CLOGGING OF HONEYCOMB CATALYSTS DURING STOVE OPERATIONS

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ABSTRACT
This research paper describes the pressure loss of the honeycomb catalyst with very high cell density caused by a gradual clogging by particulate matter produced during the real biomass stove operation. The chosen catalyst was placed in the flue gas duct right at the flue gas outlet of two combustion units. Experimental combustion tests were carried out on two stoves (automatic pellet stove and wood log stove). Both stoves were connected to real chimney with ceramic flue gas path creating real chimney draught to simulate real home use of the units. During the tests, the static relative pressure at the catalyst inlet and at the catalyst outlet was measured, from which the pressure loss of the catalyst was determined. During both long-lasting combustion tests, problems with the clogging of the catalysts occurred (after several days of operation). These problems may cause significant safety risk, which was to be solved. Consequently, the decreasing influence of catalyst on mass concentration of carbon monoxide (CO) during the catalyst clogging was observed. Obtained results confirm the importance of finding an appropriate connection between chosen catalyst and newly produced combustion equipment. Consequently, the obtained results confirm the importance of solving the clogging problem by installing the catalysts as the retrofitting systems for old combustion units in flue gas duct in some kind of easy cleanable bypass, such as the rotation one, or by using catalysts with lower cell density.
Keywords: catalyst, stove, biomass, combustion.

1 INTRODUCTION

Nowadays, air pollution is a serious and intensively debated global issue. One of the sources of the air pollution is the combustion of solid fuels, which produces gaseous and particulate pollutants. More than 2.7 billion people in the world heat their homes by combustion of biomass in small burning equipment [1]. As there are almost 26 million used stoves in Europe, the individual states and European Union are constantly issuing new regulations for maximum amount of pollutants emitted from mentioned equipment into the air [2]. These regulations are progressively becoming more stricter and manufacturers of the combustion equipment must continuously improve the design of their products to comply with all regulations.

The changes of combustion equipment, from the design point of view, which prevent the formation of pollutants, are called primary measures. The primary measures are: better combustion air distribution in combustion chamber, adjustment of physical and chemical properties of the fuel, optimization of air excess ratio, combustion chamber material, etc. [3]. The primary measures, which affect the combustion process quality and, consequently, can reduce the amount of pollutants in the flue gas, are not limitless from the technical point of view. Location of the wood-burning stove at homes (usually in the living room) causes another design limitation by necessary reduction of a flue gas leakage during the door opening and by secondary function of the stove – decorative element in the home (improving the quality of combustion process at the expense of the appearance of the stove is usually not desirable) [4].

WIT Transactions on Ecology and the Environment, Vol 260, © 2022 WIT Press
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/SC220061

Secondary measures can partially solve the described problem. Secondary measures are those which treat already generated flue gases (usually behind the combustion chamber) in order to reduce the mass concentrations of pollutants, such as electrostatic participates or catalysts. In general, a catalyst is a substance that participates in chemical reactions, accelerates them and helps them to proceed, as, for instance, in synthesis of higher hydrocarbon compounds (so called liquefaction) [5]. Catalysts used in the field of small-scale stoves stay unchanged after the chemical reaction (presumption of heterogenous catalysts' behaviour) [6].

In case of small combustion unit, the catalyst can be used in combination with a new combustion unit to comply with all regulations, or it can be used in old combustion units as a retrofit. The catalyst used in the combustion unit consists of the body, the wash coat and catalytic material. The catalysts body is usually ceramic or metal monolith with honeycomb structure. The washcoat is a layer of material with large surface area, such as titanium dioxide, silicon dioxide, aluminium oxide, etc. The catalytic material is made of precious metals, mainly platinum, palladium or rhodium [7]. These precious metals are the catalytically active elements and are deposited on the washcoat layer. In the case of catalyst installation right into the combustion unit, the catalyst may be placed in the combustion equipment itself or in the flue gas duct. During the combustion unit operation, the catalyst allows or facilitates the oxidation reaction of CO to carbon dioxide (CO_2) and organic gaseous compounds (OGC) to carbon dioxide (CO_2) and water (H_2O).

