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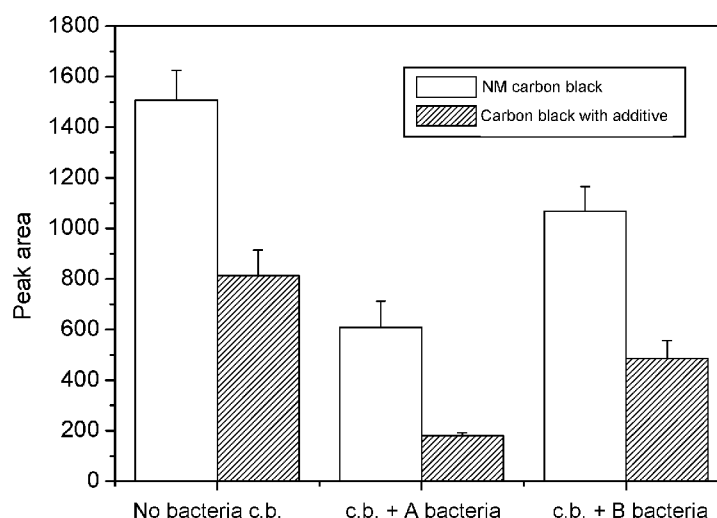
(54) **Title:** ECOLOGICAL SOLID FUEL ADDITIVE, REDUCING SOOT FORMATION

Fig.1

(57) **Abstract:** The invention concerns the ecological fuel additive, composed of triferric tetroxide, nitrates containing 30-60% in weight of triiron tetroxide (Fe_3O_4), 10-30% in weight of potassium nitrate(V) (KNO_3), sodium nitrate (V) (NaNO_3), ammonium nitrate(V) (NH_4NO_3), or mixture of the abovementioned nitrates(V), 5-30% in weight of sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$) and 10% in weight of anti-caking agent. Advantageously, the anti-caking agent is powdered burnt clay and Fe_3O_4 used for production of fuel additive is free from FeSO_4 . The solid fuel additive according to the invention is ecological thanks to this that the production of carbon black and toxic compounds present in carbon black is reduced.

Ecological solid fuel additive, reducing soot formation

The subject-matter of the invention is the ecological solid fuel additive, reducing soot formation. The fuel additive for soot combustion applied in operations of hard coal, lignite, fine coal, coke, anthracite, peat, pellets, coal briquettes and wood-burning furnaces as well as low, medium and high efficiency furnaces and boilers.

To this moment, the fuel additives, chemical composition of which could produce corrosion of steel and ceramic components of the heating installation or contribute to increased release of toxic pollutants formed in the combustion process, have been used.

There are certain fuel additives containing the mixtures of inorganic and organic soils, primarily chlorides and transition metal compounds, for the most copper, known.

The effective fuel additive allowing for reduction by deposit volume at the exchanger by 45-55% is known from the Chinese patent CN 1010483. The fuel additive is a mixture of potassium nitrate (60-80%), ammonium nitrate, triiron tetroxide (0.1-1.0%), charcoal, borax, trisodium phosphate as chelating agent, magnesium, aluminum, sodium chloride and powdered sulphur. The additive is used in household and industrial installations and industrial coal-burning boilers. The additive modifies chemical and physical soot properties improving at the same time heating efficiency of the heat exchanger. The fuel additive is decomposable in 485°C, forming a coating on the heat exchanger surface and protecting it against corrosion. Coal additive to coal of low calorific value known from the Chinese CN 103305313 patent description contains 20-100% of active substance. Mixture of active substances contains 30-80% in weight of calcium cobaltite ($\text{Ca}_3\text{Co}_4\text{O}_9$), 0-30% in weight of triiron tetroxide (Fe_3O_4) and cerium dioxide (CeO_2) and potassium oxide of several percents in weight. The fuel additive revealed in this invention decreases the fuel ignition temperature by 3-15°C, enhancing the combustion effectiveness and making coal combustion with fuel additive less polluting to the air comparing to fuel combustion without the fuel additive.

The soot combustion catalysts containing copper sulphate, sodium chloride and ammonium chloride are known from PL 207482 and PL 165406 patent description. Despite its advantages in combustion of lesser quantities of coal and lower risk of carbon deposits ignition in the flue pipes, this is not environmentally safe operation.

The ecological aqueous liquid fuel additive containing among others hydrated fusel oils and ethyl alcohol is known from Polish patent PL 202335.

The solid biomass additive containing among others the carboxylic acid salts and one or more metals from among the alkaline earth, lanthanide and ferrous metals; fatty acid esters and fatty

acids or acidic resins, is known from the EP 0 725 128 B1 patent. The fatty acid esters are, advantageously, methyl esters, in particular of rape oil esters. The described additive enhances mechanical properties of biomass in the course of processing and reduces production of toxic fumes. The disadvantage of the described solution is no opportunity to apply the additive to any other fuels than pulverized one.

Known fuel additives may be harmful to the environment (copper and chlorine compounds), cause excessive corrosion of boiler and flue pipes (chloride and sulphur compounds, fatty acid oxy-degradation products) and have pathogenic effect (cerium compounds).

Despite numerous research and attempts to solve the problem of ecological fuel combustion and soot formation, smog and damages to the environment, the quest for enhanced additive ensuring more effective and safer to the environment fuel consumption has been continued.

The subject-matter of the invention is the ecological solid fuel additive, composed of triiron tetroxide, nitrates, most frequently potassium nitrate(V) containing 30-60% in weight of triiron tetroxide (Fe_3O_4), 10-30% in weight of potassium nitrate(V) (KNO_3), sodium nitrate(V) (NaNO_3), ammonium nitrate(V) (NH_4NO_3), or mixture of the abovementioned nitrates(V), 5-30% in weight of sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1,5\text{H}_2\text{O}_2$) and 10% in weight of anti-caking agent.

Advantageously, the anti-caking agent is powdered burnt clay.

Advantageously, Fe_3O_4 used for fuel additive production is free from FeSO_4 .

Advantageously, soot production and toxic compounds present in soot is limited.

Ecological solid fuel additive reducing soot production presented in the invention is a proposal for environment-friendly solid fuel combustion, preventing environmental contamination with soot accompanying pollutants such as: polyaromatic hydrocarbons (PAH), persistent organic radicals and heavy metals, whereas reduction of carbon black production prevents additionally the excessive fuel consumption (carbon black decreases the heating efficiency of a boiler) and increases combustion effectiveness.

Solid fuel additive according to the invention is characterized by that it contains 30-60% in weight of triiron tetroxide (Fe_3O_4), 10-30% in weight of potassium nitrate(V) (KNO_3), sodium nitrate(V) (NaNO_3), ammonium nitrate(V) (NH_4NO_3), or mixture of the abovementioned nitrates(V), 5-30% in weight of sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1,5\text{H}_2\text{O}_2$) and 10% in weight of anti-caking agent e.g. powdered burnt clay.

It is important that Fe_3O_4 used for fuel additive production is free from FeSO_4 (FeSO_4 may act as the raw material for Fe_3O_4 production, which explains its presence). FeSO_4 presence in small quantities does not change the activity of fuel additive towards reducing the carbon black production, however carbon black obtained in presence of even small quantities of FeSO_4 is significantly less biodegradable (negative environmental impact).

The additive according to the invention, introduced to the combustion chamber with fuel or at the surface of the combusted fuel, is subject to partial thermal decomposition and releases the large volume of gaseous products. Fuel additive components are activated in the temperature range of 80-650°C. Gaseous products of nitrates and sodium percarbonate decomposition reaction transport part of Fe_3O_4 quantity onto the carbonaceous deposit surface covering the heat exchanger. Fe_3O_4 particles in contact with heated fuel reach high temperature and then are transported on the carbonaceous deposit surface along with flue gas, where using its energy and catalytic oxidation properties catalyze the reaction of complete and total fuel combustion for hours.

Thermal decomposition of nitrates(V) is connected with production of atomic oxygen, which, at the moment of production (*in statu nascendi*) is highly reactive thanks to which it may easily oxidize the carbon black deposits covering the heat exchanger.

Decomposition of sodium percarbonate produces the peroxide and hydroxyl radicals, which, by means of chain reactions, are able to initiate the carbon black oxidation reaction.

Advantageously, application of fuel additive results in significant lowering of carbon black oxidation temperature. When applying the said fuel additive, carbon black, thanks to lowering the energy of oxidation initiation in low-oxygen atmosphere, begins combustion in temperature of 300°C, whereas in the process without added fuel additives this temperature is >700°C.

