Modifiers used in the combustion process of fuel oil and solid fuels

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Introduction
Preventing environmental pollution today is a task of paramount importance. Due to the rapid growth of the human population, it is essential to address the issue of shifting proportions between the flora and fauna, and thus the changing composition of atmosphere, hydrosphere and soils. A particularly important role in this matter falls to the hands of chemical sciences and industry [1].

The combustion processes of liquid and solid fuels emit pollution into the atmosphere in the form of non-combusted organic residues, nitrogen oxides and sulphur oxides. The levels of gas emissions into the atmosphere in technological processes and technical operations, as well as acceptable pollution levels in the air are regulated by applicable legislation. After Poland’s entry into the European Union the acceptable levels of certain pollutants in the atmosphere should be reduced [2, 3]. Basing on European requirements, the legislation specifies the emission standards for the installations in terms of gas or dust release into the atmosphere, and the acceptable levels for certain substances.

One of the possible solutions is the use of modifiers (catalysts) in liquid fuel combustion processes to significantly reduce the local pollution emission levels.

Catalysts in environmental protection
New stoichiometric and catalytic, environmentally friendly processes for the chemical industry, metallurgy, transport and other economy branches are extensively studied.

The role of catalysts in promoting environmental protection is illustrated on the figure below (Fig. 1).

Environmental protection catalysts find non-standard applications, among others in households:

* mobile preheaters
* catalytic deodorisation systems.

The examples above illustrate the notion that catalysis is applicable not only to chemistry, but also to everyday life.

Reducing the emission levels of volatile organic compounds and carbon oxide (CO) is one of the priorities in the protection of the atmosphere from toxic chemical substances. In practice this translates into using solutions that enable continuous conversion of pollutants such as volatile organic compounds (VOCs) and CO into carbon dioxide and water. In view of the results obtained in the field thus far, the most efficient process for nearly complete elimination of the substances in question is catalytic afterburning.

ICSO Chemical Production Sp. z o.o. offers a VOCs and carbon oxide afterburning catalyst under the trade name of Katalizator PD-I. The product is manufactured using the technology developed by the Institute of Heavy Organic Synthesis “Blachownia” (ICSO) in Kędzierzyn-Koźle. The production process involves impregnating the active carrier with precisely specified properties with platinum and nickel salts. The carrier is γ-Al2O3 in the form of granules with 4÷8 mm in diameter. In the next stage the impregnated carrier is dried and undergoes anaerobic reduction. The obtained VOCs and carbon oxide conversion rate is 97-99%, with the catalyst life-cycle of 2 to 3 years [5].

For oxidation of chloro-organic compounds a catalyst containing Cr2O3/Al2O3 has been developed. In this case, the following destructibility of chloro-organic compounds was observed [6]:

\[
CH_2 = CCl_1, > ClICH = CCl_2, > ClCH_2 = CH_2, > Cl > CH_3Cl
\]

Another example of the application of catalysts in environmental protection is the catalytic elimination of nitrogen oxides from exhaust fumes with the use of ammonia, performed mainly in large power plants. The catalysts in this reaction are transition metal oxides on the carrier: V2O5/TiO2 and V2O5-WO3/TiO2. Although the process is not particularly simple in terms of technology, it is the only one to meet all environmental protection requirements.

In the case of fuel combustion in diesel engines, the inconvenient ammonia is substituted with ammonia-containing substances, e.g. urea in the form of a 32% aqueous solution under the name of AdBlue.

The vehicle transport uses monolithic honeycomb catalysts. The catalyst is composed of monolith in the form of 2MgO-2Al2O3·5SiO2 cordierite, covered with a thin film of γ-Al2O3.

In the fuel combustion process in petrol engines the most frequently used catalysts are three-way catalysts, enabling simultaneous reduction of NOx and oxidation of hydrocarbons and carbon oxide. Diesel engines, on the other hand, use catalysts oxidising hydrocarbons and CO. Simultaneous NOx reduction is not possible due to the fact that diesel engines operate on lean mixtures.

Catalysts find broad applications in environmental protection. Table I provides examples of catalyst application, according to the pollution type and source [7].
The use of heavy fuel oils in combustion processes

In domestic conditions the electric and heat power is generated mainly in power units and systems operating on liquid and solid fuels, usually fuel oils and mineral coal. A general tendency to improve the efficiency of those installations is clearly visible, as improved efficiency translates into fuel savings and reduced emission levels per unit of generated power.