During the combustion unit operation, vacuum, which sucks the flue gas from the combustion chamber, is created in the flue gas duct and in the chimney (in modern combustion units the flue gas fan or combustion air fan can affect the pressure ratio in the flue gas duct). The vacuum is caused by a difference in density between the hot flue gas and the cooler ambient air outside the chimney.

A catalyst located in the flue gas duct can be considered as an obstruction, which reduces the vacuum. Not only the catalyst, but any object in the flue gas duct causes a so-called pressure loss (pressure loss is a difference between the static pressure at inlet and outlet of the object). The static pressure at the catalyst inlet is higher (lower vacuum) than the static pressure at the catalyst outlet due to the catalyst pressure loss. The vacuum in the flue gas duct allows not only the flue gas to be drafted, but also ensures the combustion air supply. A reduction of the vacuum can cause disruption of the combustion process.

The catalyst is designed in a way that its pressure loss is not large enough to cause the negative effect described above. However, during the combustion process, particulate matter (PM) may be deposited on the surface of the catalyst. In case of not appropriate catalyst usage in combination of not appropriate flue gas temperature and in combination of high mass concertation of particulate matter in the flue gas, the catalyst could gradually become clogged and its pressure loss increases. In the worst case, the catalyst can become completely clogged.

This study is aimed on flue gas pressure loss considering the catalyst's clogging by its operation in real flue gas environment.

2 MATERIALS AND METHODS

2.1 Fuel

Two types of fuel were used for the combustion tests. Wood briquettes were used for the tests with a manually loaded wood log stove. The briquettes were made from spruce sawdust and their elemental composition is shown in Table 1. The net calorific value of the briquettes was 17.01 $MJ.kg^{-1}$. Their diameter was 90 mm and length 300 mm. A1 class wood pellets were

used for the tests with automatic stove. The pellets were mainly made from spruce wood and their elemental composition is shown in Table 2. The net calorific value of the pellets was 17.65 MJ.kg^{-1}. The pellets were approximately 6 mm in diameter and 10 to 45 mm in length.

Table 1: Elements composition of used briquettes in raw state.

Element	Chemical symbol	Mass fraction (%)
Carbon	C^r	46.17
Hydrogen	H^r	5.37
Nitrogen	N^r	< 0.20
Oxygen	O^r	38.87
Sulphur	S^r	< 0.02
Water	W^r	8.58
Ash	A^r	0.79

Table 2: Elements composition of used pellets in raw state.

Element	Chemical symbol	Mass fraction (%)
Carbon	C^r	47.53
Hydrogen	H^r	5.7
Nitrogen	N^r	< 0.20
Oxygen	O^r	40.25
Sulphur	S^r	< 0.02
Water	W^r	6.05
Ash	A^r	0.25

2.2 Combustion unit

Two types of combustion units were selected for the tests. The first type of combustion unit was an automatic, wood pellet stove. This stove was equipped with a flue gas fan. The second type was the manually loaded, wood log stove, which was not equipped with any element for affecting pressure draught such as flue gas fan or combustion air fan. A detailed description of both combustion units is given in Table 3. The chosen combustion units were not designed for the catalyst installation originally.

Table 3: Description of the tested stove.

Parameter	Stove 1	Stove 2
Heat input	6.15 kW	9.8 kW
Feeding	Automatic	Manual
Fuel consumption	1.28 kg.h^{-1}	2.07 kg.h^{-1}
Fuel consumption	Wood pellets	Wood briquettes
Average flue gas temperature	268°C	452°C
Flue gas flow rate	19.26 m^3·h^{-1*}	16.38 m^3·h^{-1*}

Note: * = related to STP conditions.

2.3 Tested catalyst

For the experimental testing, a cylindrical (145 mm in diameter) honeycomb catalyst was chosen. This catalyst was produced for stove flue gas purification. The catalyst has a steel body, the surface of which is covered with a layer of aluminium oxide (Al_2O_3). At the surface of the catalyst, platinum (Pt) was applied as an active element. This catalyst was chosen for its high number of cells per square centimetre (inlet surface of each cell was very small), which causes relatively high flue gas pressure loss in comparison to other usually used catalysts for this application. Therefore, the worse conditions in terms of clogging by particulate matter were ensured. Detailed description of the catalyst is given in Table 4. A cleaned catalyst (without particulate matter) is shown in Fig. 1.

