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Reducing the impact of biomass combustion in residential units on local air quality by using innovative low-loading Pt-based heterogeneous catalyst

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ABSTRACT

There are several published studies evaluating the potential of platinum and palladium-based catalysts for real flue gas purification, however, the need to reduce the mass fraction of precious metals and the effect of this process is often neglected. This study aimed to assess the influence of two catalysts on the overall flue gas composition formed during combustion in a pellet burner operated to mimic the operation of a real wood log stove. Commercial Pt–Pd-based (CAT A) and Pt-based (CAT B) catalysts with innovative sol-gel coatings and a reduced amount of active substance were used. The CO, OGC and PM conversion rates of CAT A reached 87.8%, 37.0% and 25.2%, while the removal efficiency of CAT B reached 85.8%, 37.8% and 18.8%, respectively. The decrease of organic carbon by the catalysts ranged from 28% to 49% in the case of CAT A and from 13% to 60% in the case of Cat B. The concentrations of PAHs emitted seem to indicate a less carcinogenic composition when catalytic converters are used than without these flue gas treatment units.

1. Introduction

Biomass combustion in residential units is still a very popular way of heating dwellings worldwide [1]. Obvious reasons for its popularity, apart from traditionality, are, for example, the price and availability of the fuel and combustion units themselves, relatively easy operation, a feeling of energy security (in the case of a remarkable fuel reserve) and the possibility of a warm feeling from the open fire (in the case of stove usage) [2]. Nowadays, approximately 40% of the worldwide population uses heating or cooking biomass combustion equipment, while according to the model made in 2020, this share will be increasing up to 62–91% by the end of 2040 [3]. It can be challenging to track this trend, especially regarding the consumption of firewood, due to incomplete data and varying assessment methodologies used by different authorities. However, in the case of wood pellets, for which accurate production statistics are available, the trend is quite evident. For example, between 2020 and 2021, the global increase in pellet consumption is 16%, representing 6.5 million tonnes [4].

The society's transition to renewable energy sources (biomass thermal utilisation is considered carbon neutral) [5], as is forced by many national and supra-national authorities, especially in Europe, is the right way from a long-term perspective point of view [6]. One of the key points of a long-term European strategic vision for a prosperous, modern, competitive and climate-neutral economy is to "Maximise the deployment of renewables", which includes the biomass combustion [7].

It is undeniable that local heating appliances affect the local air quality [8]. The national and supra-national authorities increase the requirements on the mentioned kinds of units by legislative and also by conditions of voluntary subsidy programs [9–11]. The requirements are aimed at flue gas composition and thermal efficiency. The first one can be affected by primary measures (especially the combustion chamber design or fuel pre-treatment [12]) or secondary measures. Primary measures already run into technical limits, which means that the utilisation of secondary measures is gradually increasing. The role of the secondary measures may be significantly higher taking into consideration the inappropriate usage of household heating appliances, which

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Abbreviations list

EC	elemental carbon
EF	emission factor
FID	flame ionisation detection
GHSV	gas hourly space velocity
LHV	lower heating value
LMW	low molecular weight
NDIR	non-dispersive infrared
OC	organic carbon
OGC	organic gaseous compounds
PAHs	polycyclic aromatic hydrocarbons
PM	particulate matter
STP	standard temperature and pressure
TC	total carbon
TSP	total suspended particles
V	Volatile
^{daf}	dry ash free state
^{r}	raw state

can result in significantly worse flue gas composition and energy efficiency than the label values obtained during the certification process, where all conditions are ideal [13]. Only a few authorities have valid legislation for regular inspections of the household heating combustion units on site, which can partially ensure the maintenance of the desired quality of operation [14]. The most important parameters that affect the flue gas composition are the type of combustion unit, fuel quality, quality of maintenance of the combustion unit and operator knowledge, which means that replacing the old combustion equipment with a new one is only a fraction of the success and, in case of poor condition of other mentioned parameters, the result can be unsatisfactory [15].

Electrostatic precipitators (especially for the decrease of total suspended particles – TSP) [16] and oxidation catalysts (especially for the decrease of mass concentration of CO, organic gaseous compounds (OGC) and partially for the decrease of TSP) appear to be appropriate secondary measures for household heating combustion appliances. The role of the catalysts in the field of thermochemical processes is not only limited to flue gas purification, but they can be also used, for example, for catalytic synthesis of gases to the liquid fuel [17], for production of hydrogen by catalytic steam reforming of methanol [18] or for the ennoblement of carbon dioxide by catalytic bi-reforming of methane [19].

Most of the oxidation honeycomb catalysts in the field of flue gas purification formed during the operation of small-scale combustion units are well-shaped bodies with a significant ratio between their volume and surface [2]. On this body, the carrier is applied, which is the support for the active substance. The type of active substance (composition and parameters), together with flue gas parameters, affect the catalyst's conversion rate of certain pollutants [20].

The impact of oxidation honeycomb catalysts on the flue gas composition of products of incomplete combustion was demonstrated in several previous studies. The study of Carnö et al. [21] described the behaviour of Pt and MnO–CuO-based catalysts formed as pellets 4.4 mm in diameter. The laboratory tests were performed in a laboratory-scale reactor at high overpressure (10 kPa). The Pt-based catalyst was considered more active for the oxidation of CO, naphthalene and methane. A study by Ahlström-Silversand [22] described the behaviour of two wire-mesh catalysts with Pt–Pd and V_2O_5–CuO as active substances. Their comparison was performed only under laboratory conditions, while the influence of the specific surface of catalysts, the specific weight of active substances and the method of preparation of catalysts on the conversion rates of CO, propylene and tars were observed. Ozil et al. [23] described the behaviour of catalysts during the ignition and burnout phases of the combustion process, while tested Pt, Pd and Ce-based catalysts were additionally equipped with an electric heating element for faster heating of the catalyst at operating temperature. To verify the function of the catalyst, a characterisation method based on a comparison of separate combustion tests on a real combustion unit was used. The same method was used by Hukkanen et al. [24], where a Pd–Pt-based wire mesh catalyst was tested in real conditions with relatively poor results of CO and OGC conversion rates. On the contrary, Bindig et al. [25] reached high conversion rates of CO (up to 99 %) and OGC (up to 89.1%) with Pd–Pt based catalysts (wire mesh and monolithic body), while a characterisation method based on comparison of separate combustion tests in a real combustion unit was used. A different method called "democat" based on the comparison of flue gas composition divided into two flows (one stream flows through the dummy catalyst without the active substance and the second stream flows through the catalyst with the active substance) was used by Reichert et al. [26] and Klauser et al. [27]. Both studies were aimed at testing commercial Pd–Pt based catalysts, which reached conversion rates of CO up to 95 %, OGC up to 60% and TSP up to 30%. Klauser et al. [27] also evaluated the influence of the catalysts on PAHs, TC, EC and OC. Kaivosoja [28] studied the influence of a specific wire-mesh catalyst on PAHs, PCDD/F and chlorophenol in the flue gas.

The conversion rate of CO by a Pt–Pd-based catalyst was also studied by Vicente et al. [29], who compared its removal efficiency with that of an electrostatic precipitator. A methodology based on parallel flue gas sampling at the catalyst inlet and at the catalyst outlet was used by Ryšavý et al. [30]. The authors described basic connections between the CO conversion rates of two catalysts and the flue gas parameters. The same testing method was used by Ryšavý et al. [31] during the uncertified fuel combustion (pistachio shells) in a home combustion unit with the simultaneous use of a catalyst that has proved the significantly positive influence of the flue gas composition (conversion rates of CO up to 82.1 %, OGC up to 33.1%) even under deteriorated conditions.

The trend of expanding the scope of catalyst usage is significantly linked to the increase in the mining and processing of precious metals (especially platinum and palladium) [32]. Since both mentioned processes cause a burden on the environment, and both materials are produced preferably in geopolitically unstable regions [33], there is significant downward pressure on the decrease of precious metals usage for example by the development of low-loading catalysts [18]. This study aims to compare two different catalysts (a commercially available and a prototype low-loading one) tested in the flue gas during real combustion conditions. The testing procedure was optimised for the usage of the mentioned catalysts as retrofit devices for old or new, improperly operated combustion units.

This work introduces a new sol-gel coating low-loading (reduced active substance deposition) Pt-based catalyst and compares its behaviour with widely used Pd-based catalysts with slurry coating and standard (no reduced) active substance deposition. The overall influence of the catalysts on the flue gas composition was observed including detailed TSP analyses such as size distributions (PM, PM10, PM2.5), carbonaceous matter, ions and detailed organic speciation which is another innovative aspect of this work never described before for chosen catalysts.

The research results are very important for both producers of combustion units and catalyst producers. The results have the potential to reduce the consumption of the precious metals in catalysts while maintaining a similar decrease in mass concentration of certain pollutants in the flue gas.

2. Experimental materials and equipment

The combustion tests were carried out in the accredited testing laboratory of the Energy Research Centre, VSB – Technical University of Ostrava. The chemical characterisation of the collected filter samples was carried out in the laboratory of the Department of Environmental and Planning, University of Aveiro, Portugal.

2.1. Fuel

As the fuel for the combustion tests, the certified pellets labelled as ENplus A1 produced by Mayr-Melnhof Pellets Paskov s. r.o. were chosen. The main reason for choosing this kind of fuel was its wide usage in Europe (77% of European pellet producers produce the ENplus A1 quality pellets, making them the most widely used biomass-based fuel used in solid fuel automatic boilers) stoves) [34,35].

The pellets were stored in laboratory conditions (standard room temperature ~ 20 °C) before the tests in the 15 kg bags, so there was no danger of pellets being contaminated by water or other substances. The proximate and ultimate analysis of the pellets was determined and are shown in Table 1. All tested parameters were in accordance with the declared quality, which is important, especially from the mass fraction of the sulphur. Sulphur oxides in the flue gas could damage precious metal-based catalysts and significantly decrease their life expectancy and conversion rates by transforming active substances into sulphates [36].

2.2. Combustion units and flue gas duct

For the combustion tests, a combustion equipment was assembled, using a prototype of a gutter pellet burner with a rear fuel supply and the combustion chamber, where the pellet burner was installed.