Apart from decreasing the quantity of carbon black produced in the fuel combustion process, the chemical composition of the produced carbon black changes advantageously, in effect of which it contains less harmful substances. Modification of the composition in result of application of the ecological fuel additive facilitates biodegradation of substances contained in the carbon black, including cancerogenic polyaromatic hydrocarbons (PAH).

The additive according to the invention should be used in quantity of 0.5-2 kg per 1000 kg of fuel, advantageously 1.2 kg per 1000 kg of fuel in the case of application of additive in mixture with fuel. Chemical composition of the additive is decisive for its value, however its dose i.e. weight proportion of the additive to fuel unit (1000 kg) is almost of equal

importance. During periodical application, the sufficient quantity is 50 g of additive in weekly intervals. In the cases of tendency of the heat exchanger to intensive covering with deposits resulting from quality of combusted fuel or the structure of heating installation, it is necessary to increase the fuel additive dose or its more frequent application.

Thanks to the fact that the ferrous compounds, in opposite to copper compounds, are not as toxic to the environment, the additive and produced carbon black is more environment-friendly. Combustion is more complete and produces less waste and smaller quantities of carbon black, which is additionally less toxic. There is also more energy produced. Solid fuel additive (coal, briquettes, etc.) according to the invention is a better ecological product than the additives in the composition, containing also: copper, chlorine, sulphur or fatty acids.

The most significant pro-ecological effect of the fuel additive according to the invention is reduced carbon black production i.e. cancerogenic substance causing a greenhouse effect, carrier of polyaromatic hydrocarbons, stable organic radicals and heavy metals. Carbon black is also a pathogenic agent (circulatory and respiratory system diseases). Carbon black is a chemical and physical pollutant of air, water and soils, therefore its reduction constitutes a significant component of air protection programmes as well as the low emission reduction programmes (LERP). It is known that soot is a powerful absorbent of sunlight and contributes to climate warming and melting of glaciers covered with so called dry deposition (particulates) causing the greenhouse effect. Ecological effect of the additive according to the invention results also in lowering the combustion temperature and quantity of produced combustion gases, whereas the limited amount of produced soot is both less toxic and its components are biodegradable, and demonstrates the properties stimulating plant growth, including biomass increase.

To summarize, upon application of fuel additive according to the invention, less carbon black is produced, and the produced carbon black has different composition comparing to carbon black produced upon application of commercially available fuel additives or without their application, which makes it significantly less toxic i.e. more ecological.

To illustrate the solution according to the invention, a figure was enclosed, on which:

Figure 1 presents comparison of the content of the total of 4 components of soot sample determined using the HS-GC-MS method in the soot biodegradation studies of two carbon black types;

Figure 2 presents the impact of carbon black (5% v/v) on the rate of occurrence of visible cotyledons of *A. thaliana*. NM carbon black – carbon black without fuel additive, B carbon black – carbon black with added commercially available additive containing significant quantities of NaCl and copper, A carbon black – carbon black with fuel additive according to the invention;

Figure 3 presents the impact of carbon black (5% v/v) on the rate of occurrence of the first leaf pair of *A. thaliana*. NM carbon black – carbon black without fuel additive, B carbon black – carbon black with added commercially available additive containing significant quantities of NaCl and copper, A carbon black – carbon black with fuel additive according to the invention;

Figure 4 presents the impact of the studied types of carbon black (5% v/v) on mass increase of *A. thaliana* upon 2 and 4 weeks of cultivation. NM carbon black – carbon black without fuel additive, B carbon black – carbon black with added commercially available additive containing significant quantities of NaCl and copper, A soot – carbon black with fuel additive according to the invention;

Figure 5 presents the impact of the tested soot types (5% v/v) on pigment content in *A. thaliana* upon 4 weeks of cultivation. NM carbon black – carbon black without fuel additive, B carbon black – carbon black with added commercially available additive containing significant quantities of NaCl and copper, A carbon black – carbon black with fuel additive according to the invention;

Figure 6 presents the graph of *A. thaliana* superoxide dismutases (SOD) activity upon native electrophoresis and histochemical staining of control plant homogenates (NM carbon black – carbon black without fuel additive, A carbon black –with newly-invented fuel additive, B carbon black – carbon black with added commercially available additive containing significant quantities of NaCl and Cu compounds);

Figure 7 presents the graph of fuel additive composition optimization – cubic model verification;

Figure 8 presents TGA and DSC thermograms of carbon black and carbon black with fuel additive samples;

Figure 9 presents the DP thermogram (red line - DSC, black line - TGA);

Figure 10 presents the thermovision image of Hercules auxiliary furnace (upon 8h from ignitron), whereas Figure 11 presents the thermovision image of SAS MI fine-coal auxiliary furnace (upon 10 hours from ignition).

The subject-matter of the invention is presented by the following examples of embodiment.

Example 1.

The additive containing the following was obtained:

triiron tetroxide	45 parts by weight
sodium percarbonate	30 parts by weight
potassium nitrate	15 parts by weight
powdered burnt clay	10 parts by weight

Upon mixing the components the fuel additive was obtained. The additive was introduced onto the surface of combusted fuel in coal boiler of 29 kW capacity. Quantity of carbon black covering the heat exchanger decreased 8 times, comparing to analogous combustion conditions without the additive. Thanks to this the chimney heat losses were reduced and fuel consumption was decreased. Soot deposited on the heat exchanger has lower carbon content and higher mineral component content (fly ash), comparing to carbon black produced during fuel consumption without the fuel additive. Application of fuel additive enables easier removal of deposits from heat exchanger. In addition it was observed that application of fuel additive reduces emission of nitrogen oxides in the flue gas.

Example 2.

Carbon black composition

Carbon black composition on the basis of elementary analysis was as follows:

Carbon black produced upon combustion of coal with no additives: 50.54% in weight of coal, 7.93% in weight of hydrogen and 4.65% in weight of nitrogen.

Carbon black upon application of fuel additive: coal 39.60% in weight, hydrogen 10.92% in weight, nitrogen 5.39% in weight.

Carbon black composition upon application of commercially available fuel additive based on CuSO_4 and NaCl : coal 44.66%, hydrogen 7.47%, nitrogen 5.01% (in weight).

The remaining components include non-organic matter (fly ash).

Example 3.

The additive containing the following was obtained:

triiron tetroxide	45 parts by weight
sodium percarbonate	30 parts by weight

potassium nitrate	15 parts by weight
powdered burnt clay	10 parts by weight

Upon mixing the components the fuel additive was obtained. The additive was introduced onto the surface of combusted fuel in coal boiler of 29 kW capacity. Quantity of carbon black covering the heat exchanger decreased 8 times, thanks to which the chimney heat losses were reduced and fuel consumption was decreased. Soot deposited on the heat exchanger has lower carbon content and higher mineral component content (fly ash), comparing to carbon black produced during fuel consumption without the fuel additive, which enabled easier removal of deposits from heat exchanger. In addition it was observed that application of fuel additive reduces emission of nitrogen oxides in the fumes.

Example 4.

The additive containing the following was obtained:

triiron tetroxide	30 parts by weight
sodium percarbonate	20 parts by weight
potassium nitrate	40 parts by weight
powdered burnt clay	10 parts by weight

Upon mixing the components the fuel additive was obtained. The additive was introduced onto the surface of combusted fuel in coal boiler of 29 kW capacity. Quantity of carbon black covering the heat exchanger decreased 5 times.

Example 5.

The additive containing the following was obtained:

triiron tetroxide	30 parts by weight
sodium percarbonate	30 parts by weight
potassium nitrate	30 parts by weight
powdered burnt clay	10 parts by weight

Upon mixing the components the fuel additive was obtained. The additive was introduced onto the surface of combusted fuel in coal boiler of 29 kW capacity. Quantity of carbon black covering the heat exchanger decreased 5 times.

In the description of the biological tests the following expression was used:

‘carbon black produced in result of combustion with fuel additive according to the invention’, which means carbon black produced with the additive being the subject-matter of the invention.

The other types of carbon black used in the description include:

1. non-modified carbon black i.e. produced with no additive (catalyst);
2. carbon black with fuel additive available on the market, however based on NaCl and copper (name not provided on purpose). The additive according to the invention, in contrary to the other additives available on the market, is based on iron compounds, more environmental friendly comparing to copper compounds demonstrating specific toxicity to environmental microflora.

Biological interactions of carbon black produced in result of combustion with fuel additive according to the invention in solid-fuel burning boilers.

Example 6.

Studying the impact of carbon black produced in result of combustion with the invented fuel additive on soil bacteria

In conical flasks (labelled A and B) of 100 ml volume containing 50 ml sterile liquid nutrient medium LB MIX (Table 1) each, the culture of two common soil bacteria: *Pseudomonas aeruginosa* – flask A and *Bacillus subtilis* – flask B was established.

