COMPARISON OF CATALYSTS IN THE POINT OF VIEW OF PELLET STOVE FLUE GAS PURIFICATION

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ABSTRACT
Monolithic catalysts are used as a method for the flue gases purifying by oxidation of gas products from incomplete combustion. This study is focused on three different types of monolithic catalysts and quantification of their degree of influence on mass concentration of carbon monoxide (CO) and organic gaseous compounds (OGCs) in real small-scale wood pellet stove. Catalysts were placed right behind the stove at the flue gas outlet. The comparison consisted of quantification of their influence on the selected pollutants during the few-hours steady operation of the small-scale pellet stove. Reference values of the selected pollutants were defined during the combustion test without a catalyst installed. In this article, three catalysts based on different active compounds: WO_3–V_2O_5, Pd and Pt were tested. The palladium-based catalyst has proven the best degree of conversion of CO (almost 78%). The platinum-based catalyst has proven the best degree of conversion of OGC (almost 64%). Due to a big degree of clogging by solid particles of all catalysts during the tests, it is impossible to operate the chosen stove with tested types of catalysts in normal operation at home conditions. Without any type of periodical cleaning (every few hours), there is a serious danger of leakage of the flue gas out of the stove. Further investigations should evaluate the degree of clogging in a long-term operation and should propose a method to avoid any danger of the flue gas leaking caused by the catalysts.
Keywords: automatic pellet stove, firewood combustion, flue gas purify, oxidizing honeycomb catalyst.

1 INTRODUCTION

Many countries around the world have been solving problems related to an air pollution. Different countries mean different sources of pollutants. An important part of the pollution source is a combustion of solid fuels both from heating (especially in countries with cold climate) and from cooking (especially in developing countries). In total, it means that more than 2.7 billion people burn biomass at home. With regard to the direct heating appliances in Europe, there are almost 26 million stoves, which already count about 635,000 automatic wood pellet stoves and approximately 7.6 million of cookers [1].

During the usage of these types of combustion equipment, the pollutants are forming. One of the group of pollutants is from an incomplete combustion inside the combustion chamber. The incomplete combustion could happen, for example, due to low air excess ratio or due to small temperature in the combustion chamber. These types of pollutants are released more significantly during a batch combustion than during the continuous combustion [2].

Legislative limitations of the new stoves and cookers producers are in the sense of the mass concentration reduction of pollutants in the flue gas understandable. Nowadays, producers have been reducing the mass concentration of pollutants in the flue gas by the primary measures, such as better fuel—air ratio, better construction of a combustion chamber, better construction of own burner and so on. Another reduction of the legislative limitations in future could lead to an utilization of the secondary measures, such as, for example, catalysts. There are six product groups in Europe of manually operated firewood room heating appliances and one group of automatically operated products for room heating: firewood cookers (EN 12815) [3], inset appliances and open fireplaces (EN 13229) [3], room heaters (EN 13240) [4], tiled stoves (EN 15544) [5], slow heat release appliances (EN 15250) [6] and residential space heating

ISSN: 2056-3272 (paper format), ISSN: 2056-3280 (online), http://www.witpress.com/journals
DOI: 10.2495/EQ-V4-N2-124-133

appliances fired by wood pellets (EN 14785) [7]. Each of these groups has own European standard defining limit values of mass concentration of some pollutants in the flue gas.

Catalysts can also be used for a retrofit of old combustion equipment, which can lead to a decrease of mass concentration of some pollutants in the flue gas [8].

Previous studies of Krpec *et al*. [9] and Reichert *et al*. [10] have proven a positive influence on the decrease of mass concentration of carbon monoxide (CO) and organic gaseous compounds (OGC) in the flue gas of a small scale batch combustion stove. Flue gas temperature during both tests ranged between 300°C and 500°C.

Thermal stability of metal-supported catalysts for reduction of a cold-start mass concentration in wood-fired domestic boilers has also been observed. The research of Ferrandon *et al*. [11] proved a good stability of this type of catalyst body and also showed a good efficiency of CO and methane conversion at certain flue gas temperature.

