

Operation characteristics of a bulk catalyst in a test stand under similar conditions to a firewood stove

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Introduction and Objectives

The EU climate and energy strategy for 2020 relies on a significant increase of biomass share in household energy production. In addition new building standards lead to a decrease in heat consumption of households and to a decrease of the nominal power of heating appliances. Small-scale wood fired room heating appliances will be an important solution for these requirements. They are already widespread in European households and the cost efficiency as well as the good availability of the firewood will lead to a further distribution (Mudgal et al. 2009). However, small-scale firewood stoves emit high fractions of gaseous and particular matter emissions (Schmidl et al. 2011), especially compared with automatically fired small-scale combustion units (e.g. pellet stoves). The fact that these emissions can seriously affect public health (Jalava et al. 2012, Chapman et al. 1997, Bari et al. 2010) led to legislative regulations concerning emissions from small-scale combustion units. The thresholds for gaseous and particulate emissions of new firewood stoves as well as stoves which are already in field operation will be tightened in the coming years (e.g. in the German first federal immission control ordinance (First BImSchV 2010). One option to achieve these new thresholds for emissions will be the use of secondary emission reduction systems in firewood stoves. Catalysts have a great potential to decrease emissions from old small-scale biomass combustion systems as a retrofit system as well as in new combustion systems as an integrated secondary measure (Ferrandon et al. 1999b). However, the integration of a catalyst in a combustion unit is a challenge because the operation performance of a catalyst depends on various factors like temperature, gas flow conditions and the flue gas composition. Therefore an extensive assessment of the catalyst performance is required before it is integrated into a biomass combustion appliance. Such assessment is also required in order to be able to differentiate between primary effects – induced by the integration of the catalyst (e.g. increased residence time of flue gases in the combustion zone due to lowered chimney draught) – and the catalytic effect of the integrated catalyst. This differentiation has not been investigated yet (Ozil et al. 2009, Ozil et al. 2011).

This paper aims to analyse the performance of a bulk oxidation catalyst. The influence of several parameters such as operation temperature, oxygen availability, emission concentration, residence time of flue gas in catalyst bulk layer and flue gas water content on the performance of the catalyst is investigated. For this purpose, a new laboratory test reactor is presented, which provides test conditions which are similar to conditions in a firewood stove in terms of temperature range, gas velocity and behaviour of the catalyst bed. This test reactor differs from previously published studies which used smaller catalyst samples (Carnö et al. 1996, Ferrandon et al. 1999b).

Material and Methods

All tests were conducted by using a laboratory test reactor with a synthetic gas supply. In the following the reactor, the used catalyst as well as used test and evaluation methods are described. Figure 1 shows the whole test set up.

Test reactor

The test bench consists of a reactor which is a 1990 mm long high-grade steel tube with a diameter of 50 mm. The reactor is heated by two heating jackets which allow a temperature range up to 900°C and it is isolated with 100 mm mineral wool. The catalyst is placed in a sample holder which consists of a tube (inner diameter 44 mm) with a meshed metal baffle bottom. The sample holder fits accurately into the reactor tube and it is placed on the top of the reactor. The temperature of the catalyst is measured by two thermocouples (type K) which are placed directly into the flue gas stream before the sample holder. The whole heating process of the test bench is controlled by a computerized control system.

The main component of the gas flow was Nitrogen (N₂), which was mixed with the below mentioned components in the given ranges in order to create artificial, but possible flue gas compositions for the experiments:

- Oxygen (O₂) 0 – 20 % vol. (supplied by Linde AG)
- Carbon dioxide (CO₂) 0 – 20 % vol. (supplied by Linde AG)

- Carbon monoxide (CO) 0 – 4000 ppm (supplied by Linde AG)
- Toluene (C₇H₈) 0 – 150 ppm
- Water 0 – 8.50 % vol.