Table 1. Composition of liquid nutrient medium LB MIX used for bacteria culture (pH – 7.00)

Composition	Mass [g/l]
Casein peptone	10.00
Yeast extract	5.00
Sodium chloride	10.00

The study on the impact of carbon black produced with the invented fuel additive and carbon black produced in result of combustion with no additive on common soil microorganisms - *Pseudomonas aeruginosa* and *Bacillus subtilis*. The study was performed for two concentrations (w/v) of carbon black in the nutrient medium i.e. 0.30% and 6.00%. All tests were repeated 10 times. In the case of both bacterial strains, regardless of type and concentration of carbon black, bacteria growth was observed. Thanks to the applied dilutions,

carrying-out of the quantitative tests was possible. Average number of grown bacterial cultures in each analyzed case at the highest dilution of the culture suspension was 9 ± 4 .

With regard to the above, application of fuel additive according to the invention is advantageous, since despite higher efficiency of solid fuel combustion, including decreased carbon black quantity, toxicity of this carbon black to the tested soil microorganisms does not increase.

Example 7.

Testing the soil bacterial capacity for biodegradation of the selected toxic components of carbon black with the invented fuel additive.

The tests were carried out with the use of two types of carbon black (carbon black produced in result of combustion with the invented fuel additive and non-modified carbon black (NM carbon black)) as well as *Pseudomonas aeruginosa* (A) and *Bacillus subtilis* (B) bacteria. Samples of each type of carbon black were grinded carefully in the mortar and 0.20 g to each conical flask of 100 ml volume was weighted out. Then each flask was filled with 50 ml of BSM mineral nutrient medium containing no carbon source (Table 2).

Table 2. Composition of BSM mineral nutrient medium containing no carbon source (pH 7.00)

Composition	Mass [g/l]
Potassium dihydrogen phosphate(V)	0.38
Dipotassium phosphate(V)	0.60
Magnesium sulfate heptahydrate(VI)	0.20
Ammonium chloride	1.00
Iron(III) chloride hexahydrate	0.08

The flasks with BSM nutrient medium and relevant type of carbon black were placed in the batch retort. After sterilization one of each type of the flasks with relevant type of carbon were left as control sample (no bacteria), whereas the remaining two containing the same type of carbon black were filled with the same amount of cells of one of two bacterial strains (A or B, the principle of standardization of the number of cells in inoculum was described in Example 6). The cultures were kept in darkness to prevent possible photolysis of sample components and incubated for 4 weeks (30°C, RPM 150). The test was repeated 10 times.

Upon completion of cultivations, 15 µl was sampled from each solution and streaked on LB MIX agar medium to verify, whether the inoculated organisms survived the incubation period.

The remaining part of the solutions were filtered using the Buchner funnel under decreased pressure via hard filters (degree: 390, weight: 84 g/sq m), selected with regard to the most effective recovery of carbon black from the solutions and the materials, from which these were produced (possibly resistant to high temperature e.g. 150°C used in *headspace* (HS) technique, consisting in analysis of gas phase above the solid or liquid sample). The filters were placed in glass vials and left for drying in ambient temperature for 5 days and then closed tightly.

Analogously, the control samples i.e. containing the relevant type of carbon black however with no bacteria added, were filtered. All residues on the filters and weighted portions of carbon black were analyzed using the Headspace Gas Chromatography/Mass Spectrometry (HS-GC-MS) after app. 15 minutes of vials thermostating in temperature 150°C directly before inoculation (50 µl). The dispenser temperature was set to 250°C, carrier gas stream proportion (helium) was 10:1, column flow was 1 ml/min, whereas linear speed amounted to 36 cm/sec. The analysis used the programmable temperature change method: 60°C for 1 minute, temperature increase by 10°C/minute until the maximum temperature of 250°C (maintained for 1 minute) was reached. The analyses were carried out with the use of capillary column HP-1 MS (Agilent Technologies) of 30 m length, 0.25 mm diameter and 1µm film thickness. The transfer line was maintained in temperature of 250°C, MS source temperature was 230°C, whereas quadrupole temperature was 150°C and dwell time - 100 ms.

Cumulative content of phenol ($m/z = 94$, RT = app. 7.78 min.), naphthalene ($m/z = 128$; RT = app. 10.04 min.), phenanthrene ($m/z = 178$; RT = app. 17.67 min.) and anthracene ($m/z = 178$; RT = app. 17.79 min.) was determined in the samples. The results of determination of the total of 4 selected polyaromatic hydrocarbons demonstrate the changes in the carbon black structure (Fig. 1).

The phenol, naphthalene, phenanthrene and anthracene biodegradation rate without the fuel additives and with the ecological fuel additive was researched. The highest biodegradation rate of the determined pollutants was observed for the samples of carbon black produced with the use of additive according to the invention, with added *P. aeruginosa* (A) ($77.9 \pm 3.2\%$), followed by *B. subtilis* (B) ($40.2 \pm 2.8\%$). In the case of non-modified carbon black, this rate amounted to $59.7 \pm 2.7\%$ for the culture with *P. aeruginosa* bacteria and $29.2 \pm 1.6\%$ for *B. subtilis*, respectively. In addition, it was observed that the primary samples of carbon black

produced with fuel additive according to the invention contained significantly lower quantity of determined compounds comparing to non-modified carbon black.

Application of fuel additive according to the invention is thus advantageous, since higher efficiency of solid fuel combustion, including decreased carbon black quantity, is accompanied by lower amount of toxic compounds in the produced carbon black comparing to the carbon black produced with no additive, and these compounds are easier biodegradable by common soil bacteria and do not increase mortality of these bacteria.

Example 8.

Studying the impact on carbon black produced in result of combustion with the invented on the selected physiological – biochemical parameters of plants

The impact of carbon black produced with the invented fuel additive on such physiological – biochemical parameters of plants as:

- a) seed germination;
- b) plant growth,
- c) biomass production,
- d) photosynthetic pigment concentration;
- e) anti-oxidative enzyme activity

was examined.

The tested plant was thale cress (*Arabidopsis thaliana*). *Arabidopsis thaliana* is a model plant commonly used in genetic tests (known genome) as well as biochemical, physiological and toxicological tests (certain standards in the area of assessment of different pollutants' phytotoxicity, including PAH recommend this species). Recently, the new methods of the use of this plant in the initial drug testing have been developed – to reduce the number of animal testing.

The plant was subject to the activity of three types of carbon black:

- carbon black produced with the invented additive (A carbon black);
- carbon black with the additive available on the market, produced with the use of sodium chloride and significant quantities of copper salt (B carbon black) (components present in vast majority of fuel additives available on the market);
- carbon black produced with no additive (NM carbon black).

The tests were carried out in sterile conditions, *in vitro*, and the plants were cultivated on the Gamborg B5 agar nutrient medium (Table 3).

Table 3. Composition of Gamborg B5 nutrient medium

Composition	Concentration [μM]	Concentration [mg/l]
Vitamins		
mio-inositol	555.1	100.0
thiamine-HCl	29.6	10.0
nicotinic acid	8.1	1.0
piridoxine-HCl	4.9	1.0
Mineral soils		
NaH ₂ PO ₄ · H ₂ O	1100.0	150.0
CaCl ₂ · 2H ₂ O	1000.0	150.0
MgSO ₄ · 7H ₂ O	1000.0	250.0
(NH ₄) ₂ SO ₄	1000.0	134.0
FeSO ₄ · 7H ₂ O	100.0	27.8
Na ₂ EDTA 2H ₂ O	100.0	37.3
MnSO ₄ · H ₂ O	60.0	10.0
H ₃ BO ₃	50.0	3.0
ZnSO ₄ · 7H ₂ O	7.0	2.0
KI	4.5	0.75
Na ₂ MoO ₄ · 2H ₂ O	1.0	0.25
CuSO ₄ · 5H ₂ O	0.1	0.025
CoSO ₄ · 6H ₂ O	0.1	0.025

Apart from control plants (not treated with carbon black), the plants were subject to the following concentrations of each of the tested carbon blacks: 1.25; 2.5; 5% (v/v) or only the highest of them.

Arabidopsis thaliana seeds were sterilized as follows in the eppendorf test-tube:

- seeds shaken for 1 minute in 70% ethanol solution;
- ethanol was eliminated and the seeds were treated in 10% ACE solution for 7 minutes with continuous mixing;
- upon elimination of ACE solution, the seeds were washed four times with sterile de-ionized water in the following sequence: 1x1minute + 3x5 minutes.

