New pro-ecological solutions in fuel combustion technology

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Introduction

Demographic growth determines the need to supply the growing human population in energy. The energy aspect is closely accompanied by issues related to access to specified quality fuels and effects of their combustion. The development of chemical technology allow the implementation of innovative solutions for more efficient ways of fuel-use – both: liquid and solid fuels to an industrial scale. Fuel combustion processes are the source of emissions of environmental harmful pollutants. An important aspect of sustainable proecological solutions is, contributing significantly to the quality of life, reduction of air pollution, as well as solid residues originated by combustion processes of fuels.

Additives for motor fuels

The purpose of the application of motor fuels additives is to lower the activation energy of oxidation occurring in combustion chamber of internal combustion engine. The result of downgrading in activation energy is the ability to conduct fuel oxidation process and, simultaneously, to ensure the total combustion at a lower temperature. Lowering of temperature in the combustion chamber causes limitation of maximum pressure prevailing in it and eases the mechanical operation of the engine. Simultaneously the greater pressure holds while moving the piston down providing greater completeness of combustion, and downturning primarily the reduction of pollution emissions with exhaust gases.

It was found that the higher the temperature of the fuel ignition the less speed of combustion process. Additives for motor fuels increases the speed of combustion process of fuel ingredients showing a high boiling point [1].

Using motor fuel additives, the maximum effect is obtained by the combustion of hydrocarbons with high boiling point, so in the process of exhaust afterburning [1].

There is a wide range of additives for motor fuels (petrol, diesel). Below the latest trends in this subject field.

The first group of additives are so-called oxidants. In paper [2] are the eleven most common aerobic supplements described, which can be used for both, gasoline and diesel engines. For these group of additives appertains: methyl tert-butyl-ether (MTBE) ethyl ether, tri-butyl-ether (ETBE), ethyl tert-amylo (TAEE), tert-amylomethyl (TAME), isopropyl ether (DIPE), dicarbonate (DMC), dimetoksymethyl (DMM), di-butyl ether (DBE), diethyl ether, diglikolomethyl (DGM), diethyl carbonate (DEC), 2-metoxyethyl acetate (MEA). In Table 1 the impact of the above mentioned additives on emission of HC, NO_x and particulate matter is described.

In turn, at work [11] the impact of additives such as ethanol, methyl-tert-butyl-ether (MTBE), ethyl acetate and methyl acetate on the quantity of the RON (Research Octane Number) is discussed. Combustion tests have been made with the use of gasoline, which composition was as follows: n-paraffin-26.3%, isoparaffin-38.7%, aromatic compounds-24%, naphthenes-7.3%. The temperature on the beginning of boiling for that gasoline amounts to 41°C, while the final temperature of distillation 178°C.

Table 1

Main effect on the emissions due to the addition of the oxygenated additives [2]

	CO	HC	NO_x	Emission of particulate matter (PM)
MTBE	emission fall	emission fall	various findings [5, 6]	-
ETBE	emission fall	emission fall	emission increase [7]	-
TAME	emission fall	emission fall	emission fall	-
DIPE	emission fall	emission fall	emission fall	-
DMC	emission fall	no change	emission increase [8] emission fall [3]	emission fall
DMM	emission fall	emission fall [3] emission increase [4]	emission fall	-
DBE	emission fall	emission fall	emission increase [9]	-
DGM	emission fall	emission fall	emission fall	-
DEC	emission fall	emission fall	no change	emission fall
MEA	emission fall	emission fall	no change	-

In Figure 1 the effects of various additives on RON (Research Octane Number) is shown. The initial value of RON is amounted to 81.5. As observed additives increase RON value and the highest value is obtained using ethanol as additive.

RON determines the resistance to raw spontaneous combustion of motor fuel for spark ignition engines, which may cause engine knocking. The higher the RON, the more gasoline is protected from engine knocking, so the better running engine.