O₂, CO₂, N₂ and CO were taken from gas cylinders and fed to the system by using mass flow controllers (model “red-y smart controller GSC” from Vögtlin Instruments AG). The water feeding system consists of 2.5 l water storage, a liquid mass flow controller (model “LIQUI-FLOW” from Bronkhorst High-Tech BV) and a laboratory vaporizer (model “CEM W202” from Bronkhorst High-Tech BV). The water storage was set on overpressure (2 bar) and the laboratory vaporizer was fed with demineralized water via the liquid mass flow controller. Toluene was brought to the reactor by using a wash bottle filled with liquid toluene. The wash bottle was passed by N₂ which was controlled by a mass flow controller. In order to achieve a constant temperature and thus a constant evaporation rate the wash bottle was placed into a water bath with controlled temperature. The tubing of all parts of the gas supply system was heated to 100°C to prevent condensation of water and toluene. All mass flow controllers were controlled using self-developed computer based control software.

Except the test with various residence times, all experiments were carried out by using a constant gas velocity and thus constant residence time along the catalyst in the reactor. Therefore the standard volume flow (i.e. at the reactor inlet) was varied according to the reactor temperature to achieve a constant operation volume flow at the catalyst sample of 0.8 m/s. The gas concentration measurement before the catalyst was done by using multi gas analyser (model “SGPLUS” from rbr Messtechnik GmbH) which works with electrochemical sensors for CO and O₂. The measurements after the catalyst was conducted by a multi gas analyser (model “NGA 2000” from Emerson Electric Co.) with nondispersive infrared detector (NDIR) for CO and a paramagnetic sensor for O₂. The toluene measurements before and after the catalyst were conducted by using two identical Flame Ionisation Detectors (FID) (model “Thermo-FID” from Mess-und Analysetechnik GmbH). A response factor of 1.01 was used for the toluene measurements.