Table 4: Description of the used catalyst.

Body material	Steel
Carrier	Al_2O_3
Active compounds	Pt
Diameter	0.145 m
Height	0.02 m
Active surface	0.508 m^2
Number of cells	31.8 $cells \cdot cm^{-2}$

Figure 1: Honeycomb catalyst before combustion tests.

2.4 Measuring system for a flue gas analysis

The volume fraction of oxygen (O_2) in the flue gas was determined with a continuous analyser which works on the principle of determining the paramagnetic properties of the flue gas. The volume fraction of CO, CO_2 and nitric dioxide (NO_2) were determined by another continuous flue gas analyser which works on the principle of infrared absorption. The volume fraction of OGC was determined by a continuous flue gas analyser, which works on the principle of flame ionisation (FID). All instruments were justified before the start of the measuring each measuring day.

In case of the automatic pellet stove and the wood log stove, the catalyst was placed 450 mm and 100 mm, respectively, from the stove outlet into the flue gas duct. The diameter of the flue gas duct between the combustion unit and the chimney was 150 mm. In flue gas duct of each combustion unit, two measuring points were prepared at the catalyst inlet and at the catalyst outlet. The static pressure of the flue gas was measured at both measuring points, continually. Flue gas analysis with evaluation of catalysts conversion rate was held occasionally. Flue gas samples for the analysis were sucked from the same measuring points.

The flue gas duct was further connected to the chimney. Detailed description of the used chimney was published by Ryšavý et al. [8]. The location of the catalyst in the flue gas duct and the distribution of measuring points for Stove 1 and Stove 2 are shown in Fig. 2.

Figure 2: Experimental set up of pressure loss test of Stove 1 and Stove 2.

3 RESULTS AND DISCUSSION

The combustion tests were aimed at determination of the degree of clogging and pressure loss change of the catalyst during combustion unit operation. The catalyst pressure loss was

calculated from the static pressure, measured at the catalyst inlet and at the catalyst outlet. In addition, the catalyst clogging effect on the conversion rate of CO in the flue gas was determined.

3.1 Test with Stove 1

The testing of the catalyst installed in the flue gas outlet of the Stove 1 was carried out for 8 test days. Each test day began with switching on the flue gas fan and the fuel being ignited manually by a propane-butane burner. The flue gas fan was set at a constant speed for all test days. At the end of each test day, the exhaust fan was turned off after the flame was extinguished.

The static pressure curves at the catalyst inlet and at the catalyst outlet are shown in Fig. 3 as well as the evaluation of pressure loss. As can be seen, the static pressure at the catalyst outlet was constant throughout all the test days; this was caused by a constant flue gas temperature. After warming up the stove and the chimney in the first testing day, the static pressure at the catalyst inlet was −8 Pa. In the second day of testing, the static pressure at the catalyst inlet was still below 0 Pa and the evaluated pressure loss was lower than the static pressure at the catalyst outlet. During the third day of the testing, the static pressure at the catalyst inlet exceeded 0 Pa and continually increased. The pressure loss value exceeded the static pressure at the catalyst outlet. In the following days of testing, the static pressure at the catalyst inlet and the pressure loss continued to increase. The ever-increasing pressure loss was caused by the gradual clogging of the catalyst by the particulate matter. On day eight of the test, a static pressure of 35 Pa was measured at the catalyst inlet and the pressure loss was evaluated to 50 Pa, both values still increasing. The catalyst was not completely clogged even after eight days of testing. This was probably due to the oversized flue gas fan, which did not allow further deposition of the particulate matter on the catalyst.