Upon sterilization, 10 seeds were planted on the Gamborg 5B nutrient medium and upon germination, depending on the experiment, analyzed and/or transmitted to sterile jars with the same medium – two plants to each jar. The plants were cultivated in the light of 80 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ intensity and photoperiod of 14h of light/10h of darkness.

a) carbon black impact on seed germination

In the first days of culture, seed germination rate and growth rate of control plant seedlings has not deviated significantly from the germination rate on the nutrient media containing carbon black, regardless of the type of applied carbon black (Fig. 2). One should emphasize that in the case of carbon black with the invented fuel additive, starting from the third day of the experiment, the percentage rate of the best-grown seedlings was the highest both among the tested carbon blacks and slightly exceeded the control cultures.

The similar results were obtained when analyzing further growth of seedlings. However the percentage rate of the plants treated with A and B carbon black was the lowest in the first day of occurrence of the first leaf pair among all analyzed samples, upon two days the percentage rate of plants with the formed first leaf pair among the plants treated with carbon black was the highest in the case of A carbon black (with additive according to the invention), and upon the next two days, the average experimental value did not differ from the value recorded for control, however the plants treated with A carbon black featured more repeatable values (their distribution was significantly narrower comparing to all tested samples, including the control sample) (Fig. 3).

Application of the additive according to the invention is advantageous, since the carbon black produced in the presence thereof both has no inhibiting effect on the number of germinated seeds and features properties stimulating growth of the young seedlings.

b) impact of carbon black on growth of overground parts of the plants

Growth of overground part of the plant was measured in 7th and 14th day of culture. The measurement was performed along the plant from the highest point of cotyledon or plant leaves, to the part of stem bordering the nutrient medium.

The results of the experiment demonstrating that the plants cultivated on the nutrient media containing A carbon black (with fuel additive according to the invention) reached the greatest height. This was also the only carbon black, increase of content of which in the nutrient medium resulted in the intensified growth of the plant. Upon 7 days of culture, average height of plants treated with carbon black produced in result of application of the fuel additive according to the invention, exceeded the control plants by, respectively:

- 17% at 1.25% (v/v) content of carbon black in the nutrient medium),
- 37% (at 2.5% (v/v) content of carbon black in the nutrient medium)
- 60% (at 5% (v/v) content of carbon black in the nutrient medium).

Upon 14 days of the experiment, the plants cultivated on nutrient media containing A carbon black (with fuel additive according to the invention) reached greater height. Average height of plants treated to NM carbon black, at the highest content of this carbon black in the nutrient medium (5% v/v), was higher from control plants (not treated with carbon black) by 55%. However, upon the next 7 days, growth rate of plants subject to the highest concentration of this carbon black decreased significantly and these plants exceeded the control plants only by app. 35%, whereas the plants treated with carbon black with the additive according to the invention exceeded the control plants by 70% and remained the highest plants among all plants tested in the experiment.

The plants cultivated on the nutrient medium with B carbon black (produced with the commercially available fuel additives), however higher than the control plants, featured weaker growth among the plants treated with three types of carbon blacks. In addition, average height of *A. thaliana* cultivated in presence of this carbon black decreased along with its increasing concentration in the nutrient medium, in effect of which upon 14 days, at the highest concentration of carbon black, the plant height exceeded the control plants only by 5%.

Application of the additive according to the invention is advantageous, since carbon black produced in the presence thereof, in the case of growth of green parts of the plant, demonstrates clear fertilizing properties.

c) impact of carbon black on biomass production

The results of the experiment demonstrated that both upon two and four weeks of observation among the plants treated with carbon black, the highest average mass (converted into single plant) was recorded in plants growing in presence of carbon black A (with the additive according to the invention). Average mass of these plants at lower concentrations of carbon black A (1.25% and 2.5%) was in all tested types of carbon black the most approximated to mass of control plants, however, as in the case of each type of carbon black, lower than the control value. For the highest concentration of carbon black A (5% v/v), mass of tested plants upon 4 weeks of the experiment exceeded the mass of control plants by more than 30% (Fig. 4).

It is advantageous to use the additive according to the invention, since the carbon black produced in the presence thereof demonstrates visible fertilizing properties in plant biomass production.

d) impact of carbon black on photosynthetic pigments content

Composition of the most important group of photosynthetic pigments, i.e. chlorophyll a, b and carotenoids, was analyzed. These pigments are necessary for proper course of photosynthesis and condition the effective conversion of luminous energy into hydrocarbons. Pigments deficiencies or irregularities in their proportion decrease the photosynthetic efficiency and therefore widely-understood plant production.

Pigment content was measured in four-week leaves of *A. thaliana* by sampling 4 leaves from each plant, homogenization and extraction of pigments with 80% (v/v) acetone solution.

To calculate the pigment content, absorbance of the obtained extract was measured using the Jasco V-650 spectrophotometer at the following wavelengths: 662nm, 645nm and 470nm (Lichtenthaler method, 1987):

$$c_{chlA} = 11.75A_{662} - 2.35A_{645} \text{ [}\mu\text{g/1 ml of extract]}$$

$$c_{chlB} = 18.61A_{645} - 3.96A_{662} \text{ [}\mu\text{g/1 ml of extract]}$$

$$c_{kar} = (1000A_{470} - 2.27c_{chlA} - 81.4c_{chlB}) : 227 \text{ [}\mu\text{g/1 ml of extract]}$$

The obtained results were converted into pigment content in 1g of fresh leaf mass (Fig. 5)

Excluding the plants growing in presence of carbon black with commercially available fuel additive (B carbon black), the proportions of individual pigments were correct. The plants growing in presence of B carbon black featured definitely deficient chlorophyll and carotenoids content, which may be decisive for their low productivity (low growth and biomass). The highest pigment content was observed in plants growing on the nutrient medium with carbon black with additive according to the invention (carbon black A).

The additive according to the invention stimulates plant photosynthetic pigment production, including valuable for health carotenoids, which is advantageous in context of plant growth, productivity and nutritive values.

e) impact of carbon black on anti-oxidative enzymes activity

Impact of A, B and NM carbon blacks on the activity of anti-oxidative enzymes was studied on 8-week plants. The tested enzymes were superoxide dismutases (SOD), being the metalloproteins protecting the cellular structures against oxidative stress. Depending on the bonded co-factor, they may have the form of copper/zinc, iron or manganese dismutases. *A. thaliana* contains the genes of all the above-mentioned forms. Copper/zinc dismutases (CuZnSOD) are localized primarily in the chloroplasts, peroxisomes and cytosol, whereas Iron dismutases (FeSOD) are present in chloroplasts and manganese dismutases (MnSOD) in mitochondria and peroxisomes (Kliebenstein *et al.* 1998, Małecka & Tomaszewska 2005).

Enzyme activity was tested using the native electrophoresis with histochemical staining method. Electrophoresis was carried out on polyacrylamide gels (11.6% (bottom) and 0.8% (upper)) at 180V in 4°C. Upon electrophoresis, the gels were subject to 30-minute staining to detect SOD activity (Miszański *et al.* 1998).

It was demonstrated that the plants treated with A carbon black presented no differences in context of isoform activity comparing to control plants and plants subject to NM carbon black. In all these plants, a dominating SOD isoform was iron dismutase (FeSOD). It was stated that in the plants treated with carbon black with additive according to the invention, as well as in plants treated with NM carbon black, activity of FeSOD isoform does not depend on carbon black concentration. Activity of the remaining isoforms i.e. MnSOD or CuZnSOD in plants treated with A carbon black, NM carbon black and control plants remains at similar and very low level, which makes the enzymatic profile of plants treated with A, NM carbon black and control plants in context of SOD activity identical (Fig. 6).

In the case of plants treated with B carbon black, a rapid increase in activity of copper/zinc forms was observed comparing to the control samples and plants cultivated with the two remaining types of carbon black (NM and A). CuZnSOD isoforms featured the highest activity, which increased along with increase of carbon black concentration in the nutrient medium. In plants treated with B carbon black a minor increase of MnSOD isoform activity was observed, whereas the activity of FeSOD isoform was comparable with activity in control extracts and plants subject to the remaining types of carbon black (NM and A) (Fig. 6).

The additive according to the invention applied in the production of carbon black A does not increase the oxidative stress in plant cells, both in plants not treated with carbon black (control) and growing in presence of carbon black produced with no additive.

The commonly applied and available on the market additive contributes to production of carbon black causing a harmful oxidative stress in plant cells reflecting in rapid increase of

activity of additional SOD isoforms, activity of which in the control plants and plants treated with NM and A carbon blacks was insignificant.