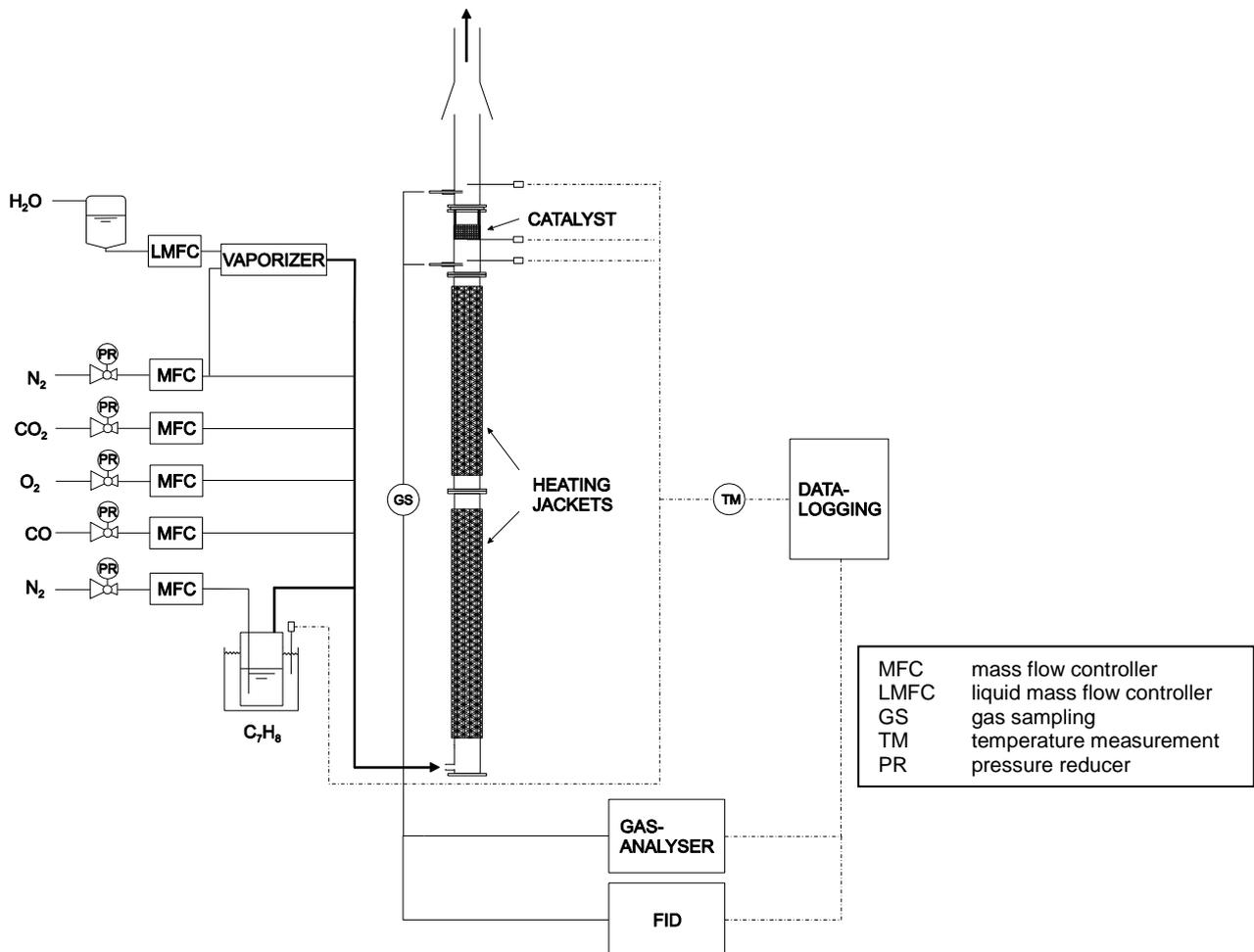


Figure 1 Experimental set-up

Catalyst

For this study a commercial bulk catalyst was used. It consists of alumina (Al_2O_3) spheres with a diameter of 4-6 mm. According to the supplier the material is coated by various noble metals with a major share of platinum. The active surface area of the catalyst was $96.1 \text{ m}^2/\text{g}$ and was determined by using the BET measurement process. The catalyst was activated by heating up to $300 \text{ }^\circ\text{C}$ for 180 minutes in a muffle oven according to the manufacturer manual. For the test bench experiments the catalyst was placed in 1.5 layers (approx. 6.5 g, 1 cm bed height) in the sample holder according to information of the manufacturer.

Test procedure

In total six different experiments were performed for this study. In the following the test procedure is described:

Carbon monoxide and toluene conversion tests:

For the CO conversion experiments three samples of catalyst were used. Two test runs per sample were performed by increasing the flue gas temperature from $50 \text{ }^\circ\text{C}$ to $500 \text{ }^\circ\text{C}$ with a heating rate of 10 K/min . For the toluene conversion experiments two samples were used and one test run per sample was performed by increasing the temperature from $50 \text{ }^\circ\text{C}$ to $400 \text{ }^\circ\text{C}$ with a heating rate of 10 K/min . A consistent synthetic gas mix according to Table 1 was used.

Other parameter tests:

All other parameter studies were performed at a constant flue gas temperature of $400 \text{ }^\circ\text{C}$. For each test one parameter was changed stepwise and the CO concentration was measured before and after the catalyst. The operating parameters of the parameter studies can be found in Table 1.

Test	Temperature ($^\circ\text{C}$)	Gas velocity (m/s)	O_2 (% vol.)	CO_2 (% vol.)	CO (ppm)	C_7H_8 (ppm)	H_2O (% vol.)
CO conversion	50 to 500	0.8	10	11	1000	---	---
C_7H_8 conversion	50 to 400	0.8	10	11	---	150	---
O_2 availability	400	0.8	0.6/10/19	20.4/11/2	1000	---	---
CO concentration	400	0.8	10	11	200/800/4000	---	---
Water content	400	0.8	10	11	1000	---	0/5/8.5
Residence time	400	0.2/1.4/1.7	10	11	1000	---	---

Table 1 Test parameters for conversion and influence factor experiments

Thermal durability tests:

For the thermal durability tests the three catalyst samples of the CO experiments were used. After the CO tests one sample each was heated to 700°C , 800°C and 900°C for 24 hours in a laboratory muffle oven in ambient air conditions. Afterwards the samples were tested again according to the CO conversion test procedure.