The Pellet burner (shown in Figure A1) was equipped with an air fan, internal screw conveyor, external fuel feeder and fuel tank. The internal screw conveyor and the external fuel feeder (connecting the burner with the fuel tank) were powered by an electric engine and together with the air fan were controlled by control unit ECOVARM RE-2009 N. Combustion air was divided into two stages. Primary air was supplied from the part under the grate and secondary air was supplied from the back part of the burner, and consequently flowed to the space under the ceramic part of the burner. The burner was designed for the nominal heat input of 20 kW (heat output is given by the combustion unit, where the burner is installed) with a possible operation range between 30 and 100%. The setting of the heat output was chosen on 11 kW of heat input, which means heat output of around 8.8 kW for heat efficiency of 80 %, so that the burner imitated the flue gas parameters of a usual wood log stove, which is the most commonly equipped by a similar type of the catalyst as was tested. Sources of the flue gas with similar heat output were used in the many published studies aimed at determination of catalysts' influence on the flue gas composition, such as in the study of Bindig et al. (7 kW) [25], Konig et al. (8.5 kW) [37] and Reichert et al. (8, 10,8, 8 kW) [38].

The combustion chamber was cylindrically shaped (250 mm internal diameter; 0.0226 m^3 volume), with a wall thickness of 2 mm made from steel without any heat insulation. The combustion chamber was designed to mount the prototype of a pellet burner by a flange on one side of the cylinder. The second part was designed as a reduction for easy connection to the regular flue gas duct with 160 mm in diameter. By using the described combustion chamber instead of a standard boiler, a very high flue gas temperature could be reached, which is one of the most crucial parameters from the conversion rates point of view as was described by Ryšavý et al. [30]. Also, in standard residential pellet boilers, high flue gas temperature could be reached, but usually at the inlet of the heat exchanger or in the heat exchanger, which would disable to test usually available cylindrically shaped catalysts (in the case of catalyst installation to the heat exchanger, catalyst shape must be optimised to fit into it).

Table 1
Proximate and ultimate analysis of the used pellets;^{r} – raw state, ^{daf} – dry ash-free state.

	abbreviation	unit	value	standard
Lower heating value	LHV^r	$MJ \cdot kg^{-1}$	17.65	EN 18125
Volatile matter	V^{daf}	$\%_{wt}$	84.2	EN ISO 22167
Carbon	C^r	$\%_{wt}$	47.53	EN ISO 16948
Hydrogen	H^r	$\%_{wt}$	5.70	EN ISO 16948
Nitrogen	N^r	$\%_{wt}$	0.2	EN ISO 16948
Oxygen	O^r	$\%_{wt}$	40.25	EN ISO 16993
Sulphur	S^r	$\%_{wt}$	0.02	EN ISO 16994
Water	W^r	$\%_{wt}$	6.05	EN ISO 181234-2
Ash	A^r	$\%_{wt}$	0.25	EN ISO 18122

The main reasons for choosing this kind of flue gas source were.

- High reachable flue gas temperature.
- Uniform operation without significant periodical process.
- Uniform operation between the testing days.
- Easy control of the combustion process to set required flue gas parameters.

During the combustion tests, the combustion chamber was connected to the uninsulated flue gas duct, where a catalyst was installed (approximately 0.9 m behind the combustion chamber outlet) without any bypass system. Catalysts filled out a major part of the flue gas duct, with a tiny layer around it, which was sealed by a heat resistant sealing cord so that all flue gas passed through the catalyst. There were two measuring points at the catalyst inlet consisting of one point for temperature and pressure measurement and one point for flue gas sampling for the analysis. At the catalyst outlet, there was one measuring point for the flue gas analysis. After that, the flue gas was directed to the hood, which was the entering part of the dilution tunnel and ensured the flue gas dilution by the ambient air. The position of the hood has been adjusted so as not to affect the natural chimney draught of the first flue gas duct section by the flue gas fan. There was a short vertical part of the dilution tunnel after the hood, followed by a horizontal section and the next vertical section. There were four measuring points in the last, vertical part of the dilution tunnel.

- Analysis of O_2 and CO_2
- PM measurement (glass filter)
- PM measurement (quartz filter)
- Particle mass size distribution

Consequently, flue gas flowed out of the dilution tunnel into the venturi tube used for flue gas flow determination. The flue gas flow was created by a flue gas fan placed behind the venturi tube. A simplified scheme of the flue gas duct with the all-important parts highlighted is shown in Fig. 1.

2.3. Catalysts

For the following experiments, two honeycomb precious-metal-based catalysts were used. CAT A is the commercially available catalyst produced for flue gas purification purpose, while CAT B is the prototype developed for the same purpose in order to reduce the material needs of precious metals used as active elements in an effort to preserve high standards of operational characteristics from the ability to decrease of concentrations of pollutants in the flue gas point of view and therefore reached cleaner operation. CAT A was prepared by standard slurry coating methodology using the active element granulometry of tens of micrometres. A commonly used slurry coating was formed by mixing powdered substances with a binder to form a paste in which the catalyst body is immersed. The catalyst was then dried and burned.

During the production of the sol-gel coating, case of CAT B, each component of active substance (only platinum in this case) started as a salt (e.g., platinum chloride or platinum acetylacetonate). The salt precursor was dissolved in a suitable solvent (e.g, ethanol or isopropanol) to form a sol. The next step involved the gelation process, which consisted of the hydrolysis and condensation of the precursor. The

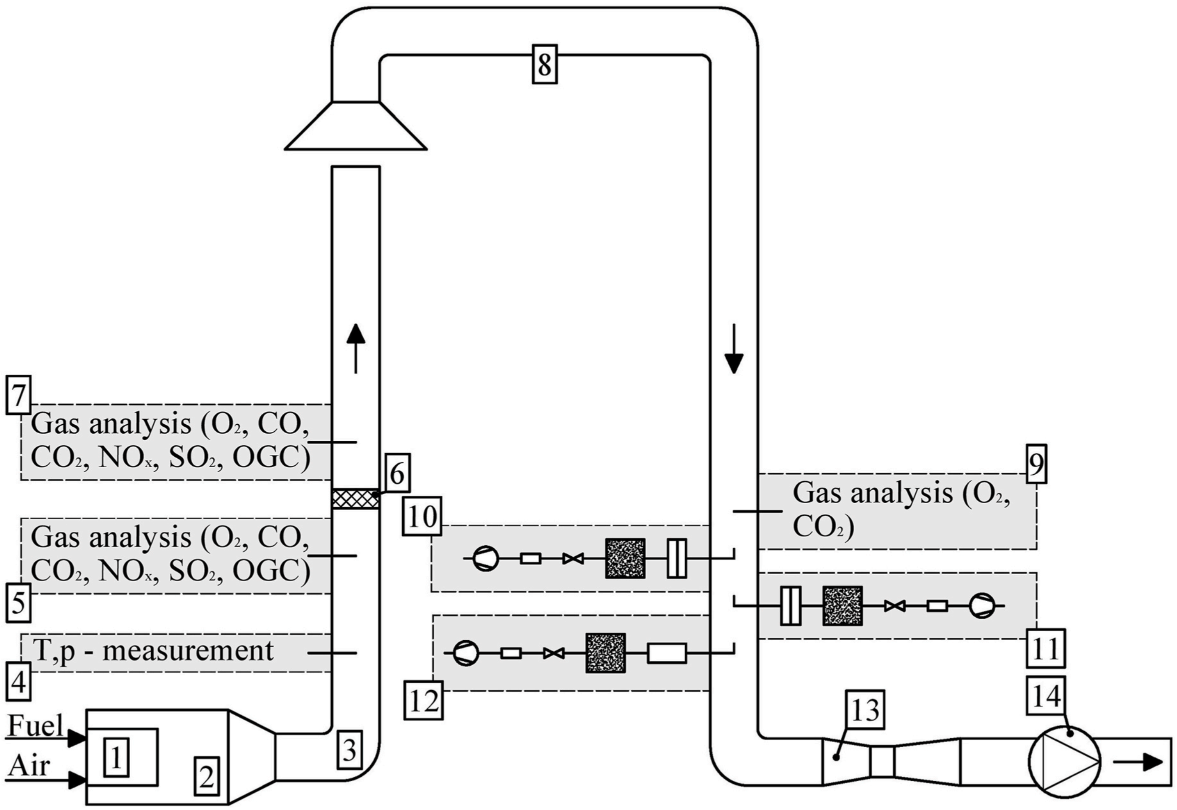

Fig. 1. Scheme of the testing equipment; 1 – Pellet burner; 2 – Combustion chamber; 3 – Flue gas duct; 4 – Temperature and relative pressure measurement; 5 – Flue gas analysis at the catalyst inlet (O_2, CO, CO_2, NO_x, SO_2, OGC); 6 – Catalyst' location; 7 - Flue gas analysis at the catalyst outlet (O_2, CO, CO_2, NO_x, SO_2, OGC); 8 – Dilution tunnel; 9 – Flue gas analysis (O_2, CO_2); 10 – PM measurement (filter holder, gas dryer, regulation valve, flow meter, gas pump); 11 – PM measurement (filter holder, gas dryer, regulation valve, flow meter, gas pump); 12 – Particle mass size distribution measurement (PM10, PM 2.5 and PM1 impactor, gas dryer, regulation valve, flow meter, gas pump); 13 – Venturi tube (temperature and pressure drop measurement); 14 – Flue gas fan.

hydrolysis step introduces hydroxyl groups, and condensation leads to the formation of the gel structure. During the mentioned chemical reactions, the adjusting of pH for instance by the addition of a base (e.g. ammonia or an amine) was crucial for reaching gel formation. The next steps are coating of sol-gel on the substrate by dipping, drying ensuring the solvent removal and formation of the stable gel layer on the substrate surface and calcination which involves the reduction of platinum ions to form platinum nanoparticles [39].

Table 2
Detailed description of the tested catalysts.

Parameter	Abbreviation	Unit		
Abbreviation	–	–	Cat A	Cat B
Type of catalyst	–	–	monolithic - honeycomb	
Body material	–	–	cordierite substrate	
Wash coat	–	–	Al_2O_3, CeO_2, La_2O_3 and Y_2O_3	
Precious metal	–	–	Pd	Pt
Type of coating	–	–	slurry coating	sol-gel coating
Precious metal loading	–	$g\cdot m^{-3}$	475	317
Inlet surface area	A_{in}	m^2	0.01628	
Height	H	m	0.05	
Effective volume	$V_{c;eff}$	m^3	0.000814	
Coated area	A_{cat}	m^2	0.56373	
Cell density	CD	cells/ cm^2	4.14	
Cell shape	–	–	quadratic	
Pressure loss	Δp	Pa	2	

Note: As the active surface of catalyst the total area, which is in straight contact with flue gas is meant. Pressure loss was determined for flue gas flow 25 m^3 h^{-1} at STP conditions.