Application of ecological additive according to the invention is therefore advantageous, since in the presence thereof carbon black does not contribute to generation of oxidative stress in plant cells.

Description of the effects of fuel additive according to the invention in the research on low efficiency boiler

Impact of fuel additive depending on share of active substances on coverage with carbon black of the heat exchanger of coal-burning boiler of 29 kW capacity was researched. The research results are presented in Table 4.

A mathematical model describing coverage of heat exchanger with soot in function of fuel additive composition was developed (Fig. 7, formula 1). Temperature range, in which the fuel additive is active for carbon black oxidation was specified (Fig. 8) followed by temperature range, in which the fuel additive is subject to thermal reactions (Fig. 9). Measurements of temperature distribution in furnace of central heating boiler were performed, according to which the furnace temperature is sufficient to activate the fuel additive (Fig. 10).

Table 4. Optimization plan for the fuel additive composition (FA)

	Fe ₃ O ₄ mass [g]	Percarbonate mass [g]	Nitrate mass [g]	Carbon black mass [g]	Coverage of heat exchanger with soot [g/m ²]
#1	45	0	0	2.46	48.81
#2	0	45	0	1.91	37.90
#3	0	0	45	1.82	36.11
#4	30	15	0	1.07	21.23
#5	30	0	15	0.94	18.65
#6	15	30	0	1.45	28.77
#7	15	0	30	1.39	27.58
#8	0	15	30	1.04	20.63
#9	0	30	15	1.72	34.13
#10	15	15	15	1.01	20.04

#11	15	10	20	0.76	15.08
#12	25	7	13	0.65	12.89

Impact of fuel additive composition on coverage of heat exchanger with carbon black was researched. Experiments #1-10 result from the experiment plan (simplex plan, grade 3 {3;3}). Experiments #11 and 12 were used to develop a mathematical model and optimize the experiment towards the extreme (minimum) of the objective function, physical sense of which corresponds to the lowest coverage of heat exchanger with deposited soot.

Fig. 7 presents the graph illustrating that the lowest coverage of heat exchanger is obtained when the chemical composition of the additive ranges between points #4, 5, 10 and 11.

$$f(\pi)=48.90x+37.76y+36.13z-82.40xy-89.06xz-42.61yz+27.38xyz-81.30xy(x-y)-93.15xz(x-z)+90.22yz(y-z) \quad (\text{formula 1})$$

where:

x –Fe₃O₄ mass,

y – sodium percarbonate mass,

z- nitrate mass,

x+y+z=15g

Coverage of coal-burning boiler heat exchanger with carbon black with no added fuel additive was, in average, $76.8 \pm 8.4 \text{ g/m}^2$ (n=5).

The new fuel additive reduces significantly the temperature of carbon black oxidation, which was presented on Fig. 8. Fig. 8 features the thermogravimetric analysis curves and differential scanning calorimetry (DSC) analysis curves, performed for the carbon black samples (black line) and carbon black with fuel additive (red line). In the case of carbon black sample, the temperature increase is accompanied with slow decrease in mass caused by organic compounds desorption. This process is of endothermic nature. In the case of carbon black with fuel additive, a clear exothermic effect is observed, which is proved by maximum on the DSC curve.

The thermal effect corresponding to carbon black oxidation in the sample containing the fuel additive is accompanied by significant mass reduction, proving the catalytic activity of fuel additive.

According to Fig. 9, complete activation of the new fuel additive takes place in temperature up to 650°C, therefore introduction of fuel additive when the boiler is well heated is advantageous. Inflow of adequate air quantity to the combustion chamber ensures relevant combustion temperature, which in low efficiency boilers may exceed even 1000°C (Fig. 10). In fine coal boiler, combustion temperature is slightly lower, however sufficient for thermal decomposition of the fuel additive (Fig. 11).

Intensive airflow via the combusted fuel results in blowing of heated catalyst particles away. Fe_3O_4 particles are transported along with fumes and transmitted at the surface of the heat exchanger, where the carbon black oxidation process takes place. Determinations of iron content in carbon black produced from fuel combustion and combustion of fuel with fuel additive demonstrate that carbon black produced in chemically – supported process has higher iron content.

Literature:

Kliebenstein D. J., Monde R., Last R.L., 1998. Superoxide dismutase in arabidopsis: an electric enzyme family with disparate regulation and protein localization. *Plant Physiology*, 118, 637-650.

Małecka A., Tomaszewska B., 2005. Reaktywne formy tlenu w komórkach roślinnych i enzymatyczne systemy obronne. *Postępy Biologii Komórki*, 32, 2, 311-325.

Miszalski Z, Ślesak I, Niewiadomska E, Baczek-Kwinta R, Lüttge U, Ratajczak R. 1998. Subcellular localization and stress responses of superoxide dismutase isoforms from leaves in the C3-CAM intermediate halophyte *Mesembryanthemum crystallinum* L. *Plant, Cell and Environment* 21: 169–179

Lichtenthaler, H.K. 1987. Chlorophylls and carotenoids: Pigments of photosynthetic biomembranes. *Methods Enzymol.* 148:350-382.

Claims

1. Ecological solid fuel additive composed of triiron tetroxide, nitrates, most frequently potassium nitrate(V),
characterized in that it contains 30-60% in weight of triiron tetroxide (Fe_3O_4), 10-30% in weight of potassium nitrate(V) (KNO_3), sodium nitrate(V) (NaNO_3), ammonium nitrate(V) (NH_4NO_3), or mixture of the abovementioned nitrates (V), 5-30% in weight of sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1,5\text{H}_2\text{O}_2$) and 10% in weight of anti-caking agent.
2. Solid fuel additive, according to patent claim 1, characterized in that the anti-caking agent is the powdered burnt clay.
3. Solid fuel additive, according to patent claim 1, characterized in that Fe_3O_4 used for production of fuel additive is free from FeSO_4 .
4. Solid fuel additive, according to patent claim 1, characterized in that production of carbon black and toxic compounds present in carbon black is reduced.