Evaluation procedure

During all experiments the gas composition was measured before and after the catalyst in the laboratory reactor. This data as well as the temperature values of the thermocouples were monitored by self-developed software with a data rate of one value per second and converted to a commercial data format.

The conversion of the catalyst is the difference of the inlet and outlet emission concentration. Based on these values the maximum conversion for each test run and the absolute conversion rate in percentage were calculated.

The results were transferred into a chart according to previously publications (Blasin-Aubé et al. 2003, Belosevic et al. 2007, Ferrandon et al. 1999a) which shows the relative conversion rate in percentage (i.e. based on the maximum conversion) as a function of temperature.

Finally the characteristic temperatures T20, T50 and T90 of the catalyst were calculated. These temperatures describe the conversion rate at a certain temperature (e.g. T20 means the temperature at which 20 % of the maximum conversion rate is observed). These temperatures can be found in product specification of catalyst manufacturers and in literature (Liotta 2010, Blasin-Aubé et al. 2003, Carnö et al. 1996, Ferrandon et al. 1999b).

Results and discussion

Carbon monoxide conversion

Figure 2 shows the CO conversion rate as a function of temperature. It can be noted that the CO conversion started smoothly already directly above 50 °C. The significant increase of the conversion rate in the range of 200 °C to 250 °C is common for oxidation catalysts in a heterogeneous oxidation reaction. This agrees well with the results of Belosevic et al. (2007) and Liotta (2010). The characteristic temperatures can be found in Table 2.

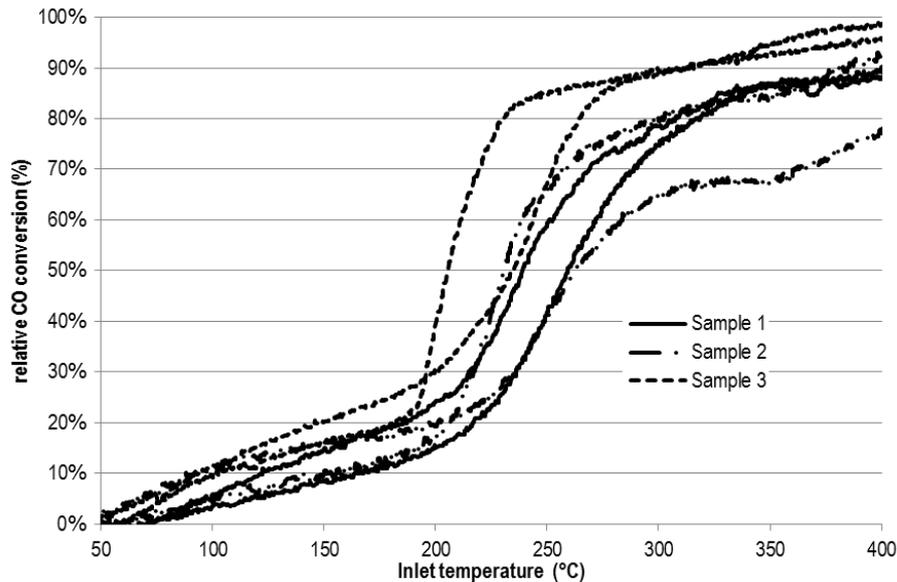


Figure 2: Carbon monoxide conversion

Toluene conversion

Figure 3 shows the results of the toluene conversion test. It can be seen that compared with the CO conversion higher temperatures were needed. A strong increase of the conversion rate in a narrow temperature range (in this case between 250 °C and 300 °C) could be determined. This phenomenon was already published by Radic et al. (2004). Table 2 shows the characteristic temperatures of the toluene conversion.

