a_{un}A^n} \quad (5)$$

where S^n and A^n = sulfur and ash values in the fuel as-received basis reduced to 1 MJ of heat, %.

$$S^n = \frac{S^p}{Q_R^p} \quad (6)$$

$$A^n = \frac{A^p}{Q_R^p} \quad (7)$$

t_{con} = water steam condensation point, °C; determined upon the partial pressure $P_{H_2O} = R_{H_2O} P$, MPa [11-13].

Since solid fuels are combusted in case of air excess, it does not affect the changes in SO_3 formation [14].

Figure 2 shows the amount of water in combustion gases for various types of fuel. As Figure 2 shows, the formation of water steam is lower for the pelleted fuel than for pine firewood. The smallest moisture content in the combustion gas is observed when burning straw pellets. It means that the water content in the combustion gas when burning straw pellets is 5% less per 1 kg of combusted fuel than for pine firewood. The moisture content in the fuel affects the dew point. The dew point has been calculated for each boiler with respect to the fuel composition for each fuel combustion experiment. After standard calculations, the partial water pressure in the combustion gas was determined for the furnace gas.

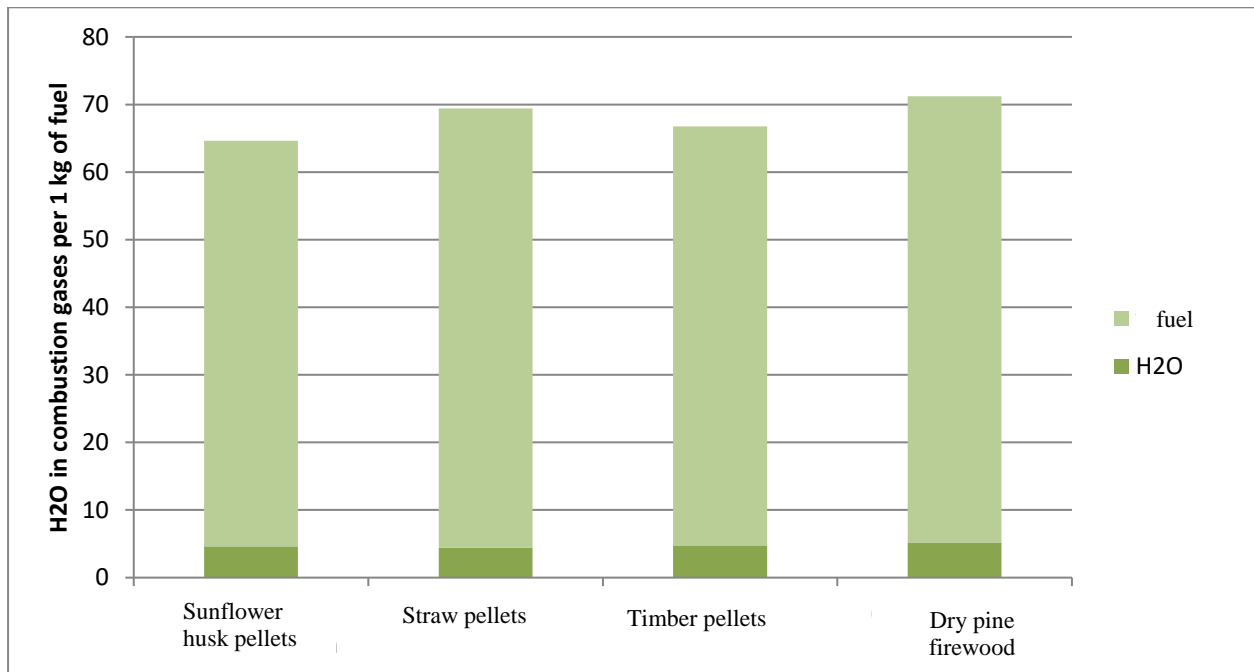


Figure 2. Amount of water in the combustion gas when burning biopellets and dry pine firewood.

By applying the equation (5), the dew point was obtained. Dry pine firewood showed the dew point of 43.5 to 44 °C. The dew point for all pelleted samples in the experimental burner combustion system was within 41 to 42.9 °C. Dry pine firewood was combusted at lower air excess than when burning pelleted biofuel. It means that the combustion gases from burning dry pine firewood contained more air than the process gas of biopellets. Since the dew point of combustion gases of pelleted biofuel is less than in pine firewood, the risk of low-temperature corrosion shall also be considered as lower.