This study was focused on the possibilities of the usage of the catalysts at the automatic wood pellet stove outlet and on the comparison of three different types of honeycomb catalysts. Two of the tested catalysts were based on precious metals, which were applied on Al_2O_3 carrier. The third one is based on titanium dioxide carrier and vanadium (V) oxide and tungsten trioxide active compounds. Catalysts based on the precious metal active compounds have been widely studied before for usage in small-scale combustion equipment. Novelty of this research is in their comparison with different types of catalyst, which was not tested in this condition.

2 EXPERIMENTAL MATERIALS AND EQUIPMENT

2.1 Fuel

For the following tests, a hard white pellets from producer M&M Pellets were selected. Elemental composition of the fuel is presented in Table 1. As is common for a biomass, it contains almost no sulfur and only very small amount of ash. The small amount of sulfur is important for the long-term functionality of many types of catalysts. Net calorific value of the M&M pellets is 17.02 MJ/kg. Mass fraction of the volatile matter is ~84%.

2.2 Combustion equipment

As a combustion equipment, a prototype of automatic wood pellet stove, further called as Prototype 1, was used. Due to a fact that stove is still in the process of development, there are

Table 1: Elements' composition of used pellets in raw state.

Element	**Chemical symbol**	**Mass fraction (%)**
Carbon	C^r	47.4
Hydrogen	H^r	6.1
Nitrogen	N^r	<0.1
Oxygen	O^r	40.0
Sulphur	S^r	<0.1
Water	W^r	6.00
Ash	A^r	0.39

no established parameters for nominal power and so on. There were three main reasons for choosing this stove:

- Flue gas temperature at the stove outlet is ~300°C, which is an appropriate temperature for operation of the chosen catalyst.
- Wood pellet stove ensures relatively uniform operation between each of tests. This means that the mass concentration of pollutants in flue gases at the stove outlet is always similar. There are no uneven states before and after a fuel batch.
- Control unit named RKU 3 made by BENEKOVterm Ltd., controls the amount of the combustion air and the supplied fuel, enables to keep the same settings without any modulation dependent on an external influences.
- The combustion air enters the stove through one duct, which enables controlling the amount of the air by a thermo-anemometer.
- Due to a different pressure loss of different catalysts, it is necessary to observe air flow at the air entrance to the stove during the tests. And with respect to this, it is necessary to change settings of a flue gas fan for the same air excess ratio between each of tests.

The settings of the control unit for fuel adding were always the same during the tests: 10/10 (s/s) adding/pause. The amount of added fuel in 1 h was investigated experimentally. This value and the known net calorific value of used fuel determine the operating input power of the stove, P = 7 kW. Hot flue gases are transmitting their heat energy to the air in a flue gas-air heat exchanger above the combustion chamber. Heated air flow was provided by an air fan. A sketch of the used automatic stove with the location of installed catalysts is shown in Fig. 1.

2.3 Tested catalysts

The aim of this research was the comparison of three different monolithic catalysts. All tested catalysts were prepared in the same dimensions, and so with the same volume. Cylindrical shape of the catalysts enables to install them at the stove outlet of the flue gas. Their detailed description is given in Table 2. A picture of all three types of catalysts is shown in Fig. 2.

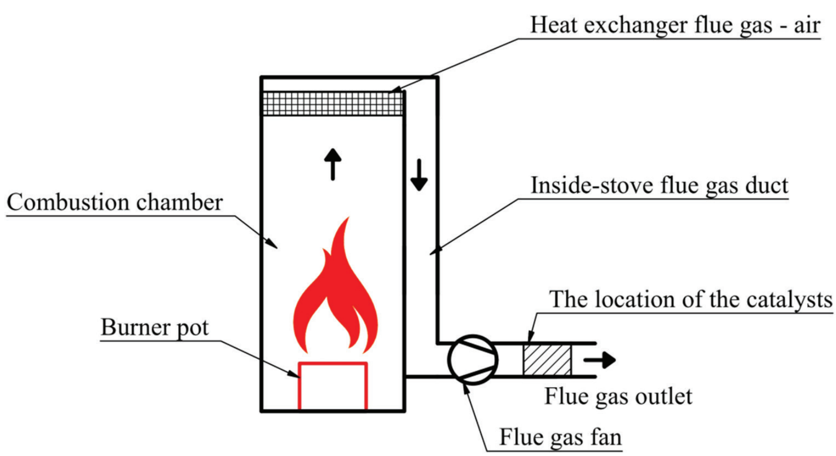

Figure 1: Sketch of used automatic stove.