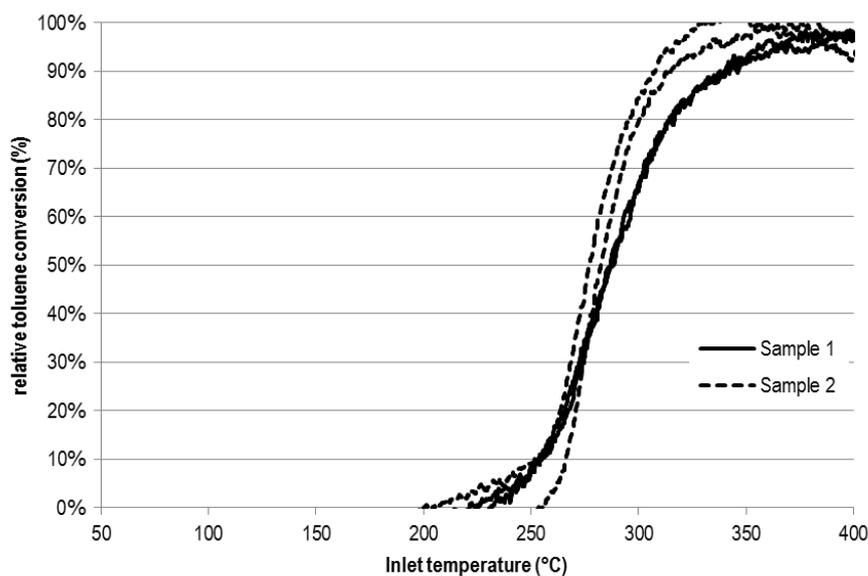


Figure 3 Toluene conversion

Test gas	T20	T50	T90
	(°C)	(°C)	(°C)
CO n= 6	190	238	381
C ₇ H ₈ n= 6	262	282	322

Table 2: Temperatures at 20% (T20), 50 % (T50) and 90% (T90) conversion of CO and C₇H₈

Influence of oxygen availability on the catalyst performance

The test runs with 0.60 % vol., 10 % vol. and 19 % vol. oxygen in the synthetic flue gas did not show any significant influence on the catalyst conversion rate of a synthetic flue gas with 1000 ppm CO (see Figure 4). Similar experiments can be found in Ahlström-Silversand et al. (1997). They also described no significant influence of the oxygen content on the performance of a catalyst.

Influence of the emission concentration on the catalyst performance

The experiments with increasing CO content in the flue gas showed an increasing efficiency (i.e. conversion rate in percentage) of the catalyst. The conversion rate at 200 ppm CO was 49 % and increased to 54 % at the 800 ppm CO test run (see Figure 4). The conversion rate at 4000 ppm was 56 %. Radic et al. (2004) described the similar correlation between emission concentration and conversion rate of an oxidation catalyst.

Influence of the water content on the catalyst performance

The test with increasing flue gas water content did not show a significant influence on the catalyst performance (see Figure 4). There are different studies published which deal with the influence of water content on the catalytic conversion. Ahlström-Silversand et al. (1997) showed no significant influence of the water content in a synthetic flue gas on the performance of a wire mesh catalyst. The results of Carnö et al. (1996) showed an increased CO and naphthalene conversion of a platinum-based catalyst in the presence of water in a synthetic flue gas. Marécot et al. (1994) determined however a decreasing activity of catalysts at higher flue gas water content.

Influence of the residence time on the catalyst performance

Table 3 and Figure 4 show the results of the tests with different gas velocities. In addition, Table 3 shows the calculated residence time of the flue gas in the catalyst bed. A clear correlation between the gas velocity and thus the residence time of the flue gas in the catalyst bed and the conversion rate was observed. This is in accordance with Carnö et al. (1996).

		Gas velocity		
		0.2 m/s	1.4 m/s	1.7 m/s
Residence time	(s)	0.0500	0.0071	0.0059
Conversion rate	(%)	84	46	45

Table 3 Calculated residence time and conversion rate of CO conversions tests

Thermal durability tests

The comparison of the catalyst performance of the unmodified catalyst samples with all thermal treated samples did not show any significant differences. Even the characteristic temperatures did not change significantly. It can be assumed that the used catalyst is thermal stable for temperatures up to 900°C.

