Emission Abatement at Small-Scale Biomass Combustion Unit with High-Temperature Catalysts

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Abstract

A newly designed downdraft wood stove achieved low-emission heating by integrating an alumina-supported mixed metal oxide catalyst in the combustion chamber operated under high temperature conditions. In the first step, a catalyst screening has been carried out with a lab-scale plug flow reactor in order to identify the potentially active mixed metal oxide catalysts. Mixed metal oxide catalysts have been the center of attention because of their expected high temperature stability and activity. The catalyst has been synthesized through two novel routes, and it has been integrated into a downdraft wood stove. The alumina-supported mixed metal oxide catalyst reduced the volatile hydrocarbons, carbon monoxide and carbonaceous aerosols by more than 60%.

Keywords: Small scale biomass combustion; Mixed metal oxide; Catalysts; Emission reduction; Pressure drop

Introduction

The use of biomass or bioenergy can be traced back to the beginning of human civilization when people started to burn wood for heating and cooking purposes. Ironically, after so many years have gone by, wood still remains the largest biomass resource in the world [1]. However, one major difference which has occurred over this period of time is the introduction of the concept “modern biomass” which states the usage of traditional biomass resources in highly efficient systems. This concept has been put into practice with more conviction and determination during the last decade, particularly in Europe, due to ever rising CO₂ levels in our environment. By now, it is an established fact that about 10-30% of total energy demand for hot water supply and domestic heating in European countries like, Austria, Germany, Sweden and Finland is provided by small scale biomass combustion systems [2]. Moreover, it has been also concluded that despite the vast spread of technologically advanced small scale combustion devices in European countries (like countries mentioned above) during the recent years, still the old biomass combustion systems (stoves and boilers) occupy more consumers [3]. These conventional systems which are based on natural draft play a pivotal role in contributing to the high emission levels of particulate matter (PM), carbon monoxide (CO), organic gaseous compounds (OGC) and polycyclic aromatic hydrocarbons (PAH). These facts and figures have triggered an enormous understanding and awareness among the researchers as well as local population concerning harmful pollutants emitted by residential biomass combustion systems. For this reason inefficient small scale biomass combustion systems have been heavily criticized and demanded to be replaced by new efficient technologies.

Speaking of older and newer technologies, it has to be mentioned here that two types of technologies exist concerning small scale biomass combustion systems. The old biomass combustion systems are based on ”up-burn” which is in a process of being rapidly replaced by “down-firing” systems (new technologies). As mentioned above, these older systems are a main source of PM, particles with diameter less than 1 µm) in European countries. It has been also concluded that such particles serve as a purpose of “support” onto which carbonaceous particles (organic compounds and soot) are deposited which are primarily responsible for the adverse health effects [4]. So in order to counter such an undesired release of pollutants, particularly from small scale biomass systems, a concept has been conceived according to which “down-firing” technology will be implemented in specially designed wood log stove in combination with catalytic treatment in order to abate harmful emissions to minimum possible values. It is noteworthy to mention here that the abatement of emissions through catalytic treatment from small scale biomass combustion systems has not been studied or implemented on a wide scale. So this novel concept of integrating catalytic components in different parts of the stove i.e. grate, walls of combustion chamber and the base will open more channels and schemes in order to accomplish the acceptable emission levels coming out of biomass combustion systems particularly, those used for residential purposes.

In the past, the process of catalysis has been strongly linked to chemical and refinery industries. However, recently the catalytic converters have been deployed and installed in automobiles, biomass fired boilers and power generation facilities in order to promote the environmentally friendly usage of technological devices. It has been estimated that the market of catalysis around the world worth around US$9 billion, out of which, one third is occupied by the environmental catalysis. So building on this ever growing trend of environmental catalysis, this article gives a further insight into the integration of catalytic components in a downdraft wood log stove to foresee the feasibility of this novel approach to resolve the problem of high emissions (e.g. carbon monoxide, volatile organic compounds, dust particles etc.) at small-scale furnaces for solid biomass.

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Materials and Methods

Setup and description of the tested equipment along with measuring techniques

A test bench has been developed (as shown in the Figure 1) in order to examine the emissions from a prototype downdraft stove. The test bench is designed in such a way that it can facilitate the analysis of dust composition.