A detailed description of the catalyst from the dimensions and composition is shown in Table 2. Catalysts are shown in Fig. 2. Catalysts will be referred to as Cat A and Cat B hereafter.

Before the tests, catalysts were new – unused, so no effect of reducing the conversion rate of the catalysts should occur. Observing the life expectancy of these catalysts was not the aim of the study, as well as the influence of the poisoning, fouling, and coking which should not occur during the proper usage of the biomass combustion unit. The standard operation temperature of the Pd-based and Pt-based catalysts is related to the pollutants conversion efficiency and the reachable parameters of flue gas ranging approximately from 300 to 500 °C [26,30,38,40].

Since sulphur and mercury act as the catalytical poisons for the catalysts based on precious metals (Pt, Pd) according to Argyle and Bartholomew [41], these catalysts should be used only in the environment of the flue gas formed during biomass combustion, where is the presumption of only negligible mass concentration of mercury and sulphur unlike the fossil and waste alternative fuels such as refuse-derived fuel, waste paper, textiles, plastics, film, tires and sewage sludge, where the mercury and sulphur content is significant [42–44].

Cordierite substrate was described as the most cost-effective option [45]. Reichert et al. [46] found that cordierite substrate is more practical than metallic substrate in real-world applications. In the mentioned study, cordierite substrate with the half-cell density in comparison to observed metallic one, was marked as the better one from the safety point of view due to lower clogging rate by solid particles in the flue gas environment from small scale combustion appliances.

2.4. *Testing procedure description*

Three separated combustion tests were performed with the same

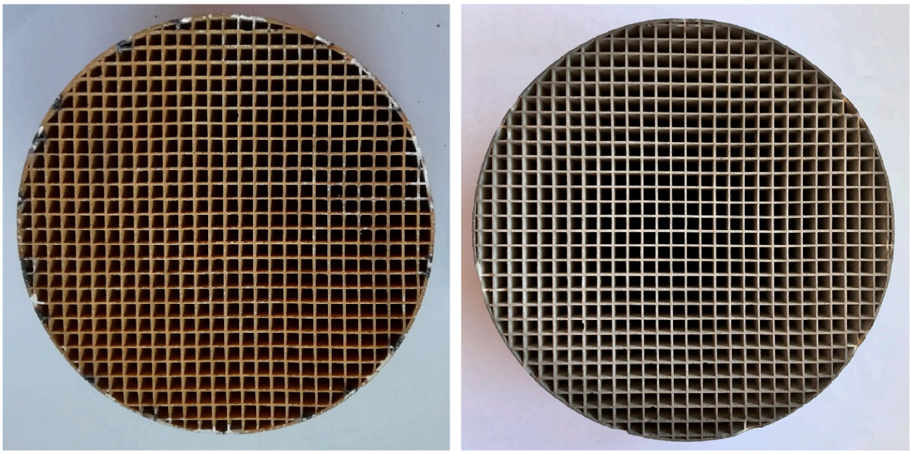

Fig. 2. Tested catalysts: on the left-side Cat A (inside the flue gas duct), on the right-side Cat B.

testing procedure. The first test (Mode 1) was set as the reference one without any catalyst usage. During the two following tests the catalysts were installed into the flue gas duct (Mode 2 – Cat A, Mode 3 – Cat B).

All tests started by auto-ignition of the first batch of pellets on the burner grate by the ceramic heating element, which is part of the burner. The setting of the combustion process (time of fuel adding, time of pause between fuel adding and rotations of the combustion air fan) was always the same throughout the tests and was not changed within the tests. Flue gas sampling started right at the same time when the ignition phase was ended and continued for 6 h. For the evaluation of the gas pollutants mass concentration in the flue gas, 5.5 h were taken into consideration excluding the first 30 min due to inappropriate operation temperature for the catalysts operation.

The burner settings (time adding the fuel, time of not adding the fuel and amount of the combustion air) were adjusted to obtain higher mass concentrations of pollutants from incomplete combustion to simulate a real household operation with an unprofessional stoker.

During each combustion test, three flue gas samples were taken to analyse solid particles. The PM sampling always started at the same relative time, which was related to the ignition (2:00; 3:30; 5:00). Each sampling lasted exactly 30 min, and all 3 p.m. sampling apparatuses started and ended right at the same time. The test period ended by changing the actual phase of the burner into the burnout phase.

2.5. Measuring system and flue gas analysis

The flue gas was sucked from 6 different sampling points.

For the determination of gaseous compounds, the sampling points were equipped with heated ceramic filters. The flue gas flowed through a heated hose (heated to 180 °C) to the analyser. At the first two sampling points (at the catalyst inlet at the catalyst outlet) the following components were analysed: CO, CO_2, O_2, NO_x and OGC. At the third sampling point, only CO_2 and O_2 were analysed to determine the dilution ratio.

The following two sampling points (in the dilution tunnel) were equipped with a filter holder, gas dryer, regulation valve, volume flow meter and pump. There was a glass fibre filter in the first, stainless steel, filter holder. The glass fibre filter served for gravimetrical determination of the mass concentration of PM in the flue gas. The glass fibre filters were heated out at 180 °C for 4 h before the test. After the heating process, the filters were stabilized in laboratory conditions (at constant temperature and relative humidity) and weighted. Exposed filters were also stabilized in laboratory conditions and weighted. Quartz filters were used in the second, titanium filter holder. The quartz filters were heated out at 815 °C for 4 h before tests. The particulate matter samples were kept refrigerated until the analysis. The exposed quartz filters primarily served for the following laboratory analysis including the carbonaceous matter, ions and detailed organic speciation.

The last sampling point was intended for the impactor used for the particle mass size distribution measurement (>PM10, PM 2.5 and <PM2.5). Settling areas of the impactor were equipped with foils while the last one (for determination of <PM2.5) was equipped with a glass fibre filter. Results obtained by weighing the deposit were used for the determination of the proportional representation of individual PM categories.

The relative pressure of the flue gas at the catalyst inlet was monitored by a differential pressure transmitter. At the same place, the flue gas temperature was monitored by thermocouples type K.

A detailed overview of measuring devices, measured components, measurement principles and accuracy is presented in Table 3.

2.6. Particulate matter chemical analysis

Organic (OC) and elemental carbon (EC) in the quartz filter samples (punches of 1.5 cm^2) were analysed using a Sunset Laboratory OC-EC analyser, following the EUSAAR-2 protocol. Initially, the

Table 3
Overview of measuring devices, measured components, measurement principle and accuracy for continuous measurements.

Device and measured component	Range	Principle	Accuracy
Sick GMS810			
OGC	0–100 ppm	FID	≤2 %
ABB AO2020			
CO (low)	0 - 1000 ppm	NDIR	≤1 %
CO (high)	0 - 50,000 ppm	NDIR	≤1 %
CO_2	0–20 %	NDIR	≤1 %
O_2	0–30 %	Paramagnetic	≤0.5 %
NO	0–1000 ppm	NDIR	≤1 %
SO_2	0–2000 ppm	NDIR	≤1 %
Thermocouple, Type K, class 1			
Flue gas temperature	−50 to 1000 °C	Thermoelectric effect	±1 °C of the measured value
Cressto SPD 211 R5UB D			
Pressure drop	−100 to + 100 Pa	Piezoelectric effect	±1.5% of the ultimate value of the measurement range
Sartorius CPA225D-OCE			
Weight	0–220 g		±0.016 mg

determination of the carbonaceous fraction is carried out under an inert atmosphere free of O_2 and at a temperature between 200 °C and 650 °C. Afterwards, an oxidising atmosphere is applied with an O_2/He mixture at a temperature between 500 °C and 850 °C. During the first stage, the volatilisation of the OC present in the sample takes place; and on the second, the EC converts to steam when exposed to a higher temperature and an oxidising atmosphere. Both carbonaceous fractions are measured in the form of CO_2 by a non-dispersive infrared detector. To ensure the quality of the measurements of the technique, an aqueous solution of sucrose (42 μg cm^{-2}) was used.

Water-soluble inorganic ions were extracted from the quartz filters (punches of 2.3 cm^2) by ultrasonic agitation for 30 min (15 + 15 min), in 6 ml of ultrapure Mill-Q water. The extracts were filtered through WhatmanTM PTFE syringe filters with a 0.2 μm pore size and transferred to glass vials for further analysis. The quantification was carried out using calibration curves obtained from high-purity grade standard solutions from Sigma-Aldrich. The determination of cations (Li+, Na+, K+, NH4+, Mg2+ and Ca2+) was performed using an ICS 1100 chromatograph equipped with a CS 12A column and a 30 mM solution of methanesulfonic acid (MSA) as eluant in isocratic mode at 1 ml min^{-1}. Anions (Br^-, Cl^-, F^-, SO_4^{2-}, PO_4^{2-}, NO2-, and NO3-) were determined using an ICS 1000 chromatograph equipped with an AS4A SC column and a 1.8 mM Na2CO3/1.7 mM NaHCO3 solution as eluent in isocratic mode (2 ml min^{-1}).

Two 47 mm diameter circles were removed from the quartz filters for organic speciation. These were extracted in 3 steps, involving a first stage with dichloromethane, followed by two stages with methanol. The combined extracts were concentrated to 1 ml in an evaporation system (TurboVap, Biotage) and brought to dryness under a gentle nitrogen flow. The dry extracts were separated in a silica gel column into 5 distinct organic fractions by eluting with solvents of different polarities. The solvents of each organic fraction were again concentrated in the TurboVap workstation and dried under nitrogen. The EPA 8270 semi-volatile internal standard mix (Supelco), with six deuterated compounds (acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene- d4, naphthalene-d8, perylene-d12, phenanthrene-d10), benzo [a] pyrene-d12 (Supelco) and fluorene-d10 (Aldrich) were used to spike the PAH extracts. Before analysis, the extracts of the two most polar organic fractions, containing alcohols, phenols, acids, sugars and other compounds with OH and COOH groups, were silylated by addition of N,O-bis (trimethylsilyl)trifluoroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco) and pyridine containing 3 internal standards (1-chlorohexadecane and 1-chlorododecane, both from Merck, and tetracosane-d50, from Aldrich). The reaction mixture was heated in an oven at 70 °C for 3 h. The quantification of the compounds was carried out by chromatography–mass spectrometry (GC-MS, GC model 7890B, MS model 5977A, GC Sampler 80, Agilent Technology Inc.). The GC housed a Tekno TRB-5MS column (0 °C-325 °C, 60 m × 250 μm × 0.25 μm), with helium as a carrier gas at a flow rate of 1.0 mL min^{-1}.