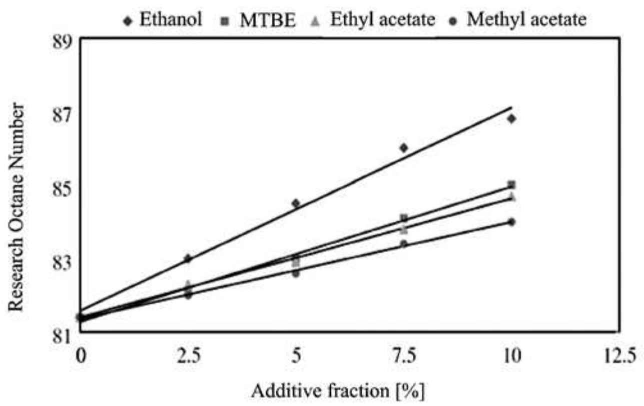

Fig. 1. Research Octane Number (RON) graphics for the gasoline mixed with 2.5%, 5%, 7.5% and 10% of ethanol, MTBE, ethyl acetate and methyl acetate [11]

The benefits arising from the use of aerobic additives are as follows:

- reduction of the emission of carbon monoxide (for a new generation of cars)
- reduction of emissions of hydrocarbons (for a new generation of cars)

- reduction of the emission of particulate matter
- ability of use for petrol and diesel engines
- increase of RON.

Another group of additives are compositions containing metal, which are discussed below.

In studies of diesel combustion organic compounds containing element of the first, second or transition group are used as additives [1]. Their concentration is of few ppb on the metal content basis. The use of such additives in such small quantities did not affect the contamination of combustion chamber or spark plugs. In Table 2 the emissions of harmful exhaust components during normal combustion of diesel oil and diesel oil with 0.01% of additive are compared.

Table 2

Emission of harmful substances with flue gases [g/kWh] [1]

Pollutant	Diesel oil	Diesel oil with 0.01%of additive	Reduction of content of mentioned pollutant in exhaust gases [%]
CO	1.43	1.23	16.3
HC	0.49	0.47	4.2
NO_x	11.33	10.76	5.3

Test results (Tab. 2) allow to assess the compliance of the operating engine with the requirements of the EURO, and attest to the overall performance of additive.

In turn, at work [12] the impact of such additives as: MnO_2 and MgO on the diesel engine is discussed. These additives were added to diesel oil in quantities of 8 μmol/l and 16 μmol/l. The impact of metallic additives on the properties of tested diesel fuel is shown in Table 3.

Table 3

Effects of metallic based catalysts: MnO_2 and MgO on fuel properties of diesel fuel [12]

	Diesel fuel	Diesel fuel + 8μmol/l MnO_2	Diesel fuel + 16μmol/l MnO_2	Diesel fuel + 8μmol/l MgO	Diesel fuel + 16μmol/l MgO
Setting point [°C]	-23	-27	-31	-26	-28
Cloud point [°C]	-6	-8	-10	-7	-8
Viscosity in 40°C [cSt]	2.6	2.5	2.3	2.4	2.2
Flash point [°C]	73	68	62	69	65

Both additives are improving such properties of diesel oil as: viscosity, flash point, cloud point and the setting point. A study shows that the use of diesel oil enhanced with an metal containing additive has dropped in fuel consumption by 4.16%.The decline of CO about 16.35% and a decrease in smoke generation of about 29.82% was also noted. However, in case of NO_x an increase in emissions has been noted [12].

Another example of metallic additives affecting an operated diesel engine are: MnO and CuO [13]. Equally as in the case of MnO_2 and MgO [12], there has been a positive effect of additives on the properties of diesel fuel noted.

Catalyst for the combustion of fuel oils

The use of fuel oil produced as a mix of heavy crude oil distillates containing different deposits each of the refinery processes, causes reduction of the effectiveness of the operating boiler, increase of the cost of maintenance, and is associated with significant adverse effects on the environment.

Shrinkage of the effectiveness of the operating boiler, as well as raising of maintenance costs are mainly caused by the slagging of deposits on its heating surfaces. Also, this process is accompanied by low and high-temperature corrosion phenomena.