For the determination of flue gas and combustion chamber temperature profiles, the thermocouples of Type K (manufactured by the company “Newport Electronics GmbH”) have been used. For this purpose, a set of various thermocouples has been inserted into the grate, in the middle of upper and lower combustion chambers as well as in the walls of the lower combustion chamber. Moreover, the pressure conditions were recorded with the help of pressure sensors, inserted into the combustion chambers (upper and lower) as well as into the exhaust pipe. The measurement of static and dynamic pressures in the flue gas has been done with the aid of Prandtl tube produced by the company “Testo AG”. The continuous transmission and data recording of Prandtl tube and pressure nozzles in the combustion chamber is carried out through data logging module provided by the company “Ahlborn”. The data of the thermocouples have been recorded through a data logger of the company “National Instruments” along with the help of the software “Labview”.

The emissions coming out of the stove are measured by means of a gas analyzer which consists of a Fourier Transform Infrared Spectrometer (FTIR, Manufacturer: Calcmet), a Flame Ionization Detector (FID, Manufacturer: Mess- & Analysentechnik GmbH, Typ: thermo-FID ES) and a paramagnetic oxygen analyzer (Manufacturer: M&C, Type: PMA 100). The infrared spectrum of FTIR can measure simultaneously organic as well as inorganic components. At the moment, about 44 different components can be recorded through FTIR.

The Volatile Organic Compounds (VOC) can be recorded by means of both FID and FTIR measuring devices. In case of VOC, the concentrations ranging under 50 mg/m³ (at standard conditions i.e. \( =0°C, 1 \text{ atm} \)) can be considered from the FID measuring device. On the other hand, the values above 50 mg/m³ (at standard conditions i.e. \( =0°C, 1 \text{ atm} \)) can be assumed from the FTIR measuring device. Following parameters can be measured simultaneously:

1. Oxygen \( \text{O}_2 \) (paramagnetic analyzer)
2. Carbon dioxide (FTIR)
3. Moisture in the flue gas i.e. \( \text{H}_2\text{O} \) (FTIR)
4. Carbon monoxide \( \text{CO} \) (FTIR)
5. Volatile organic compounds (VOC) as organic carbon (Org.-C) (FTIR and FID)
6. Nitrogen oxide as nitrogen dioxide equivalent (NO\(_2\)equi) (FTIR)
7. Sulphur dioxide \( \text{SO}_2 \) (FTIR)
8. Methane \( \text{CH}_4 \) (FTIR)
9. Organic compounds like, alkanes, alkenes, aromatics, aldehydes as well as ketones (FTIR)
10. Flue gas temperature, gas velocity and draft conditions.

The recording of the above mentioned parameters took place on continuous time basis except for the dust measurement. During the evaluation of the data, the average values of the pollutants were calculated for each dust sampling cycle whereas each cycle lasts for 30 minutes. With the aid of a chimney fan, a constant negative pressure of 12 Pa has been maintained in the chimney stack in order to achieve a fuel thermal output from 8 to 9 kW.

The gravimetric analysis of total amount of dust was done in accordance with VDI guidelines 2066-1, according to which a partial volume flow must be taken in isokinetic manner out of the main flue gas stream. In this process, the accompanied particles can be deposited on the already weighed plane filter. Since the filter housing is located outside the flue gas pipe, this sampling procedure is termed as “out-stack process”. The filter system was heated up with a heating jacket in order to prevent the falling down of temperature under saturation temperature of the flue gas. The temperature of the filter was maintained at 70°C so that the semi-volatile hydrocarbons could also be deposited on the filter. After the experiment, the deposited dust amount was determined gravimetrically and then can be specified by taking into consideration the measured partial volume and oxygen concentration. The plane filter was made of micro-glass fibers having a diameter of 45 mm.

Catalyst synthesis techniques

In this work, two different synthesis routes have been developed in order to coat aluminium oxide foams with a mixed metal oxide active
phase. These two respective techniques cannot be yet described in detail because of ongoing patent approval.

**Results and Discussion**

**Reference experiment**

At first, a reference experiment was carried on the downdraft stove in order to determine the emissions, temperature profiles and pressure conditions during the operation of the stove in an unmodified state. This reference test is vital in the context of evaluating the effect of different modifications and changes in the stove which will be done in upcoming experiments. In Figure 2, the temperature profiles of different sections of the stove have been depicted. For every burning cycle, the stove was operated for the first 30 s in “up-draft” mode. After that, it was operated in downdraft (Twinfire mode) for the next 29.5 minutes. The average temperature in the grate was calculated to be around 750°C whereas, the temperature in the walls of the lower combustion chamber, where catalysts are planned to be installed in future experiments, was found to be ca. 650°C. In Figure 3, the time-dependent behavior of CO, VOC (Org.-C / THC) and aromatics (sum) has been depicted. These concentrations are recorded for four burning cycles of the reference test (Table 1).