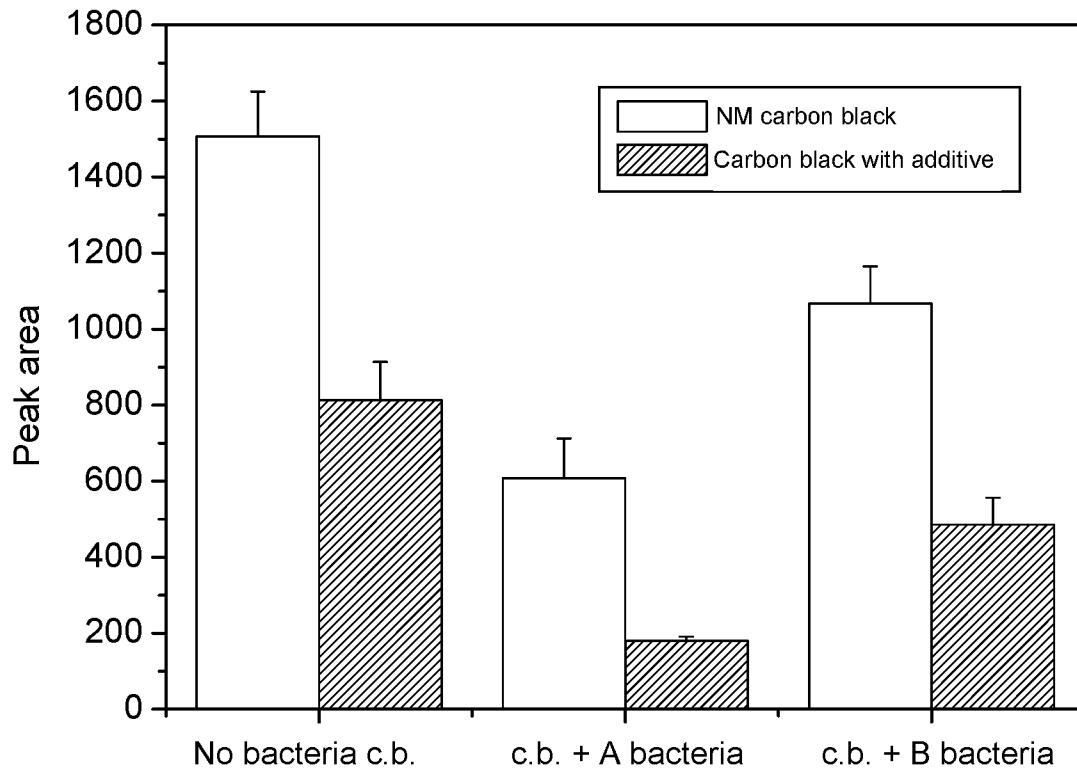


Fig.1

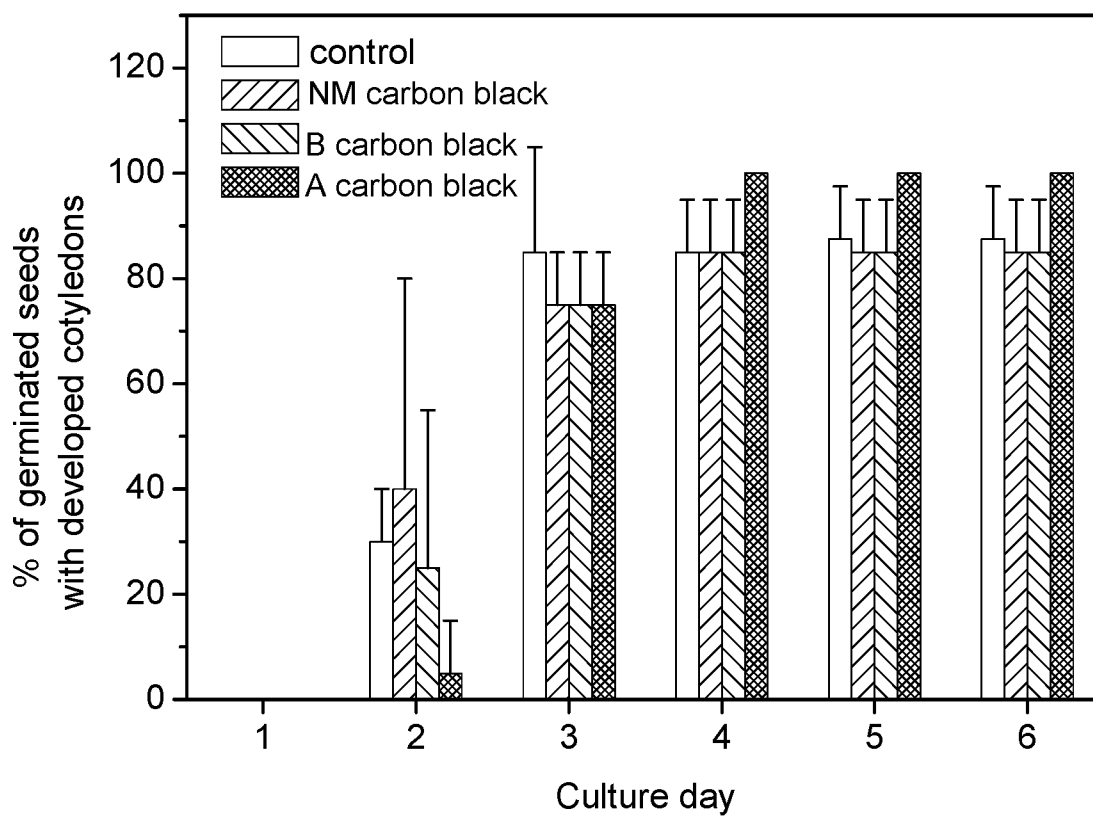


Fig.2

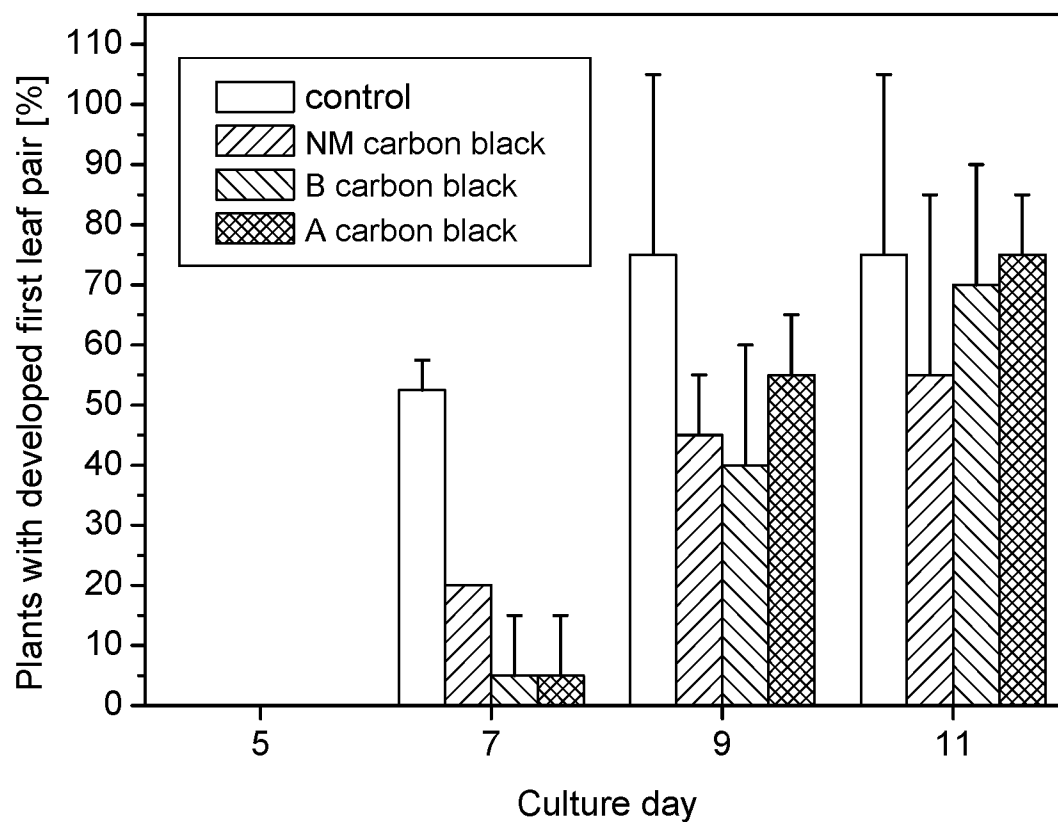


Fig.3

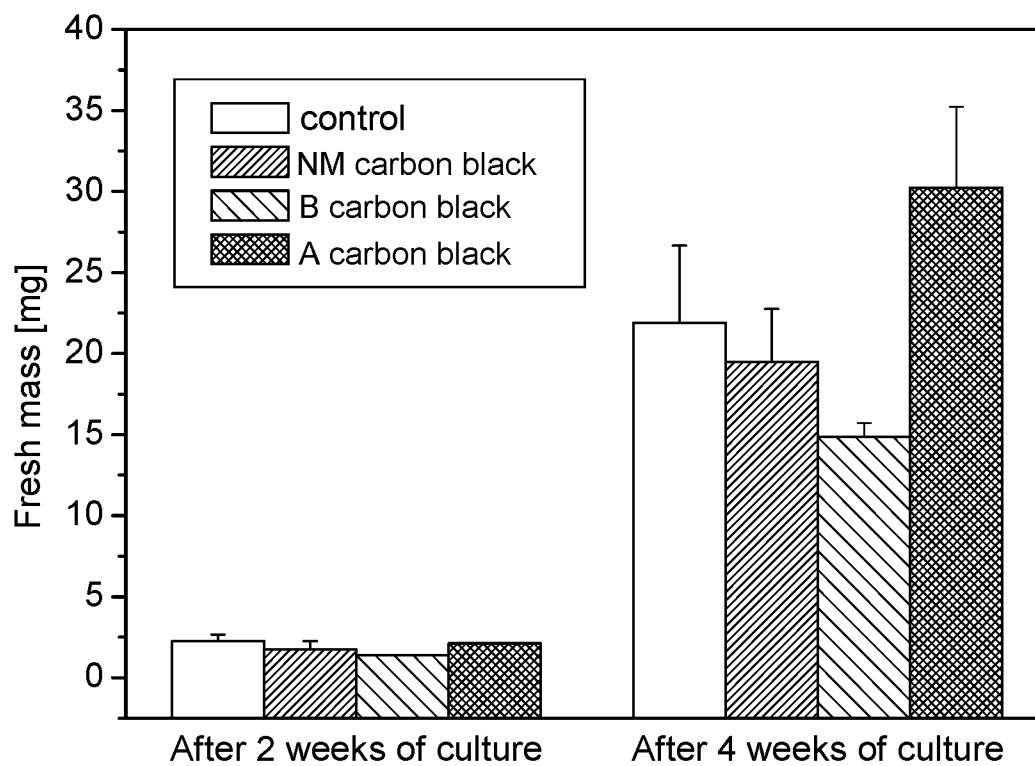


Fig.4

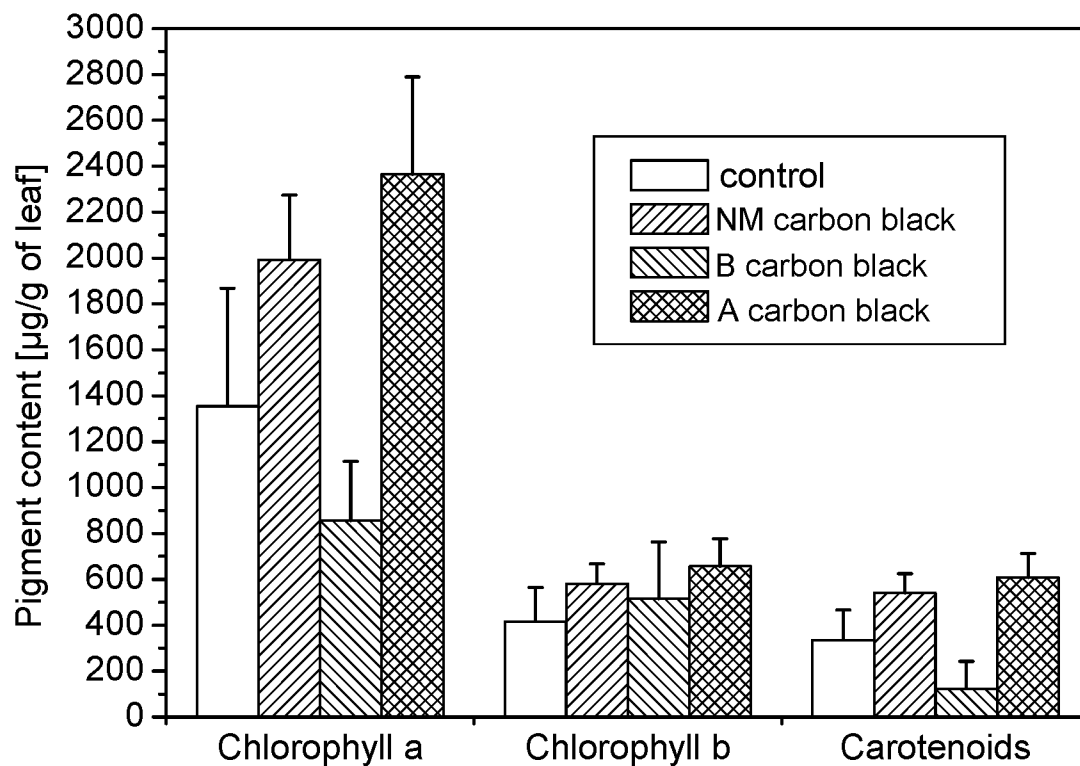


Fig.5

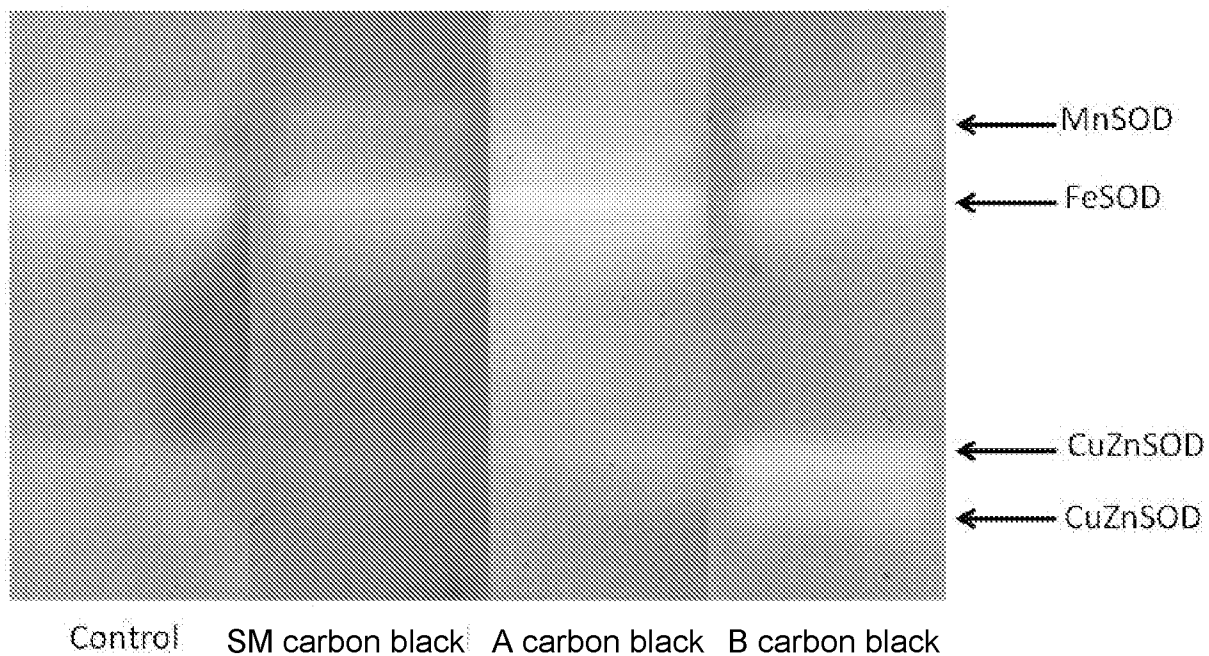


Fig.6

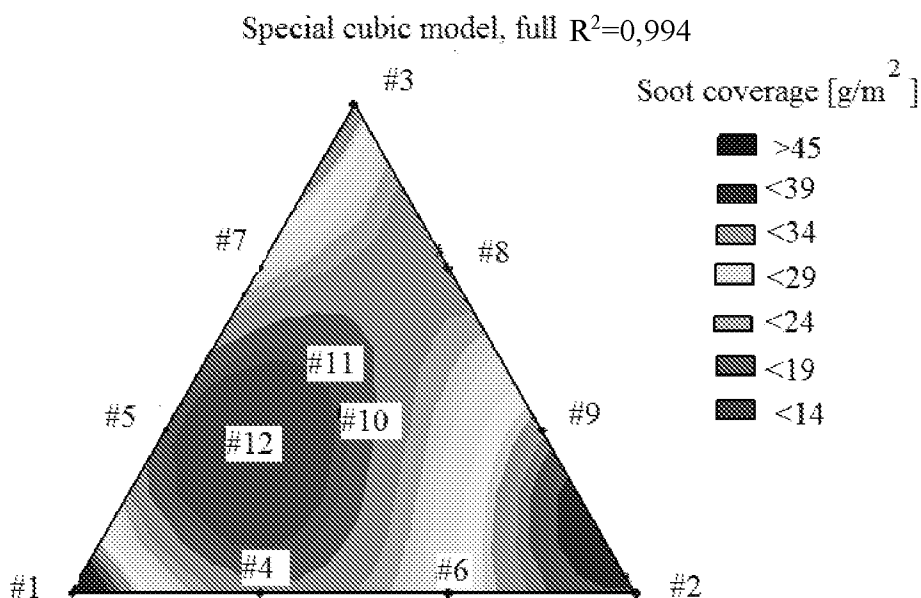


Fig. 7

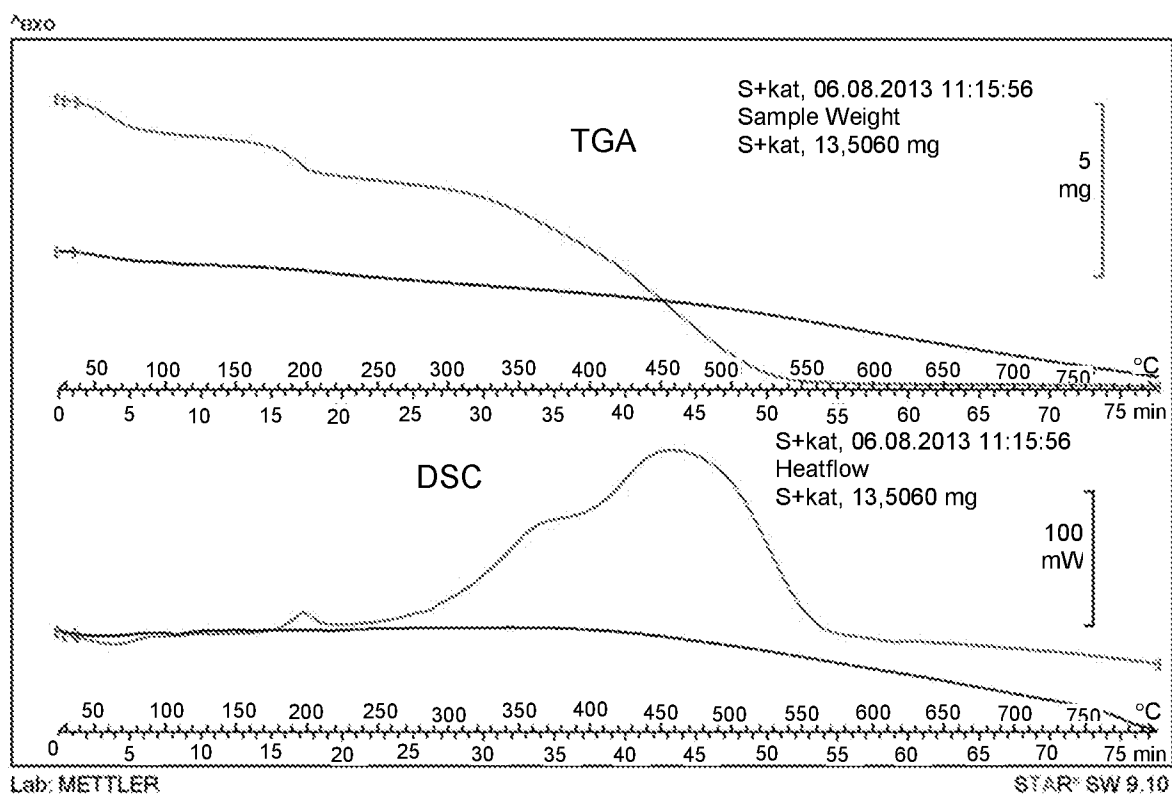


Fig. 8

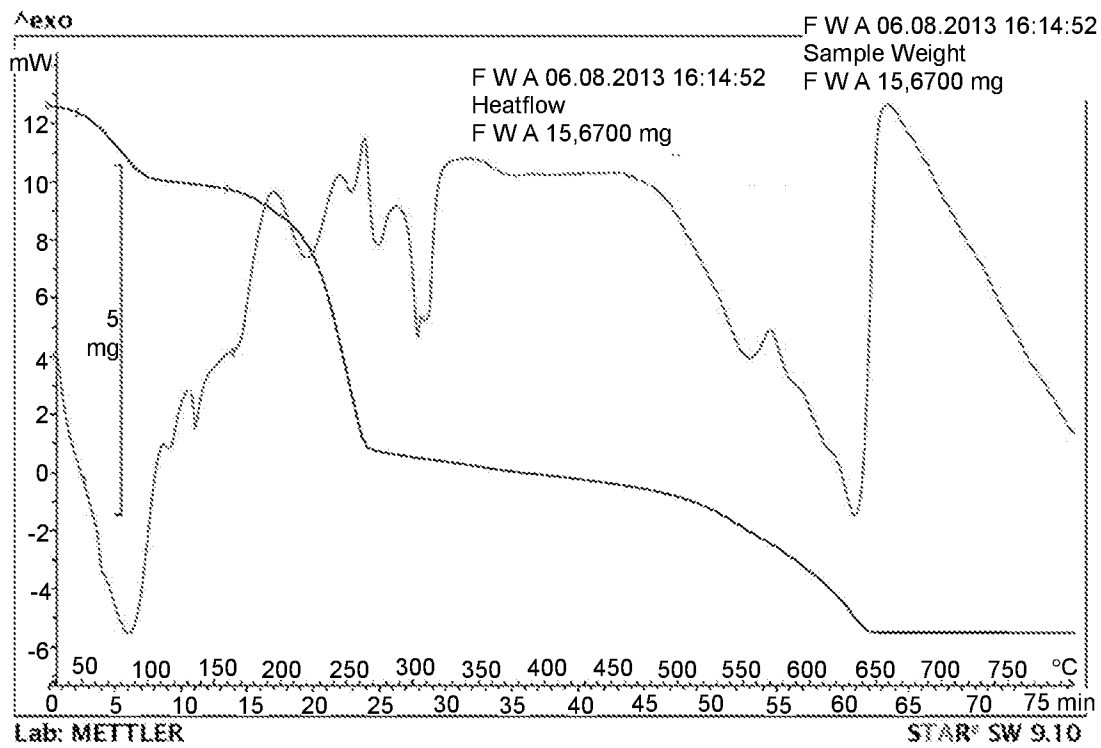


Fig.9