Table 2: Detailed description of the tested catalysts.

Name		**cat 1**	**cat 2**	**cat 3**
Catalyst type	–		Monolithic-honeycomb	
Body material	–	SiO_2	Ceramic	Steel
Carrier		TiO_2	Al_2O_3	Al_2O_3
Active compounds	–	WO_3-V_2O_5	Pd	Pt
Diameter	m		0.15	
Height	m		0.02	
Volume	m^3		0.00035	
Active surface	m^2	0.35343	0.23770	0.50800
Number of cells	Cells/cm^2	5	8.7	31.8
Pressure loss*	pa	3	3	9

* The catalyst pressure losses were determined at the flue gas flow rate of about 25 m^3/h.

Figure 2: Tested catalyst; from left: cat 1, cat 2, and cat 3.

Additional information about the catalysts:

- Two of them (catalysts 2, further referred to as cat 2 and catalysts 3, further referred to as cat 3) were delivered with specified shapes, one of them was delivered as a big cube (catalysts 1, further referred to as cat 1) (40 × 40 × 40 cm) and the final shape was cut out of it.
- Producer did not provide an information about operating temperature of the catalysts (cat 2 and cat 3), but their dimensions enable to place them only at the stove outlet of the flue gas. Usual operating temperature of cat 1 is between 300°C and 500°C.
- A catalyst's layer thickness was not observed and producer did not provide this information.
- The producer did not provide a conversion efficiency diagram for the catalysts for the oxidation reaction of CO and OGC.
- Producer did not provide any information about active catalytic layer thickness.

2.4 Measuring system for a flue gas analysis

The flue gas was at first purified from solid particles in a ceramic filter. Then it went through a heated tube to analyzers ABB AO2020 and SICK GMS810. The mass concentrations of

CO, CO_2, O_2, SO_2, NO_x and TOC in the flue gas were determined by these machines. Before each test, the analyzers were justified by calibration gases. For the catalysts' comparison, at least 3-h period was evaluated in a steady-state operation.

2.5 Data evaluation

The mass concentration and temperature of the observed pollutants in the flue gas were recorded as average per minute. All final values are counted as average values of mass concentrations of the pollutants (reported as mass concentrations in mg/m^3) in a dry flue gas. Also, the final values represent the whole period of each test and are recalculated for normal conditions ($T = 273.15$ K; $p = 101{,}325$ Pa) and a reference volume fraction of oxygen in the flue gas $\varphi_{\mathrm{ref;[O2]}} = 13\%$. Before the tests with catalysts, a test without any catalyst was done. This test determined the reference values of mass concentration of pollutants in the flue gas. Measured values of mass concentrations of pollutants from following tests with catalysts were related to these values.

Degrees of conversion of the catalysts were calculated from a comparison of the mass concentrations of pollutants in the flue gas without and with the catalyst present according to eqn (1).

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

X is the degree of conversion of a pollutant as flowing through the catalyst (%);
ρ_{Bo} the mass concentration of a pollutant without usage of any catalyst (mg/m^3) and
ρ_B the mass concentration of a pollutant during the test with catalyst (mg/m^3)

3 RESULTS AND DISCUSSION

The measurement was aimed at the catalysts' behavior during the steady-state operation of the stove. All tests start with a process of ignition of pellets at a burner pot. The amount of the ignited pellets was always the same. A gas burner was igniting the pellets for exactly 1 min. After that, the stove door was closed and was not opened during the test again. And after approximately 20 min, the process of burning was considered stable and the flue gas analyzer was connected behind the stove outlet.

3.1 Degree of pollutants' conversion by tested catalysts

CO and OGC degrees of conversion are presented in Fig. 3. Comprehensive information about the flue gas composition during each test is presented in Table 3. Courses of CO mass concentrations, OGC mass concentrations and flue gas temperatures during each mode are presented in Figs. 4, 5 and 6, respectively.