Performance degradation occurs as a result of the decrease in heat exchange, caused by fouled heat-exchange surface and resulting in a smaller yield of heat gain from the fuel unit, and less efficient combustion process and an increased amount of hydrocarbon waste gases in exhaust.

An increase in emissions of nitrogen oxides (NO_x), sulphur oxides (SO_x), carbon monoxide (II) (CO), and particulate matter is also associated with the combustion of heavy fuel oil. Problems concerning the fuel oil combustion in boilers, depending on area and phase of its prevalence, can be classified as follows: pre-combustion zone, combustion zone and post-combustion zone (Tab. 4).

Table 4

Problems relating to operation in the various combustion zones [14]

Pre-combustion zone	Combustion zone	Post-combustion zone
Sludge, deposits plugging corrosion in storage and handling system	Formation of SO_x NO_x CO C_xH_y PM	Slagging deposits high- and low-temperature corrosion environmental problems

Most of the problems emerging in the burning zone are associated with the problems existing already in the pre-combustion zone. Similarly, the situation in case of environmental problems that dependens on the processes taking place in the combustion zone. The best conditions for an operating boiler can be obtained by applying of the catalysts in the pre-combustion and combustion zone.

Catalysts to improve the combustion process according to their course of action are classified in Table 4 in compliance with the operational problems of boilers presented in Table 5.

Table 5

The effect of catalysts depending on their functions [14]

Additives for improvement in pre-combustion zone	Additives for improvement in combustion zone	Additives for improvement in post-combustion zone
Fuel stabilisers	Combustion improvers	Corrosion inhibitors
Sludge reducers	SO_3 depressants	Deposits depressants
Solvents	NO_x reducers	Scavenging agents
Detergents	PM reducers	-
Pour-point dispersants	CO reducers	-
Flow improvers	-	-
Corrosion inhibitors	-	-
Acidity neutralisers	-	-
Demulsifiers	-	-

Whereas measures aimed at prevention related to low-temperature corrosion, catalysts should meet two basic functions. First of all should raise the melting point of ash components above the melting temperature of metals contributing to the low-and high-temperature corrosion. Such elements as sodium, vanadium, nickel and sulphur are meant. Secondly catalysts should modify the ash to more crumbled form, to facilitate easier removal of heating system.

Application of catalysts can help to reduce the low-temperature corrosion by preventing the origination of SO_3, neutralizing the acidity of sulfuric acid and protecting of surfaces susceptible to damage.

Application in the form of suspension of two catalysts based on magnesium and on an organometallic compound, contributes to limitation of the corrosion degree and to reduction of the amount of produced pollutants [15, 16].

Organometallic catalysts for burning of heavy fuel oils influence primarily the reduction of soot [17]. Catalysts are composed of organic chain and metal. Organic part gives the ability of homogeneous mixing with liquid hydrocarbons, while metal catalyzes the combustion process.

The efficiency of using of catalysts is significantly affected by such factors as: the operating conditions while boiler performance, the construction characteristics of the installation, the method of catalyst's batching and the properties of fuel.

Currently, there is a small quantum of scientific publications about catalysts for an improved process of fuel oil combustion [18÷20], therefore, more research in this direction is needed.

Catalyst for the combustion of solid fuels

The use of coal as an energy carrier is the reason of origination of inter alia: smog, acid rains and precipitation of particulate matter. The formation of soot, tar products and carbon monoxide is further conduced to the low oxygen content in the atmosphere. Concerning the wide use of coal as an energy source many kinds of catalysts to reduce the nuisance of that fuel combustion are developed.

Oxidation of tar products and soot in the place of their origination causes destruction of many by-products arising from incompleted combustion of coal which show an of carcinogenic, mutagenic and/or toxic activity. Next to carbon monoxide what should be mention are, first of all, polycyclic aromatic hydrocarbons (PAHs).