In modern boiler installations automatic regulation systems are widely used and the air fed to the boiler is carefully controlled, which enables the operator to maintain the watt-hour efficiency of the device at a relatively high level. A potential solution for enhancing the watt-hour efficiency of the boilers is the application of modifiers added to fuels. The modifiers improve the combustion efficiency i.a. by afterburning heavier hydrocarbon fractions in the fuel, thus reducing the loss from incomplete combustion. At the same time, the modifiers reduce the levels of emission into the atmosphere.

It is also generally accepted that modifiers have a beneficial impact on the heating surfaces of the boilers that have been in operation for a long period of time. It should be pointed out that there is no comprehensive scientific information available on the impact of various modifiers on the combustion process, its efficiency and the emission levels of specific compounds.

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In the heating systems, particularly new generation ones, a major role is played by the fuel oil.

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In the recent years a significant increase in production of heavy fuel oils has been visible. In 2011 the production of heavy fuel oil rose by more than 68% in comparison to 2009. Such major increase in production is associated with increased crude oil processing in domestic refineries, as well as launching new processing plants and modernising the existing ones [8].

Heavy fuel oils are characterised by high content of slow-burning, heavy paraffin waxes and tars. The combustion of those fuels without pre-processing causes emissions significantly exceeding the limits, particularly of benzopyrene and dust. The refinement of the heavy fuels in question by adding modifiers (catalysts) can considerably improve their combustion, thus reducing the emission levels of unwanted substances.

**Combustion catalysts of heavy fuel oils and solid fuels**

The literature of the subject provides numerous examples of combustion process modifiers, however, usually applicable to engine fuels. In the case of heavy fuel oils the available information is limited.

Global power industry knows a number of modifiers that improve the fuel combustion conditions. Those include mainly modifiers associated with cleaning the boiler heating surfaces and reducing emission levels of NOx, SOx and unburned organic residue. Those modifiers are usually fed into the combustion chamber in the form of a powder or emulsion [9-12].

Efficient fuel combustion modifiers include e.g. magnesium oxides which are found in the form of a suspension in the heavy oil or can be dispersed in the oil with the use of surfactants. Another solution is the use of Fe, Mg and Cu chlorides in the form of a suspension in the oil. However, the use of the aforementioned catalysts is associated with considerable difficulties with feeding them into the oil and the stability of the resulting suspensions.

Also sodium (NaOH, NaCl and Na2CO3) and potassium (KOH, KCl, K2CO3) compounds are used as fuel combustion catalysts. The aforementioned catalysts improve the efficiency of oxidation if the reaction takes place at 650 -710K. The activity of those catalysts is arranged in the following order: NaOH > Na2CO3 > NaCl > no catalysts and K2CO3 > KOH > KCl > no catalysts [13].
Another group of catalysts comprises mainly organometallic salts of rare earth elements, principally Ce, Pr and Nd, suspended in aromatic organic solvents. The salts are produced in the reaction of the water-soluble metal or metal hydroxide salt with carboxylic acids containing 6 carbon atoms in the molecule. The literature of the subject provides examples of attempts to substitute the costly rare earth element with a cheaper element, e.g. Mg, Fe, Ca and others, without significant loss of the catalyst properties. The catalysts are introduced into liquid fuel in the volumes of 10 to 100 ppm, as converted into metal. In the case of combustion of e.g. heating oil which contains high asphaltene volumes, the catalyst is absorbed on the surface and enables full oxidation [14-16].

The review of additives for heavy fuel oil combustion available on the market is provided by Paulikkas in [12] (Tab. 3).