As can be seen from the degree of CO conversion point of view, cat 2 with almost 78% of conversion was the best from the three tested catalysts. Cat 1 and cat 3 proved to be a bit lesser of abilities to convert CO. During the tests of both mentioned catalysts, an increased rate of mass concentration of CO in flue gas was observed. These situations were created by the clogging of pellets inside the tube, which leads from a screw conveyor to a burning pot. After the release of this clogging, pellets fell down into a burning pot in greater amount, which influenced the mass concentrations of pollutants in the flue gas.

From the degree of OGC conversion point of view, the rate of mass concentration of this pollutant in the flue gas was similar for all three tests, except for the two malfunctions described above.

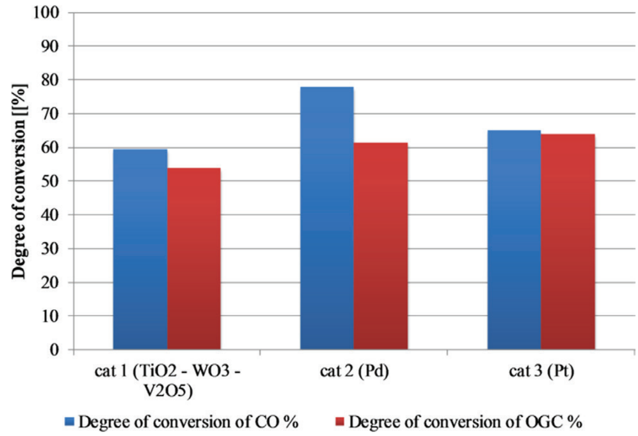

Figure 3: Catalysts' degrees of conversion of CO and OGC.

Table 3: Overall results of the tested catalysts (mass concentrations are given at temperature, T = 273.15 K and pressure, p = 101,325 Pa; final concentration of mass concentration of NO_x is recalculated to NO_2, nd means "not detected").

Mode			**Without catalyst**	**cat 1 (TiO_2-WO_3-V_2O_5)**	**cat 2 (Pd)**	**cat 3 (Pt)**
Test period		h	3.0	3.0	3.0	3.0
Space velocity		1/h	–	67,676	76,684	60,555
Flue gas volume flow		m^3/h	30.3	23.9	27.1	21.4
Flue gas temperature inside the catalyst		°C	–	293	282	307
Volume fraction of O_2 in flue gas		%	16.2	14.8	15.6	14.1
Air excess ratio		–	4.34	3.40	3.85	3.02
Reference volume fraction of O_2 in flue gas		%	13	13	13	13
Mass concentration of pollutants in dry flue gas with reference volume fraction of oxygen	CO	mg/m^3	649	264	144	227
	NO_x	mg/m^3	117	108	119	121
	SO_2	mg/m^3	nd	nd	nd	nd
	OGC	mg/m^3	39	18	15	14
	CO_2	g/m^3	149	150	150	150

Degree of conversion of CO	%	–	59.4	77.8	65.0
Degree of conversion of OGC	%	–	53.8	61.2	63.8
Degree of conversions related to mode:	–	–	Without catalyst	Without catalyst	Without catalyst