An important advantage resulted by limitation of soot pollution is minimizing of its ignition risk in ducts, what eliminates the cause of fire and damage to the structural elements of buildings. Further, the accumulation of soot on the walls of the installation results restricted chimney draught that causes an exhaust discharge from combustion chamber more difficult and increases the concentration of toxic gases in burnt gases. Effect of catalysts for reduction of CO_2 emission is based on improving of the process of oxidation CO to CO_2 and on ensuring the patency of the exhaust ducts [23].

The most commonly used solid fuel catalysts are copper compounds and sodium chloride. Introduction of NaCl to the medium positively affects the process of hard coal combustion. The optimal dose is set out at 7–8g NaCl/m^2 on the furnace surface. Catalyst is generating higher heating efficiency of installation and simultaneously reduces the emission of CO and NO_x into the atmosphere.

Moreover it has created an opportunity to reduce the coefficient of excess air number that is fed into the combustion chamber, and to reduce heat losses in the exhaust gases by about 12% [24]. Sodium chloride in conditions operating in the combustion chamber is partly decomposed in hydrogen chloride and sodium oxide. Hydrogen chloride reacts with oxides – chlorides of metals are forming a solid residue, which removal from the heating system is easier than removal of sintered oxides.

In turn, the use of ammonium chloride will protect the installation against low- and high-temperature corrosion. However, it is a source of chlorine for synthesis of toxic group of pollutants, inter alia dioxins.

Fossil fuels contain some amount of inorganic compounds, including chlorides of metals: copper, manganese, chromium, iron. These compounds catalyze many chemical reactions – therein synthesis of dioxins. Inhibitors introduced into the combustion zone may show reducing activity on already created pollutions. There is also ability to inhibit the origination of dioxins during synthesis through the application of inhibitor [23].

In Table 6 are compared two groups of substances, that ultimately contribute to reduction of dioxins level in exhaust gases.

A good example of an inhibitor is sulfur and its compounds presented in Table 6. They inhibit the synthesis of dioxin's as a result of transformation of $CuCl_2$ (the most efficient catalyst and at the same time the source of chlorine for the dioxin's synthesis) in a much less catalytic-active $CuSO_4$. Possible precursors for dioxin's synthesis: aliphatic and aromatic compounds located on surfaces of fly ashes evolved during combustion process. Dioxins originated in the presence of sulfur shows lower toxic properties.

Table 6

Chemical compounds affecting the dioxins standard in exhaust gases [23]

Inhibitors of dioxin's synthesis	Inhibitors of dioxin's synthesis
CaO	
ammonia	pyridine
ammonia sulfate, sodium sulfate	chinoline
sodium thiosulfate	urea
ammonium sodium phosphate	ethylene glycol
sulphur	amines
dolomite	EDTA

The introduction of a fitted modificator to the process of fuel combustion in industrial scale allows to reduce the amount of produced dioxins up to 90%. Simultaneously dioxin inhibitor due to its activity in the process of the DeNOx-may result in a reduction of the amount of emitted nitrogen oxides. Examples of chemical substances for outlined activity are urea and ammonia [25].

Another effective method of removing soot is procurement of a mixture of oxidants into the firebox. Thermal decomposition of inorganic salts such as nitrates(V) or manganates(VII) causes origination of oxygen with high reactivity, which oxidizes soot in a relatively low temperature. The advantage of this method of supporting combustion process is creation of large volume of gases as a result of decomposition of a small amount of introduced oxidants – these gases penetrates thoroughly contaminated surface, even in places, where mechanical cleaning is very onerous.

Catalysts having in its composition oxidants are less efficient than compositions enclosing salts of transition metals, in spite of the advantages described above. Transition metals are supporting soot oxidation processes by atmospheric oxygen derived from the air inserted into the combustion chamber. Organic and inorganic salts of copper ($CuCl_2$, $CuSO_4$, CuO • $CuCl_2$, copper naphthenate) are of great importance. High efficiency of catalyst, including a reduction of burnt gases in approximately 100°C has been achieved not only thanks to proper selection of ingredients but also refining of the grains of less than 100 μm.