The possibility of low-temperature corrosion can be reduced by maintaining reduced operating conditions and selecting proper designs.

Measuring the corrosion mass (HCl and SO_2) for all fuels used in the experiment was below 0.1 mg/nm^3 . No difference was found between burning firewood and pellets. Thus, the risk of corrosion due to sour gaseous compounds will be the same in firewood and pellets. Other types of fuel with higher chlorine and sulfur content were not included in this experiment.

Using biofuel in boilers to produce heat energy is a complicated process. High content of alkali metal chlorides, primarily KCl , can be a reason for high-temperature corrosion [15]. Small amount of hydrochloric acid (HCl) can be formed when burning biopellets containing chlorine. Apart from HCl , the chlorine contained in the fuel can be emitted as alkali metal chlorides (KCl and $NaCl$).

High corrosion activity of chlorine significantly decreases the operation time of heat exchangers and flue walls. Frequent replacement of these components is impossible due to economic considerations. Nowadays, this issue is an aspect of multiple studies.

Let us consider the emissions of solid particles in the flue. The primary components of solid particles emissions include *K*, *Na*, *S* and *l*, whereas at the heat exchanger, high amount of *Ca* is expected. The distribution of sediments in the heat exchanger is shown in Figure 3.

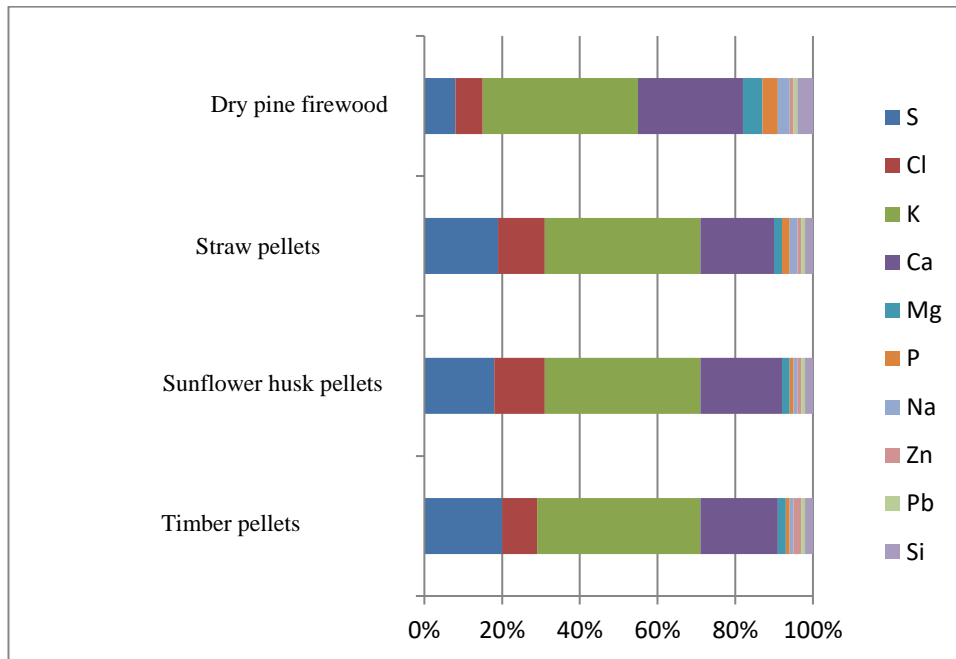
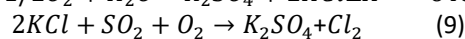
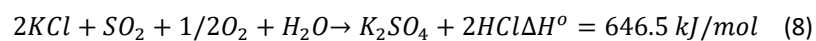


Figure 3. Distribution of individual elements of sediments in the heat exchanger.

High amount of calcium in the elemental composition is caused by different mechanism to capture calcium as compared to sulfur, potassium and chlorine. Calcium is mainly captured as solid particles in rough burning conditions that are sedimented due to impacting each other in the heat exchanger. When burning various fuels, the increased chlorine and sulfur in solid particles is observed when changing temperature and conditions of the fuel burning process. Nevertheless, the difference in the amount of sediments between various types of fuel is not apparent.