**Integration of uncoated Al₂O₃-foams as a support material**

Al₂O₃-foams were tested as a possible support material for a suitable catalyst at the start of the experimental stage. For this purpose, two such foams were inserted into the walls of the combustion chamber. However, first of all it was important to calculate the pressure drop across the monoliths in order to ascertain the smooth operation of the stove after installing the monoliths. The pressure drop across the monoliths was found to be lower than 0.5 Pa which is sufficiently low and shows the applicability of the foams.

As observed, there is no negative effect on the combustion behavior of the stove after installing the uncoated Al₂O₃-foams, so it leads to the testing of the monoliths in the combustion chamber with Mixed Metal Oxide (MMO) as an active phase.

**Reduction of pollutants with the integration of wall catalysts and heat reflecting plate:**

In order to lower the emissions, the temperature of wall catalysts in the lower combustion chamber was increased by placing a heat reflecting plate (made of vermiculite) in front of the door in the lower combustion chamber (Table 3).

**Integration of the catalyst in the walls of lower combustion chamber**

**Wall catalyst based on MMO/Al₂O₃-foam:** As evident from the Table 2, after the catalyst incorporation, the emissions of CO and VOC (Org.-C) were reduced by 21% and 42% respectively (in comparison to the reference test). Moreover, the dust emissions were also abated by 55%.

**Reduction of pollutants with the integration of wall catalysts and heat reflecting plate:** In order to lower the emissions, the temperature of wall catalysts in the lower combustion chamber was increased by placing a heat reflecting plate (made of vermiculite) in front of the door in the lower combustion chamber (Table 3).

**Integration of the MMO/α-Al₂O₃ catalyst synthesized through Technique 1:** After recording positive results concerning emission control by using a suitable catalyst, the active phase of mixed metal oxide (as used in previous experiments) was brought onto the aluminium oxide foam through a novel technique, which is termed here as “Technique 1” (described in the section 2.2).

As can be seen from the Table 4, the emissions of CO and Org.-C were reduced by 58%, clearly indicating the suitability of both the active phase and the corresponding synthesis route.
Integration of the mixed metal oxide/α-Al₂O₃ catalyst synthesized through Technique 2: On experimental basis, another technique, “Technique 2” (described in the section 2.2), has been adopted to observe the suitability of the procedure regarding better oxidation activity of the catalyst.

As evident from the Table 5, the selected synthesis route was not proved to be fruitful, as emission values were higher than using “Technique 1” (Table 6).

Aging behavior of the wall catalyst MMO/α-Al₂O₃: For the determination of the thermal and chemical deactivation of the catalyst, it was aged by fitting into a downdraft stove and subjected to real operating conditions for 630 h (equal to one heating period). The long-term/aging experiments were planned in such a way that the catalyst was exposed to real operating conditions for three weeks (except the first aging cycle was 6 weeks) and after that immediately tested for its activity. Shortly after, the catalyst was again subjected to a long-term experiment for three weeks before being analyzed again for its stability. The results have indicated that, as shown in Table 7, the catalyst showed initially quite a promising oxidation of pollutants namely, carbon monoxide, volatile organic compounds and dust (particulate matter). This behavior can be attributed to the thermal activation of the catalyst caused by the diffusion of active phase species into the support material. However, there is so far no evidence of the thermal oxidation of pollutants namedly, carbon monoxide, volatile organic compounds and dust (particulate matter). This behavior can be attributed to the thermal activation of the catalyst caused by the diffusion of active phase species into the support material, resulting into the synthesis of more active catalytic phase [5]. However, as clear from Table 7, the activity of the catalyst dwindled with the passage of time. This can be possibly due to the poisoning of the active phase on the support material. However, there is so far no evidence for the provided assumptions as catalyst characterization (e.g. XRD, XPS) is planned to be done at the end of the aging experiments (after the fifth cycle).