The silylated compounds were analysed in both full scan and selected ion monitoring (SIM) modes. Because all PAHs generate the molecular ion as the base peak in their mass spectra, the molecular ions were used for SIM. Twenty one polycyclic compounds were targeted (naphthalene, benzothiazole, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, p-terphenyl, retene, benzo [a] anthracene, chrysene, benzo [b]fluoranthene, benzo [k]fluoranthene, benzo [*a*]pyrene, perylene, indeno (1,2,3-cd)pyrene, dibenzo [a,h]anthracene and benzo [g,h,i]perylene). Calibrations were performed with authentic standards (Sigma- Aldrich) in five different concentration levels. Additional details of the entire procedure can be found in a previous publication of Alves et al. [47].

2.7. Data evaluation

The composition of the flue gas, flue gas temperature, relative pressure in the flue gas duct and pressure drop in the venturi tube were continuously recorded and presented as average values per minute.

Pollutants' mass concentrations in the flue gas were listed as mass concentrations in a dry flue gas and were recalculated to STP conditions (standard conditions for temperature and pressure; $T = 273.15$ K; $p = 101{,}325$ Pa) and the reference volume fraction of oxygen in the flue gas $\varphi_{\mathrm{ref};[O2]} = 13$ %. Final mass concentrations of NO_x were recalculated to NO_2. Mass concentrations of the PM and division of PM into individual categories were based on the determination of filter weights and sucked volumes of the flue gas through the filters.

Conversion rates of the catalysts were calculated from the comparison of the mass concentrations of pollutants in the flue gas at the catalyst inlet and in the catalyst outlet according to eqn (1).

$$X = \frac{\rho_{BO} - \rho_B}{\rho_{BO}} \tag{1}$$

X - the conversion rate of a pollutant [%]

ρ_{Bo} - mass concentration of a pollutant at the catalyst inlet [$mg \cdot m^{-3}$].

ρ_B - mass concentration of a pollutant at the catalyst outlet [$mg \cdot m^{-3}$].

Gas hourly space velocity (GHSV), was calculated according to eqn (2) as the ratio of wet flue gas volume flow at STP conditions ($\dot{V}^{wet}_{flue\_gas}$) and the effective catalyst volume (V_{eff}).

$$GHSV = \frac{\dot{V}^{wet}_{flue\_gas}}{V_{eff}} \left[h^{-1}\right] \tag{2}$$

3. Results and discussion

3.1. Overall test results

The overall results of the performed combustion tests were presented in Table A1.

The reached heat output of the burner was always the same between each test ranging between 8.2 and 8.6 kW which is slightly above the minimal heat output of the burner which was completely in accordance with the operation setting listed in section 2.2.

The oxygen volume fraction ranged from 7.9 to 8.2 % on average, which can easily represent well maintained and tight stove without any problems with sucking of fake air. The flue gas temperature reached in the catalyst section of the flue gas duct was always very high (also due to low air excess ratio), ranging from 335 °C (test without the catalyst) to 393 and 402 °C (test with the catalyst). It is obvious that oxidation processes on the catalyst surface, which is a strongly exothermic reaction, affected the flue gas temperature.

Considering the mass concentration of pollutants in the flue gas right at the outlet of the combustion chamber, the values were very similar between each combustion test what was the intention for comparison of the mode without the catalyst with modes with the catalyst. The flue gas temperature in the sampling part of the dilution tunnel ranged between 42 and 45 °C within all tests.

The GHSV at STP conditions as the function of several input parameters (fuel composition, fuel consumption and catalyst dimensions) ranging in average between 19,386 and 19,942 h^{-1}. This range corresponds to an attempt to imitate the operation of a standard wood log stove. This range is also in accordance with previous research of catalysts describing their utilisation for flue gas purification such as the study of Ryšavý et al. where the GHSV reached on average around 30,000 and 33,000 h^{-1} during the testing of slightly less bulky catalysts (by 27%), the study of Ferrandon et al. [48] where the GHSV during the laboratory testing was adjusted on 19,100 h^{-1}, while during the real stove testing GHSV reached approximately 32,000 h^{-1} and the study of Reicher et al. [26] while consideration of the result obtained with similar catalyst dimensions.

3.2. Carbon monoxide in the flue gas

The average CO mass concentration ranged between 2750 and 2814 mg m^{-3} and the emission factor (EF) ranged between 1235 and 1272 g MJ^{-1}. The courses of the mass concentration of CO in the flue gas for each test are presented in Figure A2.

The first part of the combustion process (after ignition) was characterised by a high mass concentration of pollutants in the flue gas. The ignition phase took place for approximately 15 min when the mass concentrations of pollutants started to decrease dramatically. The rest of the combustion process can be marked as the “burning phase”. The burning phase was characterised by a continual increase in the mass concentration of CO and OGC in the flue gas. This was related to the continual filling of the fuel filling of the burner grate by the fuel. It usually takes some time to fill the whole grate with the fuel, which turns into ash which settles down in specific positions (between the air inlets) and prepares some stable conditions on the grate. Since the minimal heat output of the burner was tested the amount of the combustion air was equally low, which worsens conditions and reduces the likelihood of ash blowing off the grate. The burning phase was also characterised by fluctuations of mass concentration of pollutants from minute to minute, which was given especially by the low amount of added fuel equal to the minimal heat output. In the case of all three combustion tests, the time courses were very similar. The statistical evaluation of the mass concentration of CO in the flue gas for each test is presented in Fig. 3. The main range of CO mass concentrations at the combustion chamber outlet was 462 to 7491 mg m^{-3}, 206 to 5454 mg m^{-3} and 388 to 7366 mg m^{-3} for the test without catalyst, with catalyst A and with catalyst B respectively. The reached mass concentrations of CO were very similar as in the study of Vicente et al. [29] (CO ranging between 2800 and 3300 mg m^{-3}), study of Klauser et al. [27] (CO ranging between 2400 and 3400 mg m^{-3}), and study of Ryšavý et al. [30] (CO ranging between 1800 and 3100 mg m^{-3}), where usual wood log stoves were used.

Regarding CO mass concentration in the flue gas, the pellet burner set up was found to be adequate for simulating the operation of standard wood log stoves without the periodic operation disadvantage. This was observed for example in the study of Bensaid et al. [49], where La–Na–CrO_3 catalyst was tested under real life conditions at the flue gas outlet of manually loaded wood log stove.

The average mass concertation of CO at the catalysts’ outlet was 343 and 390 mg m^{-3} for Cat A and Cat B respectively. The average conversion rate of CO by catalysts (comparison of the flue gas composition at the catalyst inlet and at the catalyst outlet) reached 87.8 (mainly ranged between 80.4 and 94.8%) for Cat A and 85.8 % (mainly ranged between 77.0 and 94.4%) for Cat B.

Even though the precious (active) element loading was lower about 33% in the case of Cat B than in the case of Cat A the difference between the average conversion rates was only 2% under given conditions.

In this study, Cat A achieved a higher average conversion rate of CO compared to previous studies. For example, it was higher than the average conversion rate of 73% reported by Krpec et al. [50] as well as the average conversion rate of 69% (and 79% at a flue gas temperature of around 400 °C) observed by Ryšavý et al. [30]. Additionally, it was higher than the 77% conversion rate reached in another study conducted by Ryšavý et al. [40]. In the mentioned previous studies, the pure Pd based catalysts were used with the same loading of active element on the surface, but with lower active surface (given by different dimensions; 0.38, 0.42 and 0.23 m^2 respectively) than presented Cat A in this study (0.56 m^2).

The conversion rate of CO (on average) reached by Cat B in this study was higher than 65% reached in the study of Ryšavý et al. [40] and lower than 96 % reached (on average) in the study of Krpec et al. [50]. In the all mentioned previous studies, the pure Pt based catalysts were used with a higher loading of the active element (475 g m^{-3}) than in presented Cat B in this study (317 g m^{-3}). The active surface of the used catalyst in previous studies was generally (0.51 m^2 for both cases) lower than the active surface of Cat B in this study (0.56 m^2). Further comparison of new results including CO, OGC and PM conversion rates with the abovementioned studies and also with other studies where the catalysts with a combination of platinum and palladium-based catalysts were used as well as with the catalysts with metal oxides-based catalysts is shown in the overview Table A2. In the previous studies, different approaches for the measurement were applied such as: methodology of several divided consecutive tests comparison, methodology of division of the flue gas duct including dummy usage, methodology of continual measurement at the catalyst inlet and at the catalyst outlet flue gas composition (this study). Consequently, many influencing parameters were different between the tests such as fuel quality, combustion unit quality, and operator quality.

Therefore, the comparison of the mentioned overall results mainly listed as an average value for the whole test may not be too accurate and completely telling.

3.3. OGC in the flue gas

The average mass concentration of OGC ranged between 92 and 105 mg m^{-3} and EF ranged between 41.4 and 46.3 mg MJ^{-1} taking into consideration the flue gas composition at the combustion chamber

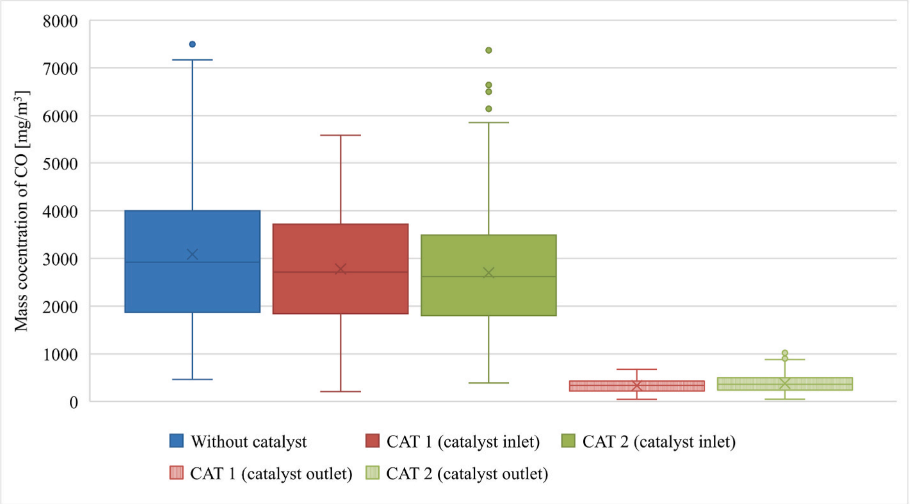

Fig. 3. Statistical graph of mass concentration of CO in the flue gas.

outlet. The courses of the mass concentration of OGC in the flue gas for each test is presented in Figure A3. It is evident from the OGC mass concentration courses that as in the case of CO, the stabilisation phase took place for 3 h. A short time deterioration around the time 5:30 after ignition occurred.