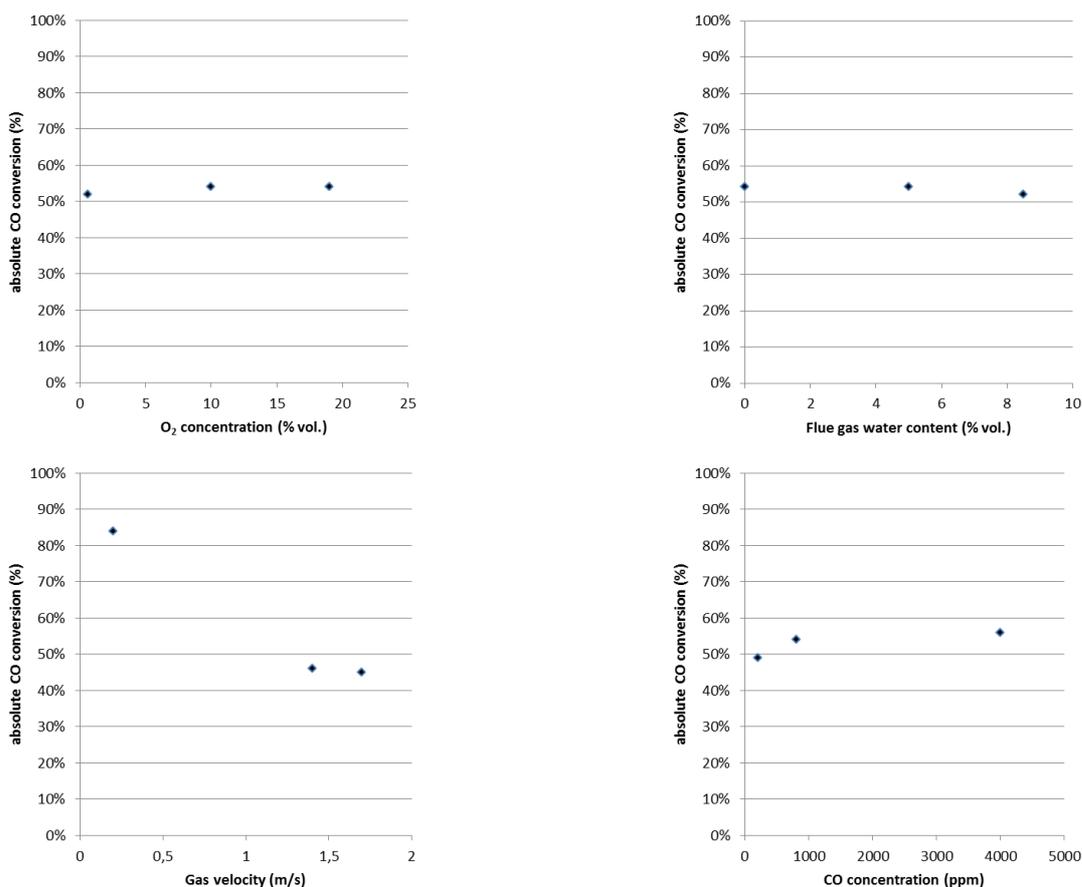


Figure 4 Results of the influence factor analysis (according to test conditions in Table 1)

Conclusion

In this study a bulk oxidation catalyst was characterized by using a new developed laboratory test reactor which provides test conditions which are similar to application conditions in a small-scale firewood stove in terms of temperature range, gas velocity and behaviour of the catalyst bed. The results show a beginning conversion of carbon monoxide in a synthetic flue gas above 50 °C with a strong increase of conversion above 200 °C. For toluene conversion temperatures above 200 °C are necessary to start the catalytic conversion. Several influence parameters on the catalytic performance were studied and can be summarized as follows: The conversion process was not influenced by low oxygen availability (in the range of 0.60 % vol. to 19 % vol.). Water content in the synthetic flue gas (up to 8.50 % vol.) also did not show a significant effect on the catalytic performance. However, the catalytic performance was influenced by the gas velocity and thus the residence time in the catalytic bed. A longer residence time increased the catalyst performance significantly. In addition experiments with thermally treated catalyst samples showed a thermal durability up to 900 °C.

The result of this study will be used for the integration of the bulk catalyst in primary optimized small-scale firewood stoves. The stoves will be used for further investigations in terms of real life influence factors such as deposit formation from particulate and condensable emissions and changing of the draught conditions.

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