Unlike timber biofuel, the given examples of agricultural crops show small content of sulfur and chlorine of 1 and 0.005%, respectively. The values of the relation Cl/S must be considered when selecting biofuel for boilers. The limit value of this relation is 0.454. For lower values, the intensity of corrosion activity of chlorine is reduced due to higher tendency to form mineral sulfur components in the boiler furnace [14]. It has been believed that S content may augment the issues related to corrosion of sediments by chlorides using the sulfation mechanism [17]:



The stoichiometric ratio $2S/Cl$ is a sign of high-temperature corrosion risk. The stoichiometric ratio was determined under GOST R 54215 – 2010 (CEN/TS 15289:2006).

Figure 4 shows the stoichiometric ratio of sulfur and chlorine ($2S/Cl$) in the studied fuel samples. The $2S/Cl$ ratio for wood pellets is lower than in standard pine firewood, which indicates a slightly higher corrosion potential. Another pelleted fuel shows a higher ratio than wood pellets, which is most likely caused by the composition of the initial feedstock.

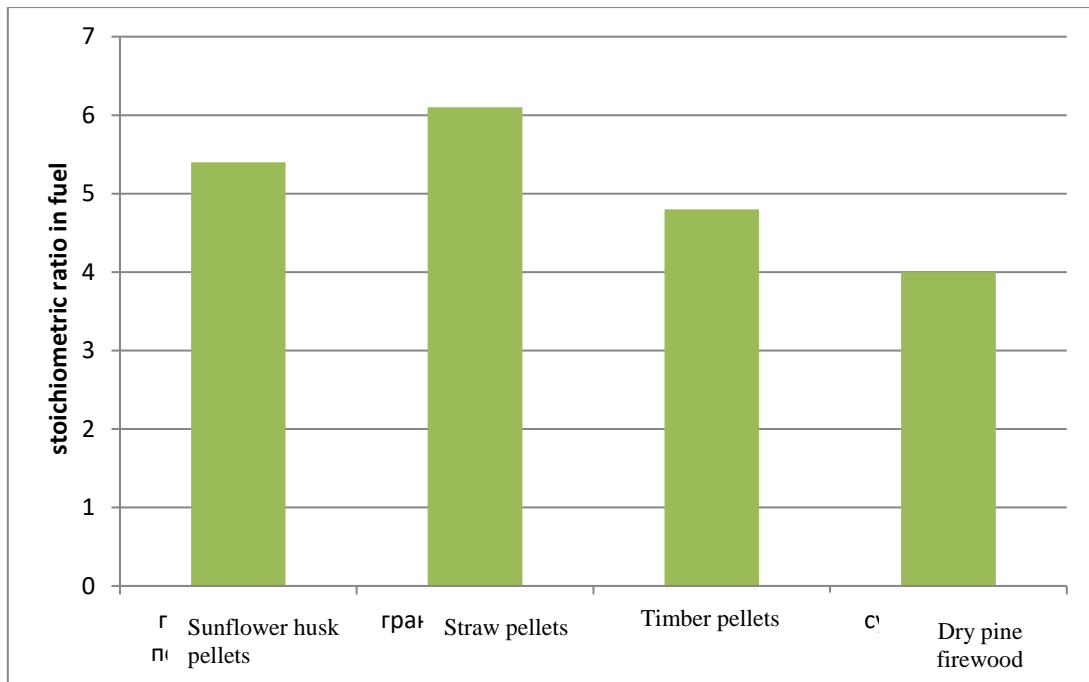


Figure 4. Stoichiometric ratio of sulfur and chlorine in the studied fuel samples.

The *Cl* concentration grows when the *2S/Cl* ratio in the fuel decreases, whereas the sulfate concentration falls down. When the *2S/Cl* ratios in the fuel become <2, even if the *Cl* excess in the form of aerosols predominates, it proves serious corrosion risks that shall be accounted for. Correspondingly, corrosion risks in husk pellets and straw pellets increase.

Attention should also be paid to the risk of high-temperature corrosion. High-temperature corrosion occurs due to reduced density and strength of the metal oxide film when it is heated. As a result, the oxygen is in direct contact with clean metal and it constantly oxidizes it.

Samples were tested under GOST 9.908-85 Methods to Determine Corrosion Parameters and Corrosion Resistance to check the corrosion effect in the heat exchanger. Samples were tested in special conditions at the relative humidity of 75% and the temperature of 50 °C. Salt formation on the heat exchanger surface is shown in Figure 5 and Table 2.