The statistical evaluation of the mass concentration of OGC in the flue gas for each test is presented in Fig. 4. The mass concentrations and EFs of OGC were in the range of previously presented studies by Reichert et al. [26,38] (OGC ranged between 25 and 538 mg m^{-3} in the first study and between 32 and 601 mg m^{-3} in the second study), where typical wood log stoves were used.

From the OGC mass concentration in the flue gas point of view the pellet burner set up was adequate for simulation the operation of standard wood log stoves without their disadvantage of periodic operation.

The average mass concertation of OGC at the catalysts' outlet was 58 and 60 mg m^{-3} for Cat A and Cat B respectively. The average conversion rate of OGC by catalysts (comparison of the flue gas composition at the catalyst inlet and at the catalyst outlet) reached 37.0 (mainly ranged between 6.8 and 54.1%) for Cat A and 37.8 % (mainly ranged between 10.2 and 54.0%) for Cat B. The difference between the obtained conversion rates of CO was almost negligible, while the reached conversion rate range was even smaller in the case of Cat B.

The statistical evaluation of the separate conversion rates of CO and OGC obtained by separate calculations for each 1-min interval is shown in Fig. 5.

The conversion rate of OGC (in average) reached by Cat A in this study was higher than the 10% reached (on average) in the study of Krpec et al. [50], higher than 4% (considering the average value of only C_3H_8 conversion) reached in the study of Ryšavý et al. [30] and were lower than 61.2 % reached in the study of Ryšavý et al. [40].

The conversion rate of OGC (in average) reached by Cat B in this study was higher than 14% reached (on average) in the study of Hukkanen [24], lower than 63.8% reached in the study of Ryšavý et al. [40] and lower than 50% reached (on average) in the study of Krpec et al. [50]. The differences between the catalyst used in this study and the catalysts used in previous studies are listed in section 3.2.

3.4. NOx in the flue gas

The mass concentration of NO_x ranged between 73 and 91 mg m^{-3} and EF ranged between 32.3 and 41.6 mg MJ^{-1}. The reached mass concentrations and EFs of NO_x were very similar as in the study of Bäfver et al. [51] (NO_x ranging between 74 and 110 mg m^{-3}) and in the study of Ryšavý et al. [30] (NO_x ranging between 92 and 96 mg m^{-3}), where usual wood log stoves were used. Platinum and palladium based catalysts should have a minor effect on NO_x mass concentration in the flue gas [2]. Regarding NO_x mass concentration at the catalyst inlet and at the catalyst outlet, there was a slight decrease of 8 and 11% in the case of Cat A and Cat B, respectively.

3.5. PM in the flue gas

Considering the PM mass concentration during the test without the catalyst, which is a reference for consequence evaluation of catalysts' influence on flue gas composition, average mass concentration from three measurements ranged from 141 to 206 mg m^{-3} and EF ranged between 62 and 90 mg MJ^{-1}. PM was categorised into three categories PM (particle of all sizes), PM10 (particles of size smaller than 10 μm) and PM2.5 (particles of size smaller than 2.5 μm). Of the mentioned categories, PM2.5 was the most represented one with a 97% share. This particle mass distribution (PM2.5 is significantly dominant) is usual for the small scale combustion units with overfired constructions (standard wood log stove, overfire boiler) [52].

The reached PM mass concentrations and EFs were in the range of the ones reported by Bäfver et al. [51] (PM ranged between 19 and 82 mg MJ^{-1}) and by Hedberg et al. [53] (PM2.5 mass concentration was 80 mg MJ^{-1} in average), where traditional wood log stoves were used. Overall, the pellet burner set up was adequate for simulation the operation of standard wood log stoves without their disadvantage of periodic operation.

The average mass concertation of PM at the catalysts outlet was 125 and 136 mg m^{-3} for Cat A and Cat B respectively. The average reached conversion rate of PM by catalysts (comparison of the flue gas composition without the catalyst and with the catalysts) reached 25.2 (ranged between 21.8 and 28.1% comparing the first, second and third sampling at the same times after the ignition) for Cat A and 18.8% (ranged between 2.6 and 26.7% comparing the first, second and third sampling at the same times after the ignition) for Cat B. The statistical evaluation of the mass concentration of PM in the flue gas for each test is presented in Fig. 6. The decrease of the PM mass concentration by flowing of the flue gas through the catalysts was caused by several processes including PM precipitation on the catalyst surface and oxidative destruction of organic and elemental carbon species.

Cat A achieved a conversion rate that was almost 7% higher than that of Cat B. However, the average value of Cat B was significantly affected by one sampling which had a very low conversion rate. In terms of the PM conversion rate, Cat B with higher precious metal loading was a more stable option. The conversion rate of PM (on average) reached by

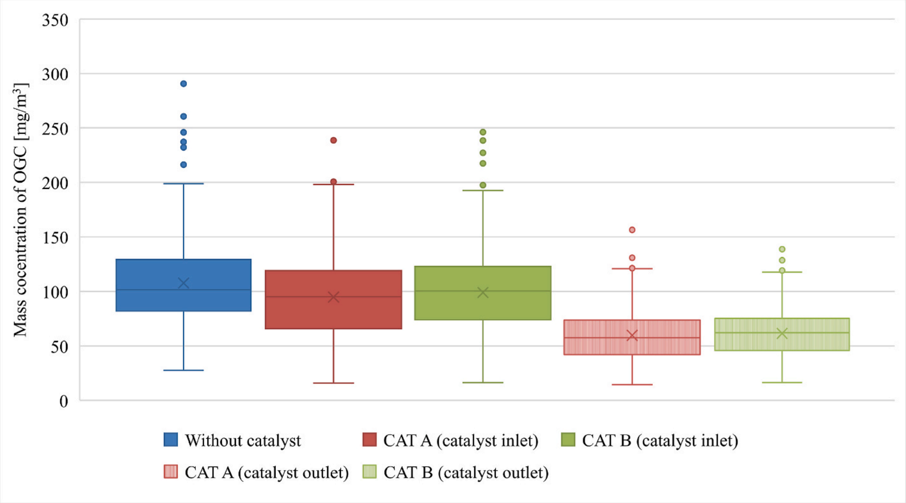

Fig. 4. Statistical graph of mass concentration of OGC in the flue gas.

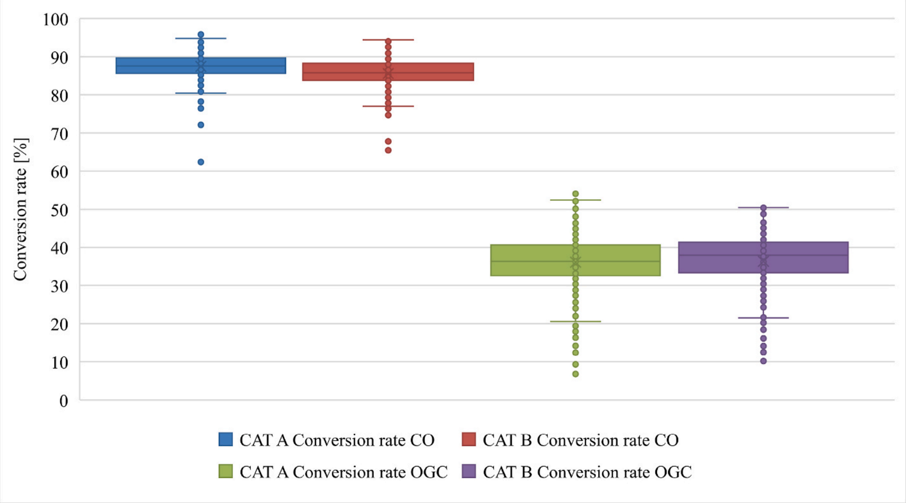

Fig. 5. Statistical graph of conversion rates of CO and OGC by CAT A and CAT B.

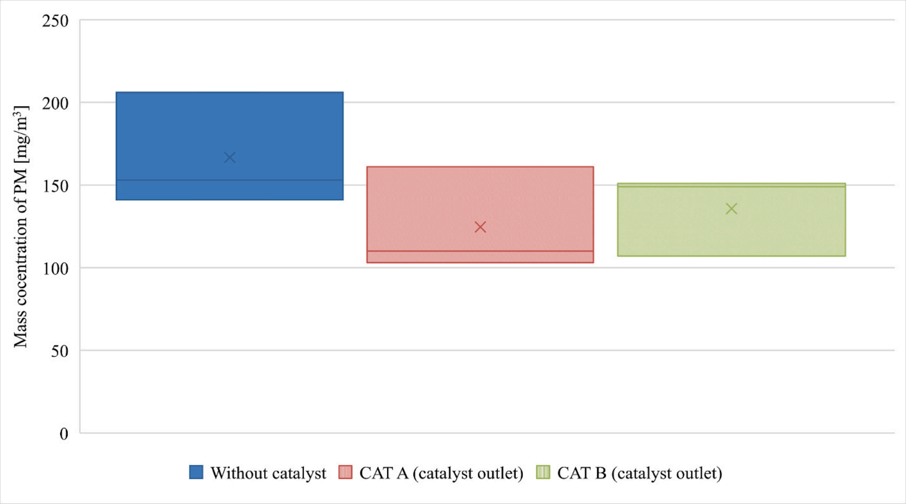

Fig. 6. Statistical graph of mass concentration of PM in the flue gas.

Cat A in this study was higher than −5% reached (on average) in the study of Krpec et al. [50].

The conversion rate of PM (on average) reached by Cat B in this study was higher than 30% reached (on average) in the study of Hukkanen [24] and higher than 10% reached (on average) in the study of Krpec et al. [50]. The differences between the catalyst used in this study and the catalysts used in previous studies are listed in chapter 3.2.

