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

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Please cite as: CHEMIK 2012, **66,** 11, 1203-1210

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 soil 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 pollutions 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).

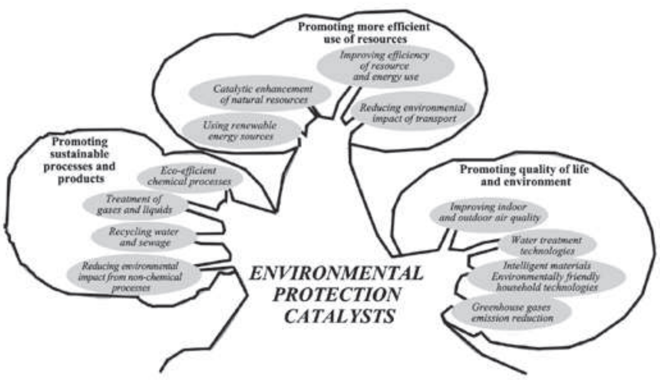

Fig. 1. Tree diagram of the role of catalysis in environmental promotion [4]

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

- catalysts for water treatment, based on MnO_2 and carbon filter, eliminating Cl_2 and HClO
- equipment for drainage and refrigeration
- household catalytic combustion chambers
- 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 pollutions 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-1. 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-Al_2O_3 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 Cr_2O_3/Al_2O_3 has been developed. In this case, the following destructibility of chloro-organic compounds was observed [6]:

$$CH_2 = CCl_2 > ClCH = CCl_2 > ClCH_2 - CH_2Cl > CH_2Cl_2$$

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: V_2O_5/TiO_2 and V_2O_5-WO_3/TiO_2. 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 $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$ cordierite, covered with a thin film of γ-Al_2O_3.

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

Catalysts find broad applications in environmental protection. Table 1 provides examples of catalyst application, according to the pollution type and source [7].

Table 1

Examples of applications of heterogenic catalysts in environmental protection [7]

Source	Pollution type	Applied catalysts
Petrol engines	Nitrogen oxides (NO_x), hydrocarbons (HC_s), carbon oxide (CO)	$Pt/Pd/Rh/Ce_xZr_{1-x}O_2/(La, Ba)-Al_2O_3$ on ceramic and metallic monoliths
Diesel engines (light vehicles)	NO_x, HC_s, CO	$Pt/Pd/Rh/BaO/Al_2O_3$ on ceramic and metallic monoliths
Diesel engines (heavy vehicles, lorries, buses)	NO_x, HC_s, CO	V_2O_x/TiO_2 on ceramic monoliths (NO_x elimination); $Pt,Pd/Al_2O_3$ on ceramic and metallic monoliths (CO, HC elimination)
Diesel engines	dusts	cerium oxides and iron oxides Pt/Al_2O_3 Cu, V, K
Power plants, waste incineration furnace, gas turbines	NO_x	V_2O_5-WO_3/TiO_2 on ceramic monolith
Gas turbines	CO, HC_s	Pt, Pd/Al_2O_3 on ceramic and metallic monoliths
Nitric acid production plants	NO_x	CuO-NiO/ Al_2O_3, Cu-La/Y
Nitric acid, adipic acid and caprolactams production plants	N_2O	Rh/Ce-ZrO_2, Rh
Chemical plants, paint manufacturers, refineries	Volatile organic compounds (VOCs)	Pt, Pd/Al_2O_3 on ceramic and metallic monoliths
Refineries	H_2S, CS_2, COS	Al_2O_3 or TiO_2 (Fe_2O_3/Al_2O_3)
Sewage from chemical and petrochemical plants, paper mills and manufacturers of electronics	Organic compounds	Ru/TiO_2 TiO_2 (anatase)
Hospitals and public facilities	Organic compounds, bacteria	TiO_2 (anatase)
Air inside houses and offices	CO and odours	Nanostructured Au/TiO_2
Air inside houses and offices	formaldehyde	Pt, Pd/SiO_2

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.

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

In 2011 Poland produced 2.943 million cubic metres of heavy fuel oil, which amounts to 12% of the total liquid fuel production (Tab. 2).

Table 2

Comparison of liquid fuel production in the years 2000÷2011, in thousands of m^3 [8]

Fuel type	2009	2010	2011
Petrols	5 641	5 504	5 219
Diesel	11 297	12 080	13 199
LPG	485	539	448
JET fuel	815	819	1 075
Light fuel oil	1 338	1 244	933
Heavy fuel oil	**1 746**	**2 552**	**2 943**
Total	**21 322**	**22 708**	**23 817**

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 NO_x, SO_2 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 Na_2CO_3) and potassium (KOH, KCl, K_2CO_3) 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>Na_2CO_3>NaCl>no catalysts and K_2CO_3>/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 7 8 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 Paullikkas in [12] (Tab. 3).

Table 3

Additives for heavy fuel oils, their composition and properties [12]

Item	Additive	Properties	Additive introduction site
1	Stable magnesium oxide suspension	Complete protection against low- and high-temperature corrosion. Elimination of carbon black.	Front bottom wall of the boiler
2	Aqueous suspension of purified magnesium oxides	Complete protection against low-temperature corrosion. Elimination of carbon black.	Front bottom wall of the boiler
3	Organometallic mixture of magnesium, iron and asphaltenes	Protects the boiler from gathering of residues and corrosion. Reduces the volume of unburned coal by 50%.	Front bottom wall of the boiler
4	Mixture of surfactants, dispersants and catalysts	Purifies residues in heavy fuel oil installations. Reduces the volume of unburned coal by 80%. Reduces NO_x emission levels by 20%. Reduces SO_3 by 50%.	Reservoir tank
5	Mixture of iron-based organometallic surfactants	Improves combustion, reduces SO_3 volume in exhaust fumes, reduces unburned coal volume, eliminates air surplus.	Reservoir tank
6	Mixture of iron- and magnesium-based organometallic surfactants	Improves combustion, reduces SO_3 volume in exhaust fumes, reduces unburned coal volume, eliminates air surplus.	Reservoir tank
7	Organic, non-metallic fly ash residue	Eliminates all residues from the tank, improves filtration and combustion, reduces corrosion and emission levels.	Reservoir tank

The authors of this paper also study the subject of catalysts for heavy fuel oil combustion [17, 18]. In the conducted research, the authors used metallic catalysts based on iron salts and iron and cerium salts of fatty acids dissolved in the fuel oil. The metallic salts of fatty acids are characterised by high solubility in fuel oil. The obtained catalyst solution exhibit low viscosity. Thus far, the following monometallic catalysts have been analysed: Fe and bimetallic: Fe/Ce. Fe and Fe/Ce catalysts are characterised by low viscosity and high stability in time. The monometallic catalysts contained 200 g of Fe/dm^3, while the bimetallic contained 150 g of Fe and 50 g of Ce per 1 dm^3 of the solution. The catalyst solutions are highly soluble in the analysed fuel and do not undergo separation.

In the combustion process analysis fuel without catalysts was used, with the addition of monometallic (Fe) and bimetallic (Fe/Ce) catalyst.

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 SO_2 emission levels by 7%, NO_x 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 NO_x 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 SO_3 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 SO_2 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, NO_x, SO_2, 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.

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