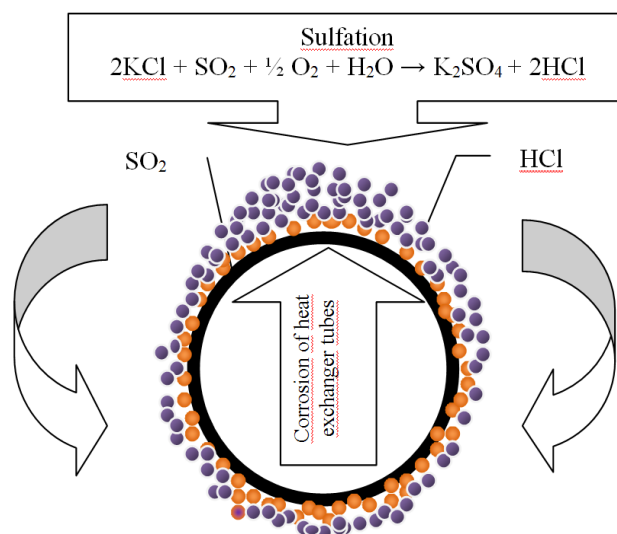


Figure 5. Mechanisms of heat formation and surface sedimentation on heat exchanger tubes [17].

Table 2. Salt formation on heat exchanger surface.

| Temperature level: | 30 °C | 40 °C | 50 °C |
|---|---------|-------|-------|
| Saturated salt solution | % ratio | | |
| <i>NaCl</i> | 75 | 74.7 | 74.4 |
| <i>KCl</i> | 83.6 | 82.2 | 81.2 |
| <i>KOH</i> | 7.4 | 6.3 | 5.7 |
| <i>K₂CO₃</i> | 43.2 | - | - |
| <i>CaCl₂·6H₂O</i> | 21.6 | 18.4 | 16.3 |

In biopellet combustion, the primary components of solid particles emissions include *K*, *Na*, *S* and *Cl*. When burning, *K* from the fuel in the combustion gas at high temperatures may cause mainly *KCl* or *KOH* to appear. When decreasing the temperature, taking into account *SO₂* being present in the combustion gas, *KCl* or *KOH* can be transferred into sulfates by using homogeneous reactions in the gas phase (highly exothermic reaction that is thermodynamically favorable for lower temperatures) as shown in the equation (8). *K₂SO₄* becomes highly over-saturated since it is only formed by extra low steam pressure. Nevertheless, in accordance with kinetic considerations, the equilibrium transformation in the gas phase in *K₂SO₄* may not always be possible, e.g., only some part of *K* in the steam phase is converted into *K₂SO₄* [18]. The remaining part may manifest itself as *KCl* or *K₂CO₃*. The fuel was tested for combustion (Table 1). Sediment samples were taken from the heat exchanger and processed with silicate. The sediments of tested fuel types showed that dry pine firewood has the lowest probability of corrosion, and straw pellets show the highest corrosion probability.

CONCLUSION

To study the corrosion effect on boilers, standard testing methods were used. It has been found that the corrosion hazard is related to the composition of biogranules. Any biological fuel subjects the burner to corrosion risk during operation. The lowest corrosion probability is shown by timber and pellets made of it. Sunflower husk and straw pellets cause higher corrosion probability in the furnace during combustion.

The primary issues in boilers during biopellet combustion are related to high-temperature corrosion. Three corrosion formation mechanisms are relevant:

1. Gaseous *HCl* and *Cl₂* directly getting on the heat exchange surfaces;
2. Formation of alkali sulfates and alkalis (alkali corrosion) that dissolve the protective oxide layer of the heat exchanger surface;
3. Sulfation of alkali metals or chlorines of heavy metals in the pipe next to the sedimentation layer. In this mechanism, *Cl* is released and affects the pipe surface (so called active oxidation) [17].

Currently, various technologies to reduce the amount of ash segmentation and related corrosion issues are under study. It is a common practice to use sulfur or *SO₂* as additives during combustion, or combined combustion of biofuel with the fuel showing lower trend to fouling [16, 19-20]. Nevertheless, it is very complicated to select optimal additives. In this connection, the authors believe that continuing the work to optimize the combustion conditions by using dynamic control parameters to decrease corrosion seems perspective.

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