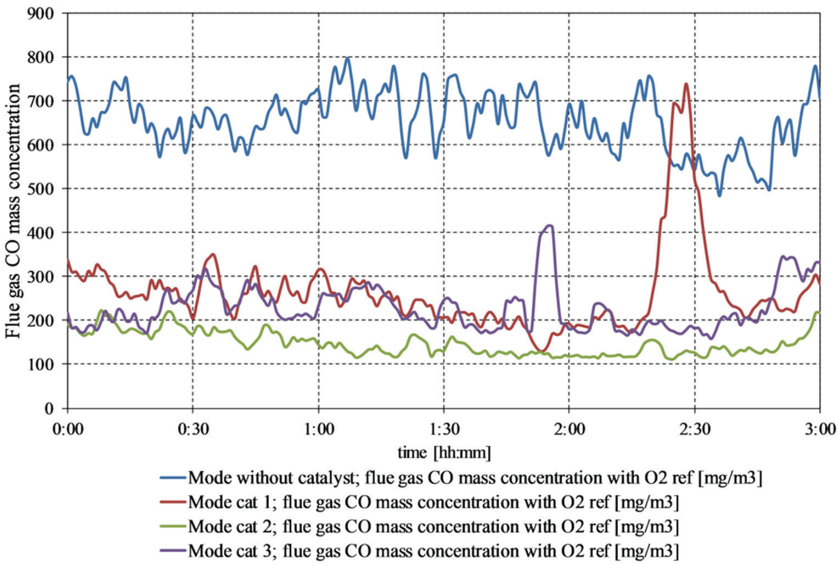

Figure 4: Process of CO concentration during each mode.

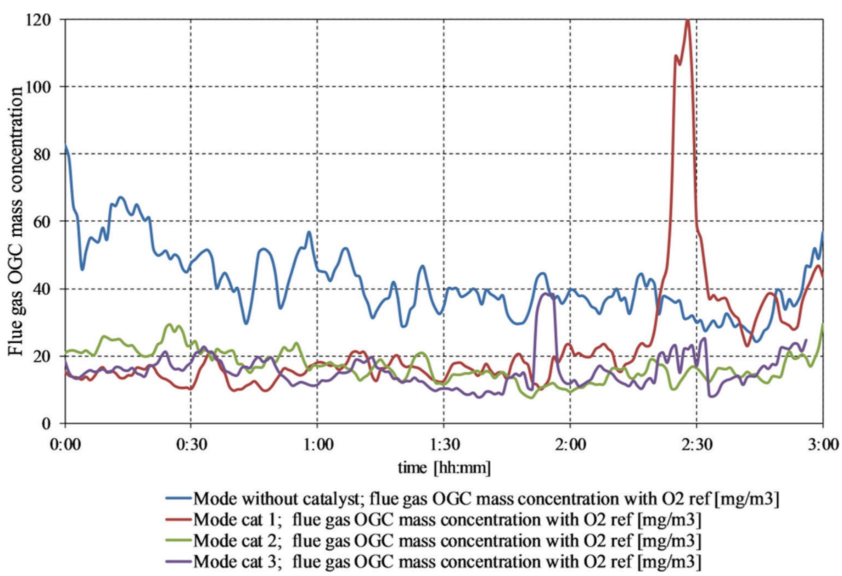

Figure 5: Process of OGC concentration during each mode.

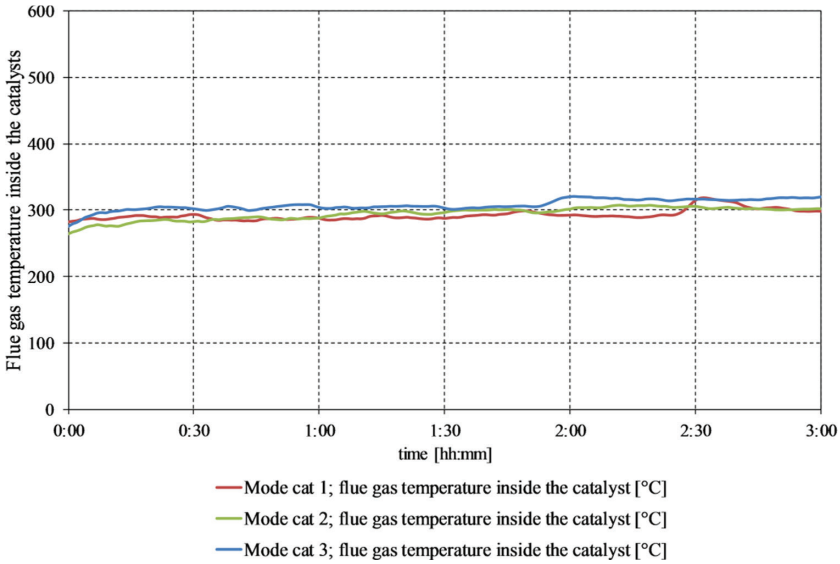

Figure 6: Process of flue gas temperatures during each mode.

Temperatures of the flue gases inside the catalysts were ranging approximately between 280°C and 300°C during all the tests. The water vapor content in the flue gas was approximately 6% and was always the same because of the same fuel composition, and the same air moisture content during the tests.