3.5.1. *Carbonaceous content*

Particulate matter emissions were dominated by carbonaceous material, which accounted for 72.8 ± 5.74, 67.8 ± 5.39 and 72.7 ± 6.30% wt. of the TSP mass for the reference condition (without catalysts) and the combustion tests with Cat A and Cat B, respectively. The carbonaceous content was mainly composed of EC, regardless of the tested condition (Table A3). The predominance of EC in emissions from pellet combustion was also reported in previous studies [54,55]. The decrease of OC by the catalysts was visible and ranged from 28% to 49% and from 13% to 60% with Cat A and Cat B, respectively. EC concentrations in the flue gas were reduced from 23% to 33% with Cat A, whereas the catalytic effect appeared to be less effective with Cat B. The latter allowed a maximum reduction of 31% but showed an increase in EC concentrations in one of the samples. In a previous study with the aim of testing the reduction efficiency of a Pt–Pd catalyst applied to emissions from the combustion of birch wood in a conventional sauna stove, the authors also pointed out that the catalyst seemed to be more effective in reducing OC than EC [24]. On the other hand, Klauser et al. [27] reported that particulate carbonaceous fractions, both OC and EC, were not reduced using catalysts installed in a wood stove. The authors tested two Pt–Pd catalysts, with distinct honeycomb carriers and different active surfaces [27].

3.5.2. *Water-soluble inorganic ions*

The contribution of inorganic ions to total PM was, on average, 13.0%$_{wt.}$, 16.1%$_{wt.}$ and 14.9%$_{wt.}$ of the TSP mass for the reference condition (without catalyst) and the combustion tests with Cat A and Cat B, respectively. The dominant water-soluble species in TSP emissions were sulphate and potassium, regardless of the tested condition. This is in line with results previously reported for the combustion of wood pellets [54,56,57]. Along with other alkali compounds, K_2SO_4 is a main compound observed in the emissions from pellet combustion [58]. In fact, potassium has been suggested as a suitable tracer for residential biomass combustion using automatically fired combustion appliances since the higher combustion efficiency achieved favours its emission [59]. Only slight differences in the concentrations of inorganic ions for the reference conditions and using the catalysts were detected. Recorded fluctuations may result from variations in fuel composition or combustion conditions. It should be noted that, over time, deposition of alkali and alkaline earth metals may occur on the catalyst's surfaces hampering the regeneration efficiency and compromising its performance [58].

3.5.3. Particle-bound organic compounds

3.5.3.1. Polycyclic aromatic hydrocarbons. Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds composed of two or more fused aromatic rings, resulting from incomplete combustion or pyrolysis of organic materials, such as biomass. Many PAHs are highly toxic, mutagenic and/or carcinogenic to humans [60]. In the present study, particulate matter emissions were dominated by 4-ring PAHs, which accounted for 58.3 ± 7.3, 65.3 ± 5.7 and 63.0 ± 3.0% of the total polyaromatic mass fractions for the reference condition and the combustion tests with Cat A and Cat B, respectively. Among them, the one that stood out the most was fluoranthene (Table A4). Lighter molecular weights, such as benzothiazole, naphthalene, acenaphthylene, acenaphthene, carbazole, and *p*-terphenyl, were always absent in particulate matter samples. Anthracene was present in only one sample of each catalyst, while retene was detected in one of the 3 filters for each condition. It is worth mentioning that during combustion processes, naphthalene and other lighter PAHs have been found to exist predominantly in the gas phase. These lighter PAHs usually have higher concentrations compared to the heavier ones [61–63]. For instance, in emissions from three fuel-stove systems, Oanh et al. [62] reported that the most volatile PAHs (ranging from naphthalene to anthracene) were detected primarily in the gaseous phase (>98–99%). Therefore, future research should focus on measuring both gas and particle-phase compounds, using appropriate methods for sampling emissions from biomass burning, and ensuring a more comprehensive understanding of the gas-particle distribution of PAHs [61]. Heavier compounds, with 5 or 6 rings, accounted for 37.2 ± 7.6, 26.5 ± 7.7 and 30.8 ± 5.0% of total particulate-bound-PAHs ($\sum$21 PAHs) in emissions without and with catalysts A and B, respectively. It has been suggested that the gaseous products are converted to low molecular weight (LMW) PAHs through incomplete combustion during devolatilisation. These LMW PAHs are progressively pyrosynthesised into medium and high molecular weight PAHs through the so called "zig-zag addition process" [64]. Given that these reaction mechanisms are highly temperature dependent, the amounts and types of PAHs formed can vary throughout the combustion cycle.

The particulate mass fractions of total PAHs in this study (1072, 883 and 1206 $\mu g \cdot g^{-1}$PM for the reference condition, Cat A and Cat B, respectively) were higher than those obtained by Vicente et al. [54] for the combustion of certified and noncertified pellets in a 9.6 kW residential stove (277–315 $\mu g\ g^{-1}PM_{10}$). It has been observed that although more modern combustion technologies contribute to reducing total PM emissions, higher combustion temperatures can generate higher PAH emissions. On the other hand, the raw material for wood pellets (hardwood versus softwood) can also influence the emission of PAHs with softwood leading to higher amounts in the flue gas [65].

On average, the overall removal of PAHs by Cat A was 45%, while the decrease with Cat B was only 17%. Gaze et al. [66] tested the removal efficiency of different catalysts (copper, manganese, titanium, and platinum) on the flue gas emissions from a standard 15 kW retort boiler powered by three types of pellets. The PAH removal rates ranged from 5 to 15%. The platinum catalyst was found to be the most effective solution for decreasing PAH emissions. Kaivosoja et al. [28] burned birch logs in a wood-fired stove (18 kW) with and without a catalytic converter with palladium and platinum as catalysts. On average, total PAH concentrations were 24% lower when the catalytic converter was employed. Klauser et al. [27] evaluated the impact of two commercially available oxidising platinum/palladium catalysts with either metallic or ceramic honeycomb carriers on the emissions from a firewood room heater (10 kW). The metallic catalyst led to a reduction of 63% of PAH emissions, while the ceramic unit allowed only a slight decrease.

In the present study, the use of catalytic converters decreased the emitted amounts of heavier PAHs with 4–6 benzene rings. Considering that the carcinogenicity of PAHs increases with the number of rings [67,68], it appears that PAH emissions with catalytic converters are less carcinogenic than without them. Nevertheless, to draw meaningful conclusions, a gas-particle partitioning assessment should be performed in future research.

3.5.3.2. Polar organic compounds. Several polar organic compounds were detected in the particulate matter (Table A5). These compounds can be volatilised molecules of the original naturally occurring compounds in the pellets that recondense into the particulate phase or, instead, chemical products of pyrolysis during combustion. Among the analysed polar organic compounds, the most abundant in the flue gas of the reference condition were palmitic, stearic and glycolic acids. The latter is a hydroxy acid that has been previously described in emissions from biomass combustion [67,69] and as a constituent capable of driving particle formation as well as the initial growth of aerosols in the atmosphere [70]. The two saturated fatty acids (palmitic and stearic) have also been identified as major primary compounds in biomass burning emissions [71]. Monoglycerides were also abundant in the untreated flue gas. Although these are major constituents of aerosols from cooking [72], their presence in smoke particles from wildfires was documented as well [47]. Various PAHs with carbonyl groups were also quite expressive in the flue gas in the absence of catalyst. Oxygenated PAHs and derivatives are a result of incomplete combustion either with or without sufficient oxygen. Additionally, they can be formed after precursors have left the combustion chamber when temperatures decline [73]. Levoglucosan and its isomer mannosan were also detected in emissions, but at particulate mass fractions lower than those reported for fireplaces and woodstoves. These anhydrosugars have been widely used to estimate the impact of biomass burning emissions on ambient particulate levels. Their emissions have been described to be largely dependent on combustion temperature, registering maximum concentrations for values below 300 °C [65].

For most compounds a significant decrease in emissions was recorded with the use of catalytic converters. However, for some constituents there was an increase in the concentrations emitted after the gas passed through the honeycomb units. This is the case of levulinic acid, succinic acid, azelaic acid, diethylene glycol, glycerol and two aromatic diones for Cat A. For Cat B an enrichment in diethylene glycol, hydroxybenzyl alcohol, 2,4-di-tert-butylphenol and two aromatic diones was registered. Excluding these compounds, the removal rate for the remaining constituents averaged 37% and 34% for Cat A and Cat B, respectively. Kaivosoja et al. [28] observed that catalytic converters can be used to decrease organic compounds, but platinum and palladium could also catalyse the oxidation of precursors of some other constituents leading to higher concentrations at the exit of the flue gas. In fact, catalysts might boost oxidative formation of semivolatile species, resulting in the formation of particulate products similar to those in secondary organic aerosols formed in the atmosphere [27]. On the other hand, the additional pyrolysis that occurs in the catalytic bed can further aromatise the natural biomass components into polycyclic structures [74]. As stated by Hukkanen et al. [24], there is a variety of organic constituents in the flue gas from biomass combustion, and these compounds have different molecular masses, spanning from liquid to gaseous forms, and thus, it is challenging to accomplish an accurate analysis of how the catalyst might affect the various emissions. Thus, it seems that PAH emissions from the combustion with this type of catalytic converters may be less carcinogenic than those not subject to any flue gas treatment.

4. Conclusions

Results of this study showed a significantly positive influence of tested catalysts on mass concentration of CO, OGC and PM in the flue gas, while conversion rates by CAT A and CAT B respectively reached 87.8% and 85.8% (CO), 37.0% and 37.8% (OGC), 25.2% and 18.8% (PM). For all tests the dominant PM size was PM2.5, while the influence of the catalysts on PM distribution into observed categories (PM, PM10, PM2.5) has not been proven.

Regarding the carbonaceous content in the TSP, the decrease of OC and EC by CAT A ranged between 28 and 49 % and between 13 and 60% respectively thus was higher, than in the case of CAT B, where the decrease of OC ranged between 23 and 33% and the increase of EC ranged between 14 and 30%. Both catalysts are considered very efficient for flue gas purification in general, while the lower precious metal loading in the sol-gel prepared coating represented an interesting solution enabling a decrease of used precious metals by about 33% while maintaining of almost identical results. The similarity of the results obtained with two different catalysts confirms the possibility of using low-loading catalysts (CAT B) as a suitable alternative to conventional ones (CAT A). The incorporation of a reduced amount of precious metals during the preparation of catalysts could potentially result in a lowered cost, thereby enhancing the accessibility and cost-effectiveness of these catalysts. The evaluation of the PM-bound PAHs composition and their mass concentrations revealed a shift in particulate PAH emissions using the catalytic converters that appeared to be less carcinogenic than those from the combustion without catalysts. However, further research is necessary to examine both gas and particle-phase compounds for a more comprehensive understanding of the distribution of PAHs in the gas-particle mixture and their associated toxicity.