Active substances in catalytic oxidation of carbon deposits are chemical compounds formed as a result of thermal decomposition of modifier. While disintegration of additive a CuO is formed, which acts as a catalyst in soot oxidation process and decreases, even by half, the temperature of its oxidation [26]. There are many components of catalysts composition for complete combustion of fuels known. To be most effective copper compounds are considered.

Study of catalyst based on a mixture of the of Cu and Mn oxides deposited on porous alumina points to a positive impact on the limitation of CO and particulate matter. That catalyst modified with titanium and zirconium oxides of high oxidative potential, indicates in the combustion chamber the possibility of emission reduction of above mentioned pollutants [27].

In the process of coal combustion, DESONOX – desulfurization and denitriding technology should be mentioned. The role of the carrier for a metallic catalyst of high dispersion is zeolite with synthetic origin. The idea of this process is based on the continual elimination of SO_3 from the operating system by binding it with furnace waste products of ash and slag type. Catalyst of DESONOX-type reduces the level of NOx in a reaction medium – determines the reduction of its content in waste gases through supporting of high temperature reactions of carbon monoxide intermediate oxidation by nitrogen oxides [28].

Summary

In view of the growing demand for liquid and solid fuels, and requirements of the European Union for environmental protection, catalysts and additives used for improved combustion process are absolutely wanted.

On the basis of the carried out literature review, it can be concluded that the use of additives and catalysts in fuel combustion processes reduces emissions of CO, SO_x, NO_x, particulate matter and PAHS into the atmosphere. Additives and catalysts also affect the combustion efficiency and prolong boiler operation, therefor these substances limit the costs associated with boiler maintaining. They also reduce the risk of high- and low-temperature corrosion of examined unit. In case of additives used for motor fuels they increase the research octane number, and hence reduce the risk of gasoline engine knocking and improve the operation of engine.

The efficiency of the application of catalysts is substantially affected by such factors as the method of catalyst's batching and the properties of fuel, as well as the performance of the boiler during operation and constructional features of the installation.