<table>
<thead>
<tr>
<th>Item</th>
<th>Additive</th>
<th>Properties</th>
<th>Additive introduction site</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stable magnesium oxide suspension</td>
<td>Complete protection against low- and high-temperature corrosion. Elimination of carbon black.</td>
<td>Front bottom wall of the boiler</td>
</tr>
<tr>
<td>2</td>
<td>Aqueous suspension of purified magnesium oxides</td>
<td>Complete protection against low-temperature corrosion. Elimination of carbon black.</td>
<td>Front bottom wall of the boiler</td>
</tr>
<tr>
<td>3</td>
<td>Organometallic mixture of magnesium, iron and asphaltenes</td>
<td>Protects the boiler from gathering of residues and corrosion. Reduces the volume of unburned coal by 50%.</td>
<td>Front bottom wall of the boiler</td>
</tr>
<tr>
<td>4</td>
<td>Mixture of surfactants, dispersants and catalysts</td>
<td>Purifies residues in heavy fuel oil installations. Reduces the volume of unburned coal by 80%. Reduces NOx emission levels by 20%. Reduces SOx by 50%.</td>
<td>Reservoir tank</td>
</tr>
<tr>
<td>5</td>
<td>Mixture of iron-based organometallic surfactants</td>
<td>Improves combustion, reduces SOx volume in exhaust fumes, reduces unburned coal volume, eliminates air surplus.</td>
<td>Reservoir tank</td>
</tr>
<tr>
<td>6</td>
<td>Mixture of iron- and magnesium-based organometallic surfactants</td>
<td>Improves combustion, reduces SOx volume in exhaust fumes, reduces unburned coal volume, eliminates air surplus.</td>
<td>Reservoir tank</td>
</tr>
<tr>
<td>7</td>
<td>Organic, non-metallic fly ash residue</td>
<td>Eliminates all residues from the tank, improves filtration and combustion, reduces corrosion and emission levels.</td>
<td>Reservoir tank</td>
</tr>
</tbody>
</table>

The initial research indicates that applying highly active bimetallic catalysts in the volume of 60 ppm in the medium fuel oil combustion tests significantly reduces the volume of produced fly ash, reduces SOx emission levels by 7%, NOx by 3%, improves boiler efficiency by 4% and reduces the volume of residues produced on the grate and in the combustion chamber. The aforementioned tests were carried out on the burner and oil boiler of 400 kW heating system by Weishaupt.

The examples of catalysts used in coal combustion include the concept of the DESONOX (desulphurization from sulphur oxides and NOx destruction) contact process. The process comprises desulphurisation and denitrification in the boiler furnace, on the level of burned coal particles. The process minimises the impact of boiler type and efficiency on the desulphurisation and denitrification of exhaust fumes. The DESONOX catalyst is composed of synthetic zeolite as the carrier of the active phase of contact and the contact itself is achieved by the double impregnation method (DIM) [20].

The concept of this process is based on continuous elimination of SOx from the reaction environment by binding it to furnace waste. The DESONOX catalyst works on the active phase produced during combustion, i.e. the liquid alloy created by very fine preparation and coal [19, 20]. The DESONOX technology eliminates sulphates together with slag and fly ash, thus increasing their weight by approx. 3-5%. The catalyst also reduces the volume of nitric oxides in flue gases, since it catalyses the reaction of high-temperature indirect CO oxidation by nitric oxides.

The analysis with the use of the aforementioned catalyst was performed in a WR-25 boiler. During the process the changes of exhaust fume concentration and boiler efficiency were monitored. It was observed that adding approx. 0.31 kg of the catalyst in question to 1 Mg of coal reduces SOx emission level by more than 50% [20].

Summary

Due to the rising production of heavy fuel oils and the EU requirements on environmental protection, the modifiers improving the combustion process of heavy fuel oils and solid fuels are becoming increasingly necessary.

On the basis of the literature review it can be concluded that the application of catalysts in the combustion process of heavy fuel oils and solid fuels enables:

- maintaining watt-hour efficiency of the boiler
- extending the life cycle of the boiler and reducing maintenance costs
- more efficient combustion by reducing the volume of hydrocarbons in flue gases (higher heat gain from a single fuel unit)
- reducing the emission levels of harmful gases into the atmosphere (CO, NOx, SOx, dust, polycyclic aromatic hydrocarbons)
- elimination of unburned residue in the form of carbon build-up in the combustion chamber, thus improving the boiler efficiency
- reducing corrosivity of exhaust fumes
- increasing the heat volume with complete combustion of the fuel.

The number of scientific publications on catalysts improving the heavy fuel oils combustion process is limited; therefore, further research in the field is required.

**Literature**

2. Rozporządzenie Ministra środowiska w sprawie standardów emisyjnych z instalacji. Dz. U. nr 95, poz. 358 z 2011 roku.
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