The results obtained in this study, using the external, retrofit solution, showed similar CO, OGC and PM conversion rates compared to other previous studies using integrated catalytic systems.

Future research should focus on the evaluation of innovative catalysts that have lower or zero precious metals loading, replaced by metal oxides. This assessment should include the overall impact of these catalysts on flue gas composition as well as their effectiveness during the combustion of uncertified fuels. Additionally, a standardised methodology for testing these catalysts should be developed to ensure consistency in the market and facilitate comparison of results from different studies.

CRediT authorship contribution statement

Jiří Ryšavý: Writing – original draft, Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Estela Alexandra Domingos Vicente:** Writing – original draft, Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Miroslav Jaroch:** Resources, Data curation. **Célia A. Alves:** Writing – original draft, Writing – review & editing, Supervision, Methodology. **Ana Sánchez de la Campa:** Validation, Supervision, Methodology, Investigation. **Jiří Horák:** Supervision.

Data availability

Data will be made available on request.

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Appendix

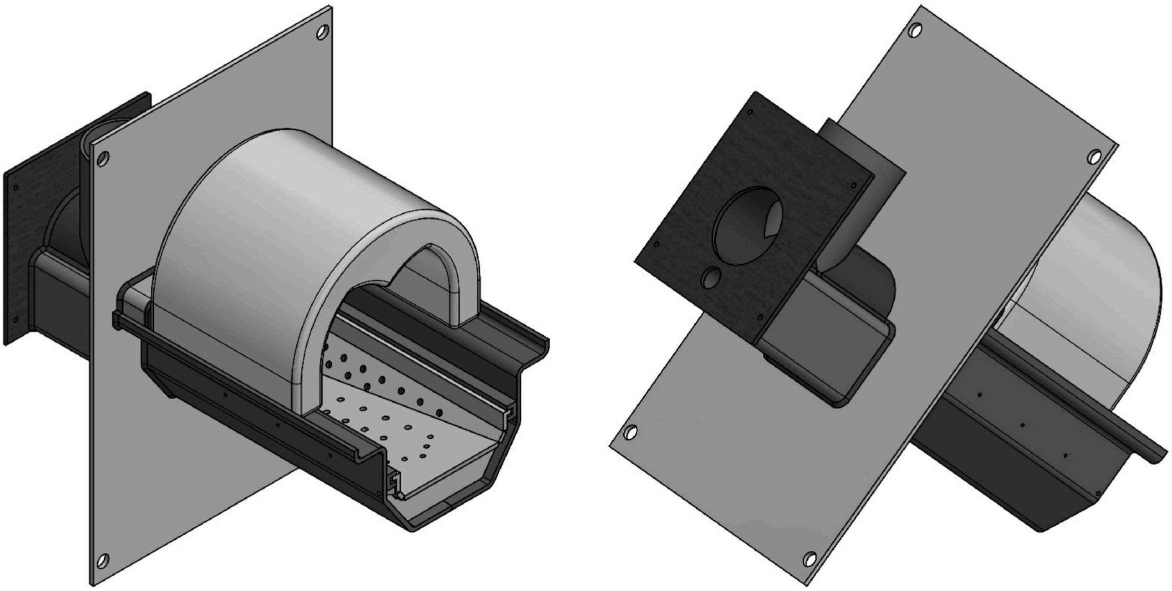

Fig. A1. Prototype of the used gutter burner for combustion of pellets.

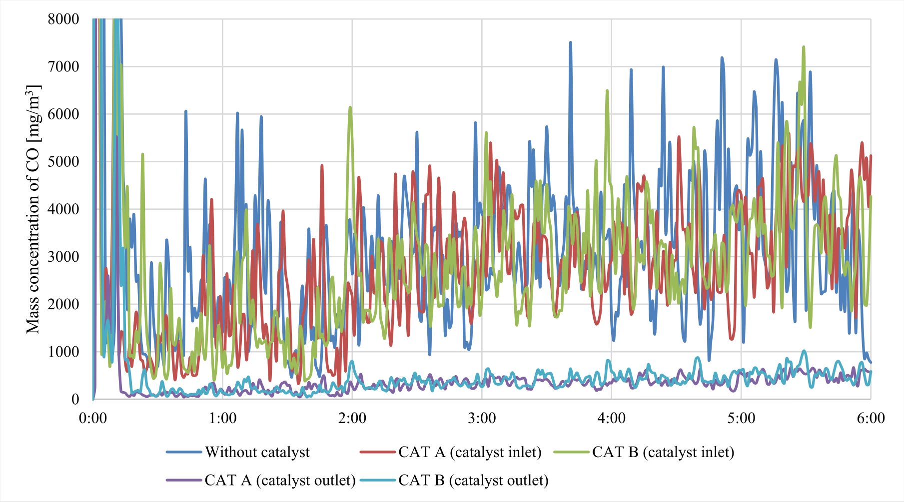

Fig. A2. Course of the mass concertation of CO of all tests.

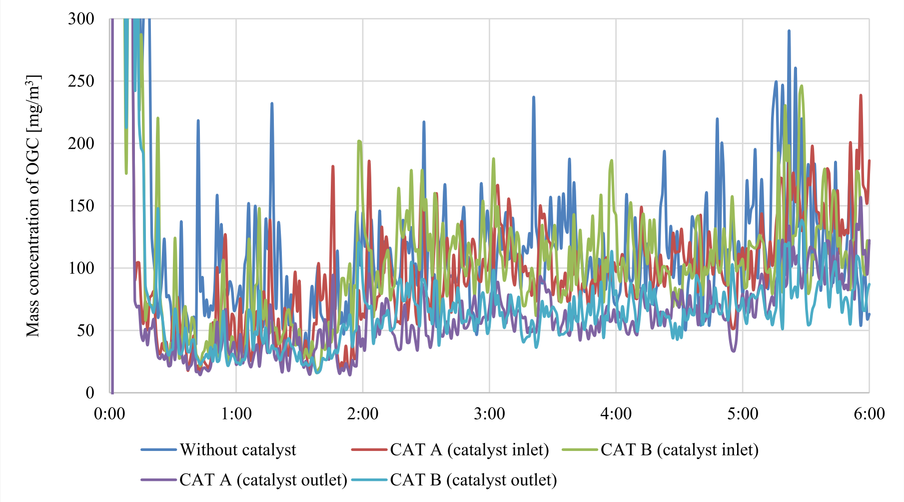

Fig. A3. Course of the mass concertation of OGC of all tests.

Table A1
Overall results of the combustion tests

Mode			without CAT	CAT A	CAT B
Sampling time (start)		h:min	0:30	0:30	0:30
Sampling time (end)		h:min	6:00	6:00	6:00
Mode duration		h	5.5	5.5	5.5
Heat output		kW	8.6	8.2	8.3
Fuel consumption		$kg{\cdot}h^{-1}$	2.2	2.2	2.2
Flue gas volume flow		$m^3{\cdot}h^{-1}$	17.1	17.6	17.6
GHSV (STP conditions)		h^{-1}	19,386	19,914	19,942
GHSV (effective conditions)		h^{-1}	43,143	49,255	48,657
Efficiency (direct method)		%	79.3	75.9	76.6
Flue gas temperature		°C	335	402	393
Chimney draught		Pa	7.2	7.1	6.8
Reference volume fraction of oxygen		$\%_{vol.}$	13.0	13.0	13.0
Volume fraction of O_2 in the flue gas at the catalyst inlet		$\%_{vol.}$	7.9	8.2	8.2
Mass concentration of flue gas components at the catalyst inlet	CO	$mg{\cdot}m^{-3}$	2806	2814	2750
	NO_X	$mg{\cdot}m^{-3}$	73	91	92
	OGC	$mg{\cdot}m^{-3}$	105	92	96
	CO_2	$g{\cdot}m^{-3}$	154	150	150
Volume fraction of O_2 in the flue gas at the catalyst outlet		$\%_{obj.}$	–	8.4	8.5
Mass concentration of flue gas components at the catalyst inlet	CO	$mg{\cdot}m^{-3}$	–	343	390
	NO_X	$mg{\cdot}m^{-3}$	–	83	82
	OGC	$mg{\cdot}m^{-3}$	–	58	60
	CO_2	$g{\cdot}m^{-3}$	–	156	156

(*continued on next page*)

Table A1 (*continued*)

Mode			without CAT	CAT A	CAT B
	PM	$mg \cdot m^{-3}$	167	125	136
	PM10	$mg \cdot m^{-3}$	166	124	135
	PM2.5	$mg \cdot m^{-3}$	162	123	134
CO conversion rate		%	–	87.8	85.8
OGC conversion rate		%	–	37.0	37.8
PM reduction		%	–	25.2	18.8

Table A2

Overall results of the combustion tests; nd – not defined

Active substance [–]	Precious metal loading [$g \cdot m^{-3}$]	Active surface [m^2]	Average flue gas temperature [°C]	Body material [–]	CO conversion rate [%]	OGC conversion rate [%]	PM conversion rate [%]	Reference [–]	Note
Pd	475	0.56	402	cordierite	87.8	37.0	25.2	this study	
Pd	475	0.38	262	cordierite	73	10	−5	[50]	
Pd	475	0.42	334	cordierite	69	ne	ne	[30]	Average values
Pd	475	0.42	400	cordierite	79	ne	ne	[30]	Values for flue gas temperature 400 °C
Pd	475	0.23	282	cordierite	77.8	61.2	ne	[40]	
Pt	317	0.56	393	cordierite	85.8	37.8	18.8	this study	
Pt	475	0.51	307	Al_2O_3	65	63.8	ne	[40]	
Pt	475	0.51	353	Fecralloy®	96	ne	ne	[50]	
Pt–Pd	ne	ne	ne	metal wire	21	14	ne	[24]	Average values
Pt–Pd	ne	ne	ne	metal wire	80	ne	ne	[24]	Values obtained during the burnout phase
Pt–Pd	ne	0.16	370	ceramic	69	27	4	[27]	
Pt–Pd	ne	0.55	370	metal	88	39	−17	[27]	
Pt–Pd	ne	0.16	400	ceramic	>80	>60	~30	[26]	
Pt–Pd	ne	0.55	400	metal	>95	>60	~30	[26]	
Pt–Pd	ne	0.16	375	ceramic	83	~30	~20	[38]	
Pt–Pd	ne	0.55	375	metal	93	~30	~20	[38]	
V_2O_5–WO_3–TiO_2	ne	0.35	293	SiO_2	59.4	53.8	ne	[40]	
V_2O_5–WO_3–TiO_2	ne	0.88	347	SiO_2	86.5	54.1	ne	[75]	

Table A3

Average TSP mass fractions and concentrations in the flue gas of OC, EC and water-soluble inorganic ions. Reduction efficiency of OC and EC.