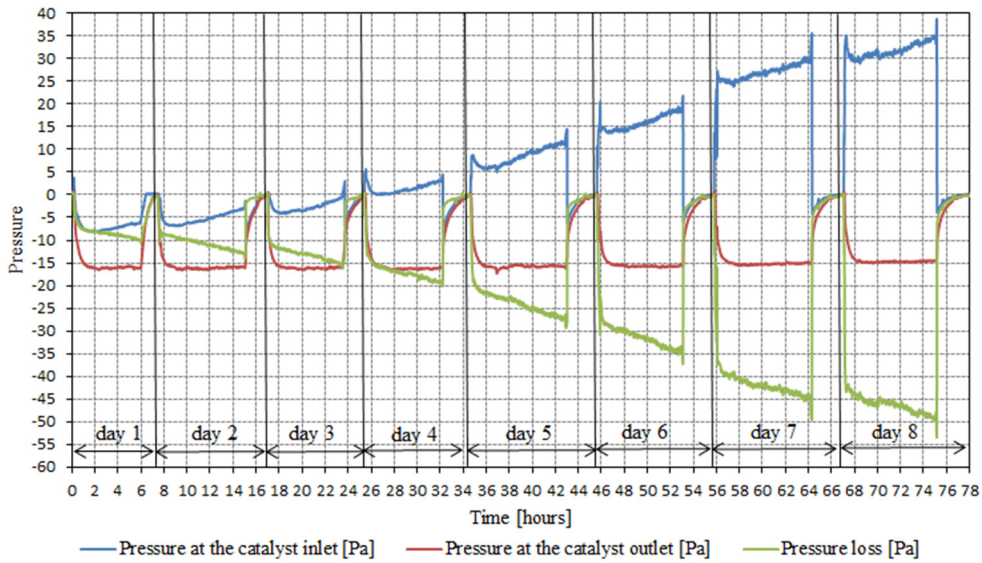

Figure 3: Course of all the measured pressures during the combustion tests provided with Stove 1.

Oversizing of the flue gas fan is also connected with high volume fraction of O_2 in the flue gas during the standard operation of the Stove 1. Since the pressure loss of the catalyst was continuously increasing and the flue gas duct used for experimental setup was not made for usage in the overpressure condition, the experimental test on the automatic pellet stove was terminated for safety reasons. In addition, due to the overpressure of the flue gas in the flue gas duct, a flue gas leakage was occurring at the connections between the flue gas duct sections. After the end of tests, the catalyst was removed from the flue gas duct and was cleaned from the settled particulate matter. A cleaned catalyst with the removed particulate matter is shown in Fig. 4.

Figure 4: Cleaned catalysts with the removed particulate matter after Stove 1 tests.

3.2 Test with Stove 2

Testing of the catalyst installed right at the Stove 2 outlet was carried out over four test days. Each test day started with the ignition of 1 to 2 kg of beech chips in the combustion chamber. The beech chips were used for ignition of the stove only. After the stove was ignited, one briquette was added to the combustion chamber. Due to the size of the combustion chamber, the briquette was halved. The burn time of one briquette was approximately 1 hour and 20 minutes. Three or four briquettes were burned each test day. The static pressure curves at the catalyst inlet and at the catalyst outlet and the evaluated pressure loss are shown in Fig. 5. As can be seen, the static pressure and pressure loss curves are similar during the first three test days. The vacuum at the catalyst outlet was slightly higher than the catalyst pressure loss. The small peaks in the static pressure curve at the catalyst outlet were caused by the change in flue gas temperature during the combustion periods.

At the beginning of the fourth testing day, beech chips were ignited manually inside the combustion chamber by the propane-butane burner as always. In the first 20 minutes of stove operation, the flue gas temperature increased and the static pressure at the catalyst inlet and at the catalyst outlet decreased. From the 20th minute of the burning process, the static pressure at the catalyst inlet started to increase up to +2.3 Pa. The pressure loss of the catalyst (−9.3 Pa) exceeded the static pressure at the catalyst outlet (−7 Pa). When the overpressure at the catalyst inlet was reached, the flue gas stopped flowing through the catalyst and the flame in the combustion chamber was smothered. The flue gas began to leak from the combustion chamber through the sealing between the stove door and the stove wall into the test room. Opening the stove door made the accumulated flue gas roll out of the combustion chamber and the fuel began to burn again with a visible flame (consequence of increase of oxygen mass fraction in combustion chamber). The state at the moment of the stove door opening is recorded in Fig. 6.