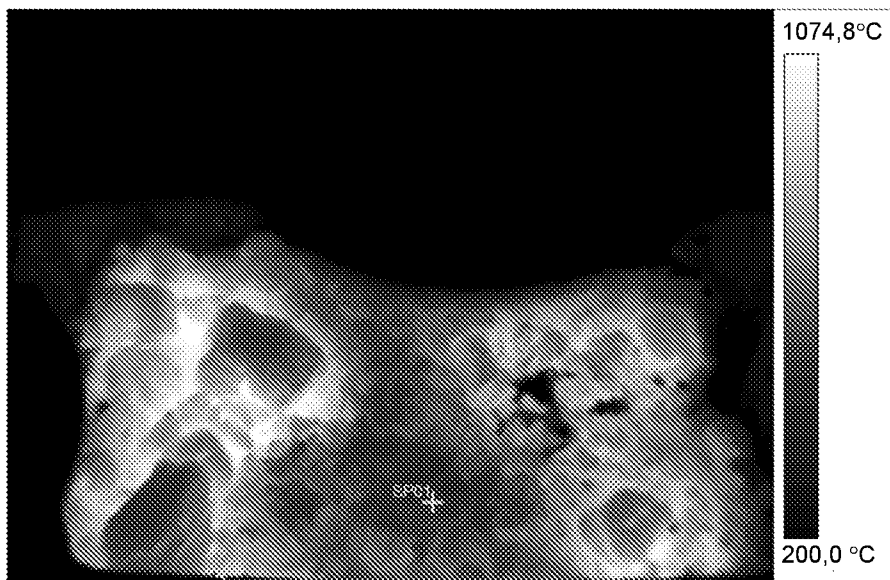


Fig.10

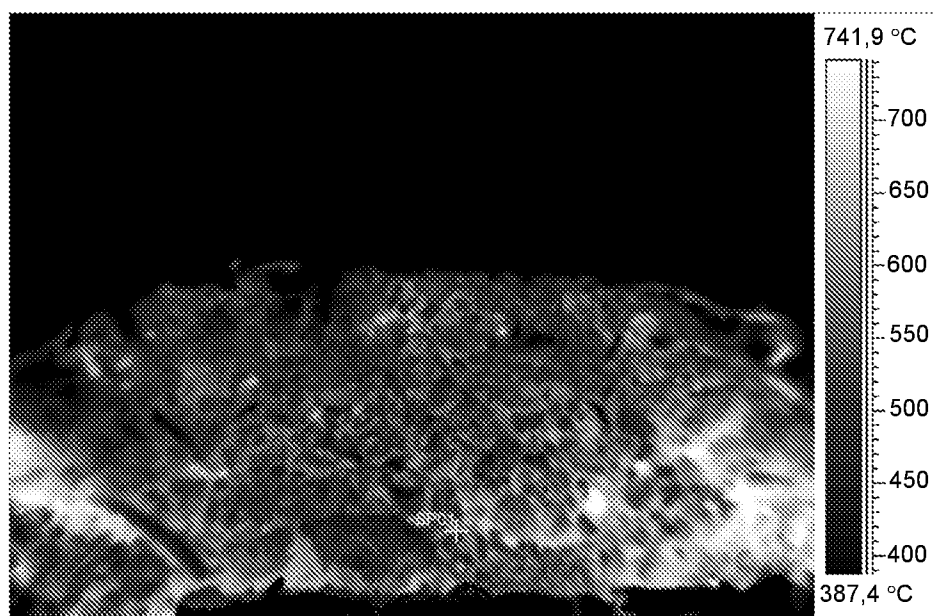


Fig.11

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/057335

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L9/10 C10L9/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011/155028 A1 (LIPSTEIN EVAN [US]) 30 June 2011 (2011-06-30) paragraph [0003] - paragraph [0016]; claims 1,4	1-4
Y	----- DATABASE WPI Week 200361 2003 Thomson Scientific, London, GB; AN 2003-637533 XP002751939, & CN 1 427 068 A (SONG W) 2 July 2003 (2003-07-02) abstract -----	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

9 December 2015

Date of mailing of the international search report

21/12/2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2015/057335

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011155028 A1	30-06-2011	CN 101665735 A	10-03-2010
		US 2011155028 A1	30-06-2011

CN 1427068 A	02-07-2003	NONE	