	Without CAT		CAT A		CAT B		CAT A	CAT B
Carbonaceous matter								
	$\%_{wt.}$ TSP mass	$mg \cdot m^{-3}$	$\%_{wt.}$ TSP mass	$mg \cdot m^{-3}$	%wt. TSP mass	$mg \cdot m^{-3}$	% Reduction (range)	
OC	8.49 ± 2.09	14.7 ± 6.76	6.46 ± 0.81	8.15 ± 2.81	6.49 ± 0.50	8.81 ± 1.61	28–49	13–60
EC	64.3 ± 4.19	108 ± 27.8	61.4 ± 4.72	77.4 ± 25.8	66.2 ± 6.32	91.0 ± 23.7	23–33	−*14*–31
Water-soluble inorganic ions								
	$\%_{wt.}$ TSP mass	**$mg \cdot m^{-3}$**	**$\%_{wt.}$ TSP mass**	**$mg \cdot m^{-3}$**	**%wt. TSP mass**	**$mg \cdot m^{-3}$**		
F^{--}	nd	nd	nd	nd	nd	nd	NA	
Cl^-	0.842 ± 0.196	1.36 ± 0.084	1.28 ± 0.380	1.52 ± 0.149	1.15 ± 0.328	1.52 ± 0.126		
NO_2^-	2.13 ± 0.432	3.47 ± 0.158	1.86 ± 1.70	2.44 ± 2.11	1.56 ± 1.35	2.33 ± 2.02		
NO_{3-}	1.03 ± 0.227	1.67 ± 0.083	1.41 ± 0.353	1.69 ± 0.071	1.31 ± 0.350	1.72 ± 0.112		
SO_4^{2-}	4.08 ± 1.15	6.55 ± 0.677	5.23 ± 1.98	6.11 ± 1.12	4.57 ± 1.43	5.99 ± 0.642		
Br^-	nd	nd	nd	nd	nd	nd		
PO_4^{3-}	0.297 ± 0.515	0.419 ± 0.726	0.404 ± 0.701	0.417 ± 0.722	0.502 ± 0.435	0.753 ± 0.652		
Na^+	bdl	bdl	bdl	bdl	bdl	bdl		
NH_4^+	bdl	bdl	bdl	bdl	bdl	bdl		
K^+	4.44 ± 1.07	7.18 ± 0.441	5.64 ± 1.84	6.65 ± 0.823	5.53 ± 1.69	7.25 ± 0.754		
Ca^{2+}	0.212 ± 0.069	0.338 ± 0.058	0.292 ± 0.111	0.344 ± 0.069	0.266 ± 0.085	0.365 ± 0.151		
Mg^{2+}	0.007 ± 0.007	0.011 ± 0.011	0.007 ± 0.010	0.008 ± 0.011	nd	nd		
Li^+	nd	nd	nd	nd	nd	nd		

Nd: not detected; bdl: below detection limit; NA: not applicable. Negative values in italics indicate increased concentrations of compounds.

OC and EC reduction efficiencies were calculated from the comparison of the mass concentrations of pollutants in the flue gas with and without catalyst collected at the same relative time in relation to the ignition (2:00; 3:30; 5:00).

Table A4
Mean particulate mass fractions, concentrations of polycyclic aromatic hydrocarbons in the flue gas and removal rates by the catalysts

	Without CAT		Cat A		Cat B		Cat A	Cat B
	μgPAH g^{-1}PM	mg·m$_N^{-3}$	μgPAH g^{-1}PM	mg·m$_N^{-3}$	μgPAH g^{-1}PM	mg·m$_N^{-3}$	%removal	%removal
Fluorene	7.86	1.34	12.4	1.37	8.02	1.10	*−2.5*	18.2
Phenanthrene	33.7	5.78	55.7	6.66	58.9	8.18	*−15.2*	*−41.4*
Fluoranthene	320	54.4	298	36.3	393	52.9	33.2	2.7
Pyrene	178	29.7	211	25.5	261	35.4	14.0	−19.2
Benzo [a]anthracene	45.4	7.89	27.5	3.31	46.6	6.04	58.1	23.4
Chrysene	78.2	13.5	49.8	5.97	69.3	9.07	55.8	32.8
Benzo [b]fluoranthene	81.7	14.0	52.2	6.13	63.0	8.36	56.2	40.2
Benzo [k]fluoranthene	65.6	11.4	40.3	4.84	68.9	9.10	57.5	20.2
Benzo [a]pyrene	53.9	9.78	32.7	3.89	55.4	7.22	60.2	26.1
Perylene	20.8	3.73	11.9	1.43	22.1	2.89	61.6	22.6
Indeno [1,2,3-cd]pyrene	68.1	12.1	33.5	4.04	62.5	8.19	66.5	32.1
Dibenzo [a,h]anthracene	2.67	0.466	1.28	0.150	2.82	0.369	67.8	20.8
Benzo [g,h,i]perylene	117	20.9	57.3	6.84	95.8	12.7	67.3	39.1

Note: Negative values in italics mean increased concentrations of compounds at the comparison of the situation without the catalyst (reference) with situations with used CAT A and CAT B.

Table A5
Particulate mass fractions, concentrations and catalyst removal rates of polar organic compounds from the flue gas

	Reference condition		Cat A		Cat B		Cat A	Cat B
	μg g^{-1}	μg m$_N^{-3}$	μg g^{-1}	μg m$_N^{-3}$	μg g^{-1}	μg m$_N^{-3}$	%Removal	%Removal
ACIDS								
Glycolic acid	1148	189	672	94.2	1147	148	50.2	21.7
Levulinic acid	46.0	7.01	103	16.0	47.5	6.20	*−128*	11.6
Hydracrylic acid	111	17.5	117	14.6	72.0	9.05	16.6	48.3
Benzoic acid	186	30.6	104	14.0	72.2	9.35	54.2	69.4
Dehydroabietic acid	13.0	2.10	13.2	1.66	10.8	1.40	21.0	33.3
1-Naphthalenecarboxylic acid	85.3	14.9	11.1	1.15	14.3	2.16	92.3	85.5
Butanedioic (succinic) acid	248	37.6	418	56.5	110	14.3	*−50.3*	62.0
Nonanedioic (azelaic) acid	40.2	6.49	83.5	11.6	34.4	4.27	*−78.7*	34.2
Dodecanoic (lauric) acid	26.7	4.34	25.4	3.36	28.9	3.66	22.6	15.7
Tetradecanoic (myristic) acid	40.4	6.65	53.0	6.31	36.0	4.68	5.11	29.6
Pentadecanoic acid	29.0	4.61	32.7	3.65	25.8	3.35	20.8	27.3
Hexadecanoic (palmitic) acid	1605	264	1404	173	1718	219	34.5	17.0
Heptadecanoic acid	23.9	3.93	28.4	3.48	18.3	2.32	11.5	41.0
cis-9-Octadecenoic (oleic) acid	38.6	6.54	10.2	1.49	41.9	5.34	77.2	18.3
Octadecanoic (stearic) acid	1242	205	1072	134	1195	149	34.6	27.3
Eicosanoic (arachidic) acid	22.2	3.58	26.2	3.30	20.5	2.57	7.82	28.2
Docosanoic (behenic) acid	10.9	1.78	8.79	1.04	10.0	1.27	41.6	28.7
Tetracosanoic acid	12.2	1.92	8.72	1.09	8.78	1.10	43.2	42.7
ESTERS								
Hexanedioic acid, dioctyl ester (Dioctyl adipate)	127	22.2	4.36	0.480	26.6	3.64	97.8	83.6
Hexanoic acid methyl ester	55.8	9.12	67.3	8.36	57.2	7.26	8.33	20.4
n-ALKANOLS								
Hexadecan-1-ol	35.0	6.91	50.4	6.48	45.9	5.90	6.22	14.6
Octadecan-1-ol	217	36.3	243	29.5	239	31.4	18.7	13.5
STEROL								
β-Sitosterol	17.6	2.94	18.7	2.22	21.0	2.71	24.5	7.82
OTHER HYDROXYL COMPOUNDS								
Diethylene glycol	209	32.6	324	39.4	305	37.5	*−20.9*	*−15.0*
Glycerol	339	51.7	517	68.7	312	45.1	*−32.9*	12.8
p-Hydroxybenzyl alcohol	22.4	3.78	21.5	2.77	35.5	4.98	26.7	*−31.7*
2,4-di-tert-butylphenol	157	26.5	118	15.2	248	31.8	42.6	*−20.0*
ANHYDROSUGARS								
Mannosan	10.4	1.68	9.06	1.07	12.6	1.64	36.3	2.38
Levoglucosan	32.0	5.14	27.7	3.84	21.9	2.88	25.3	44.0
MONOGLYCERIDES								
1-Monopalmitin	350	56.9	377	45.9	334	42.6	19.3	25.1
2-Monopalmitin	318	64.4	34.4	4.48	24.5	3.18	93.0	95.1
1-Monostearin	383	62.0	405	50.1	366	46.8	19.2	24.5
2-Monostearin	23.2	3.73	22.7	2.78	20.0	2.53	25.5	32.2
AROMATIC KETONES								
7,9-di-tert-butyl-1-oxaspiro [4.5]deca-6,9-diene-2,8-dione	146	22.9	211	24.3	171	22.8	*−6.11*	0.437
1H-Phenalen-1-one (Perinaphthanone)	289	48.22	107	13.99	157	21.7	71.0	55.0
1H-Benz [de]isoquinoline-1,3(2H)-dione (1,8-Naphthalimide)	66.8	12.5	33.4	4.99	195	29.1	60.1	*−133*
7H-Benz [de]anthracen-7-one (Benzanthrone)	143	23.7	60.0	7.38	78.1	10.1	68.9	57.4
2,6-Di-tert-butyl-1,4-benzoquinone	303	48.9	369	44.8	254	33.9	8.48	30.7
1H,3H-Naphtho [1,8-cd]pyran-1,3-dione (1,8-Naphthalic anhydride)	116	20.9	415	48.0	304	44.8	*−130*	*−114*

Note: Negative values in italics mean increased concentrations of compounds at the comparison of the situation without the catalyst (reference) with situations with used CAT A and CAT B.

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