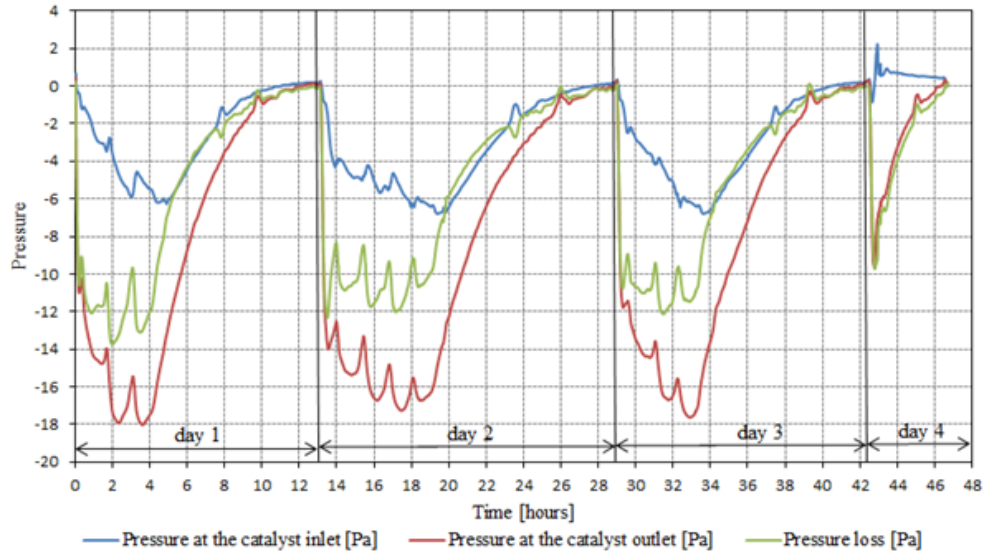

Figure 5: Course of all the measured pressure during the combustion tests provided with Stove 2.

Figure 6: Accumulated flue gas rolls out of the combustion chamber.

Figure 7: Clogged catalyst by particulate matter after four test days of Stove 2.

Results of these experiments show that the catalyst was clogged by solid particles after a few days of testing; this caused the creation of non-negligible flue gas overpressure in the flue gas duct at the catalyst inlet. In case of combustion unit usage without forced air or flue gas flow, due to catalyst blockage, the flue gas could not flow towards the chimney and the combustion air was not drawn into the combustion chamber. This issue caused the smothering of the flame and the leakage of combustion gases from the combustion unit and the flue gas duct. Overpressure in the combustion unit with flue gas fan was also created, but the flue gas was pressed through the catalyst by flue gas fan. The pressure, generated by the fan, was high enough for complete blocking of the catalyst by solid particles to be avoided in eight test days. It can be assumed that pressure loss of the catalyst exceeded the chimney draught at the end of third testing day; this created overpressure between the flue gas fan and the catalyst.

One of the catalyst characteristics that affects the pollutant's conversion rate is the surface area of the catalyst. The surface of the catalyst was gradually covered by particulate matter during the test. The solid particles gradually reduced the reaction area of the catalyst, which caused a decrease of the CO conversion rate. On three test days (during the Stove 1 testing), namely the 3rd, 6th and 8th, the flue gas composition at the catalyst inlet and at the catalyst outlet was analysed and the CO conversion rate was determined. On the 3rd day, the determined CO conversion rate was 38.9%, on the 6th day, 19.6% and on the 8th day, 8.5%. It is evident that the pollutant's conversion rate decreases with more particulate matter deposited on the catalyst surface.

It may seem that clogging of the catalyst is a purely negative process, as the CO conversion rate is reduced. Actually, the catalyst in the flue gas duct also works as a settling particulate matter precipitator. The deposition of the dust on the surface of the catalyst could help to decrease the mass concentration of particle matter in the flue gas. It is important to find the balance between particle matter separating and the catalyst clogging. The solution is

to clean the catalyst regularly or use a bypass device to prevent particulate matter deposition on the catalyst surface.

From the combustion tests carried out as part of this research, it was found that complete blockage of the catalyst, or a condition where the catalyst pressure loss was higher than the chimney draft, occurred in the natural draft stove during the first hour of stove operation when the chimney was not sufficiently heated, and the chimney draft was low. This effect, which occurred during our experimental tests, can be avoided also by using some kind of bypass device.