Literature

1. Serdiuk V.V., Serdiuk D.V., Askinazi L.A.: *Poprawa ekologicznych wskaźników pracy spalinowych silników tłokowych przez zastosowanie katalizatorów spalania.* Środkowo-Pomorskie Towarzystwo Naukowe Ochrony Środowiska 2008, **10**, 399–411.
2. Arteconi A., Mazzarini A., Di Nicola G.: *Emissions from ethers and organic carbonate fuel additives: A review.* Water Air Soil Pollut 2011, **221**, 405–423.
3. Ren Y., Huang Z., Miao H., Di Y., Jiang D., Zeng K.: *Combustion and emissions of a DI diesel enigine fuelled with diesel-oxygenate blends.* Fuel 2008, **87**, 2691–2697.
4. Lu X., Zhang J., Zhang W., Huang Z.: *Improving the combustion and emission of a direct injection compression ignition engines using oxygenated fuel additives combined with cetane improver.* Energy Fuels 2005, **19**, 1879–1888.
5. Schifter I, Diaz L. Vera M., Guzman E., Lopez-Salinas E.: *Fuel formulation and vehicle exhaust emission in Mexico.* Fuel 2004, **83**, 2065–2074.
6. Song C., Zhang W., Pei Y., Fan G., Xu G.: *Comparative effects of MTBE and ethanol additions into gasoline on exhaust emissions.* Atmospheric Environment 2006, **40**, 1957–1970.
7. Baur C., Kim B., Jenkins P.E., Cho Y.S.: *Performance analysis of a SI engine with ETBE as a blending component in motor gasoline and comparison with other blending components.* Energy Conversion Engineering Conference. Proceeding of the 25th Intersociety 1990, **4**, 337–342.
8. Nibin T., Sathiyagnanam A.p., Sivaprakasam S., Saravanan C. G.: *Investigation on emission characteristic of a diesel engine using oxygenated fuel additive.* IE (I) Journal 2005, **86**, 51–54.
9. Zannis T.C., Hountalas D.T.: *DI diesel engine performance and emission form the oxygen enrichment of fuel with various aromatic content.* Energy Fuels 2004, **18**, 659–666.
10. Yanfeng G., Shenghua L., Hejun G., Tiegang H., Longbao Z.: *A new diesel oxygenate additive and its effects on engine combustion and emission.* Applied Thermal Engineering 2007, **27**, 202–207.
11. Dabbagh H.A., Ghobadi F., Ehsani M.R., Moradmand M.: *The influence of ester additives on the properties of gasoline.* Fuel 2013, **104**, 216–223.
12. Keskin A., Gürü M., Altiparmak D.: *Influence of metallic based fuel additives on performance and exhaust emissions of diesel engine.* Energy Conversion and Management 2011, **52**, 60–65.
13. Lenin M.A., Swaminathan M.R., Kumaresan G.: *Performance and emission characteristics of a DI diesel engine with a nanofuel additive.* Fuel 2013, **109**, 362–365.
14. Prelec Z., Mrakovcić T., Dragicević V.: *Performance study of fuel oil additives in real power plant operating conditions.* Fuel Processing Technology 2013, **110**, 176–183.
15. Barroso J., Barreras F., Ballester J.: *Behavior of a high-capacity steam boiler using heavy fuel oil, part 1, high-temperature corrosion.* Fuel Processing Technology 2004, **86**, 89.
16. Barreras F., Barroso J.: *Behavior of high-capacity steam boiler using heavy fuel oil, part 2, cold-end corrosion.* Fuel Processing Technology, 86, str. 107, 2004.
17. Somasundaram G., Sunavala P.D.: *Suppression of soot in the combustion of residual furnace oil using organometallic additives.* Fuel 1989, **68**, 921.
18. Kaźmierczak M.: *Całkowite utlenianie organicznych związków siarki.* Przemysł Chemiczny 2003, **82**, 1029.
19. Kők M.V., Iscon A.G.: *Catalytic effects of metallic additive on the combustion properties of crude oils by thermal analysis techniques.* Journal of Thermal Analysis and Calorimetry 2003, **64**, 1311.
20. Paullikkas A.: *Cost-benefit analysis for the use of additives in heavy fuel oil fired boilers.* Energy Conversion and Management 2004, **45**, 1725.
21. Tic W. J.: *Metal Salts as the Homogeneous Catalysts for an Effective Combustion of Liquid Fuels.* Polish Journal of Environmental Studies 2008, **17**(3), 439.
22. Zvereva E.R., Ganina L.V.: *Effects of additives on the working properties of furnance heavy fuel oil.* Chemistry and Technology of Fuels and Oil 2009, **45**(5), str. 349.
23. Chyc M.: *Znaczenie dodatków paliwowych w procesach spalania paliw stałych.* Prace naukowe GIG górnictwo i środowisko 2012, **1**, 5–16.
24. Szkarowski A., Naskręt L.: *Poprawa efektywności i jakości warstwowego spalania paliwa.* Magazyn Instalatora 2011, **2**, 150, 24–25.
25. Long H.M., Li J.X., Wang P., Gao G., Tang G.W.: *Emission reduction in iron ore sintering by adding urea as inhibitor.* Ironmaking&Steelmaking 2011, **38**(4), 258–262.
26. Katalizator do spalania sadzy, zgłoszenie patentowe nr nr 365431, RP.
27. Doggalia P., Kusabab H., Einagab H., Bensaidc S, Rayalua S., Teraokab Y., Labhsetwara N.: *Low-cost catalysts for the control of indoor CO and PM emissions from solid fuel combustion.* Journal of Hazardous Materials 2010, **186**, 796–804.
28. Nazimek D.: *Kataliza i katalizatory w ochronie środowiska.* Przemysł Chemiczny 2006, **85**, 8–9, 1058–1060.

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