The flue gas fan speed was set with regard to the conduct monitoring of air velocity at the stove inlet. This measurement should ensure the same volume of combustion air despite the different pressure loss of the catalysts. Despite this regulation, a difference of the space velocity between tests occurred. Its value was approximately 16,000 1/h (roughly 20% of the total amount). Due to unstable operation of this type of combustion equipment, it is an acceptable inaccuracy. The flue gas flow through the catalysts is always laminar. Space velocity is equivalent value to hydraulic retention time of gas molecule inside of catalyst. It is obtained by flue gas volumetric flow rate divided by catalyst volume. Space velocity was calculated using eqn (2).

$$\text{space velocity} = \frac{\text{flue gas volumetric flow rate}}{\text{catalyst volume}} \left[\frac{1}{h} = \frac{\frac{m^3}{h}}{m^3} \right] \tag{2}$$

The limiting value of mass concentration of CO in the flue gas (recalculated to reference volume fraction of oxygen $\varphi_{\text{ref;[O2]}} = 13\%$) is 500 (during the nominal performance of the stove) and 750 mg/m^3 (during the minimal performance of the stove). This norm does not determine limiting values for other pollutants.

If the nominal heat performance of this pellet stove prototype is set to approximately 5.6 kW, using the catalyst could be a way to reach lower values of the mass concentration of CO, which is thus suffice for the limits (calculated with 80% of efficiency).

These tests lasted for only 3 h of the steady-state operation to avoid an influence of clogging caused by solid particles. Cat 1 was completely new before the test, cat 2 and cat 3 were used for ~20 h of operation in wood log stove before their tests. They were both cleaned by compressed air, thoroughly. Even after such a short test period, there were lots of settled particles at the catalysts' surface, which would definitely lead to their blockage.

3.1.1 Costs evaluation

Active compounds of the tested catalysts are different not only by their effect on the flue gas, but also by the purchase costs. Neither a thickness of the catalysts' layer, nor the density of active substances per unit area, were determined. Assuming that the density of the active substances at the catalyst surface is the same on all tested catalysts, cat 1 could be, with regard to active compounds material costs, 3.5 times cheaper than cat 3 and ~2.5 times cheaper than cat 2 [12].

4 CONCLUSIONS

This study was aimed on possibilities of the decrease of mass concentration of pollutants by the catalysts based on three different active compounds. Results of these experiments show, but for one exception, the similar degree of conversion of CO (~60%) and OGC (~60%) in the flue gas from the tested small-scale pellet stove. By that exception, the degree of conversion of CO by cat 2 (Pd) is meant. Despite the highest space velocity, cat 2 (Pd) ensured the biggest degree of conversion (~78%). The measurement of flue gas temperature at the stove outlet proved the same conditions of the operation.

From the pollutants' limitation legislative point of view, the selected combustion equipment did not comply with the standard EN 14785 without catalyst. After installing any of the three tested catalysts, CO limits were met.

From the purchase costs point of view, cat 1 is the most suitable, as it is cheaper than others.

In connection with catalysts, it is necessary to mention that every object inside a flue gas duct could be a danger in a form of clogging. All three tested catalysts have proven high inclination to clogging by solid particles contained within the flue gas, despite that each test lasted only for approximately 5 h (ignition, burning and extinction).

The degree of clogging of the catalysts could be a part of further research, as well as the possibilities of cleaning of the catalyst during its operation right inside the flue gas duct.

ACKNOWLEDGEMENTS

This article was prepared within OP RDE, the project 'Research on the identification of combustion of unsuitable fuels and systems of self-diagnostics of boilers combusting solid fuels for domestic heating', identification code CZ.02.1.01/0.0/0.0/18_069/0010049, with the financial support from the European Regional Development Fund. This article was also prepared within the project SP2019/83 'Monitoring the operating parameters of a small combustion equipment and determining its effect on condensation of water in the flue gas' and was elaborated in the framework of the grant program 'Support for Science and Research in the Moravia-Silesia Region 2018', (RRC/10/2018), financed from the budget of the Moravian-Silesian Region.

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