Bypass device works on the principle of reducing the amount of flue gas passes through the catalyst during the insufficient flue gas temperature, for example during the ignition phase. There are two commercially available designs. One of them is a bypass, mounted as a part the flue gas duct, which works on the principle of rotating the catalyst into two positions. In the first position, which is used when heating up the stove and chimney happens, the catalyst is (usually) in a vertical position (parallel to the flue gas flow direction) and the flue gas do not pass through the catalyst (just flows around it), but the catalyst is pre-heated, consequently. In the second position, the catalyst is in the operational, (usually) horizontal position (perpendicular to the direction of the flue gas flow) and the flue gas flows through the catalyst. The second bypass design is a device that is also mounted as a part the flue gas duct, but the catalyst is fixed in the horizontal position (perpendicular to the direction of the flue gas flow). Around the catalyst there are closable holes with flaps. When the flaps are open, during the heating up of the stove, the flue gas can flow through these holes instead of through the catalyst. This type of bypass does not ensure a complete flue gas flow outside the catalyst. The distribution of the flue gas between the bypass and the catalyst has not been studied so far, but it depends on pressure loss of the bypass and the catalyst. The first mentioned variant of bypass seems to be very suitable for the catalysts' installation in case of retrofitting of the old combustion equipment.

Another way to prevent the catalyst from clogging is to regularly clean it of particulate matter. Nowadays, catalysts in the field of small combustion equipment placed at the stove outlet have to be cleaned manually in certain period of time depending on catalysts' dimensions, mass concentration of particulate matter in the flue gas, flue gas temperature and also type of the installation (if the bypass is installed and used). Another way of cleaning a catalyst could be automatic cleaning, which would make the use of catalysts more convenient. Hammering the catalyst (under appropriate circumstances may be provided with the catalyst installed in a rotation bypass device) or cleaning with compressed air can be used as the suitable methods of cleaning. Further research will focus on ways of automatically cleaning catalysts.

In addition, it has to be mentioned that the chosen catalyst had very high cell density, which significantly shorted the time of clogging of the catalyst. Catalysts with lower cell density used in combination with modern combustion units with lower mass concentration of PM in the flue gas could be significantly less susceptible for the clogging.

4 CONCLUSION

For the pressure loss experimental tests on catalysts with high cell density, a catalyst with very tiny channels was used to simulate the worst possible conditions of catalyst's clogging. Already on the first day of the experimental test with the Stove 1, the catalyst pressure loss (14 Pa) was almost as large as the chimney draft (18 Pa). On day four of the test, the catalyst pressure loss (9.3 Pa) was greater than the chimney draft (7 Pa), resulting in the creation of an overpressure in the combustion chamber (2.3 Pa). The flame was extinguished, and the flue gas leaked into the surroundings of the stove.

The effect of clogging of the catalyst by particulate matter on the pressure loss of the catalyst can be seen in the results of experimental tests with automatic, pellet stove. During the tests, there was no variation in chimney draft (15 Pa), which was constant during all test days. The pressure loss of the catalyst then increased linearly each day (up to a value of 50 Pa). Despite the significant overpressure in the flue gas duct (35 Pa on the last test day), the flame was not extinguished due to oversized combustion flue gas fan that did not allow the catalyst to be completely clogged during the eight test days.

The deposition of particulate matter on the catalyst does not affect only the catalyst pressure loss. The deposition of solid particles on the catalyst fouls the catalytic active substance and reduces the pollutant's conversion rate. As part of the investigation, CO conversion rates were measured on an automatic pellet stove. The CO conversion rate was decreasing during the tests (38.9% on test day 3, 19.6% on test day 6 and 8.5% on test day 8).

Preventing or reducing the catalyst clogging rate can be done in various ways. The catalyst design has a significant effect on catalyst clogging. Smaller channels mean that higher pressure loss of the catalyst and, also, better particle separation occurs. At the same time, installing the catalyst closer to the combustion chamber can be another way of reducing the catalyst clogging rate. Higher temperatures can cause partial burnout of particulate matter on the catalyst. Other possibilities are bypass usage, or usage of different catalyst cleaning methods while the stove is in operation.

ACKNOWLEDGEMENT

This work was supported by the Doctoral grant competition VSB – Technical University of Ostrava, reg. no. CZ.02.2.69/0.0/0.0/19_073/0016945 within the Operational Programme Research, Development and Education, under project DGS/TEAM/2020-035 "Determination of oxidation catalysts characteristics during the flue gas purification".

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