Aging behavior of the wall catalyst synthesized through Technique 2: In order to get verification about thermal activation in case of mixed metal oxide catalyst, another long-term/aging experiment for three weeks before being analyzed again for its stability. The results have indicated that, as shown in Table 8, there is quite a substantial amount of reduction in the emissions. The emissions of CO and VOC (Org.-C) were reduced by 62% and 77% respectively. Clearly, there is a thermal activation effect which can be observed in regard to the selected MMO/Al₂O₃ catalyst. However, like pointed out earlier, a catalyst characterization has to be done in order to support this assumption but it is very obvious that there exists quite a high probability of thermal activation, as can be observed from multiple experimental results.

Future Work and Conclusions

The selected monoliths, primarily composed of aluminum oxide (Al₂O₃) were coated with mixed metal oxide as an active catalytic phase and later inserted into the walls of the stove in the lower combustion chamber. These Al₂O₃ foams (porosity of 10 ppi) consist of 92% α-Al₂O₃ along with the trace phases of mullite and corundite. The results revealed that the catalyst was found to be quite active in terms of oxidation of harmful pollutants e.g. CO and VOC. In addition, two different synthesis routes for mixed metal oxides on the alumina foam were discussed. It was found that, the “Technique 1” proved to be promising as the catalyst showed higher emission reductions, as compared to the one synthesized through the “Technique 2”. Perhaps, it can be attributed to the comparatively high temperature handling of the precursor, thus allowing a more mature crystallization of the active phase structure. Furthermore, the aging experiments were performed with three different wall catalysts, each consisting of mixed metal oxides but synthesized via different methods. It is quite obvious that each of the three catalysts showed a “thermal activation effect” during the long-term/aging experiments, but this assumption cannot be yet supported due to the lack of catalyst characterization, which is planned to be carried out as soon as possible.

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| Experiment Unit | Reference mg/m³ i.N., 13 % O₂ | MMO(α-Al₂O₃) mg/m³ i.N., 13 % O₂ | Reduction % |
|-----------------|-------------------------------|----------------------------------|-------------|
| CO              | 1514                          | 578                              | 62          |
| VOC (Org.-C, FID) | 109                          | 16                               | 85          |
| VOC (Org.-C, FTIR) | 132                          | 35                               | 74          |
| dust with rinsing | 37                           | 11                               | 71          |
| dust without rinsing | 33                           | 10                               | 70          |

Table 3: Emission reduction after integrating MMO/α-Al₂O₃ foams with heat reflecting plate.

| Experiment Unit | Reference mg/m³ i.N., 13 % O₂ | MMO(α-Al₂O₃) mg/m³ i.N., 13 % O₂ | Reduction % |
|-----------------|-------------------------------|----------------------------------|-------------|
| CO              | 1718                          | 725                              | 58          |
| VOC (Org.-C, FID) | 156                          | 65                               | 58          |
| VOC (Org.-C, FTIR) | 202                          | 92                               | 54          |

*The reference experiment was performed again with the new batch of same fuel type

| Experiment Unit | Reference mg/m³ i.N., 13 % O₂ | MMO(α-Al₂O₃) mg/m³ i.N., 13 % O₂ | Reduction % |
|-----------------|-------------------------------|----------------------------------|-------------|
| CO              | 1718                          | 1359                             | 21          |
| VOC (Org.-C, FID) | 156                          | 115                              | 26          |
| VOC (Org.-C, FTIR) | 202                          | 147                              | 27          |

Table 5: Emission values after fitting the catalyst (MMO/α-Al₂O₃) synthesized through Technique 2.

| Experiment Unit | Reference mg/m³ i.N., 13 % O₂ | MMO(α-Al₂O₃) mg/m³ i.N., 13 % O₂ | Reduction % | Technique 1 | Technique 2 |
|-----------------|-------------------------------|----------------------------------|-------------|------------|------------|
| CO              | 725                           | 1359                             | 21          | 1359       | 115        |
| VOC (Org.-C, FID) | 65                           | 115                              | 26          | 115        | 147        |
| VOC (Org.-C, FTIR) | 92                           | 147                              | 27          | 147        | 115        |

Table 6: Comparison between the two selected synthesis routes.

| Experiment Unit | During normal experiment mg/m³ i.N., 13 % O₂ | During long-term experiment mg/m³ i.N., 13 % O₂ | Reduction % |
|-----------------|-----------------------------------------------|-----------------------------------------------|-------------|
| CO              | 1359                                         | 518                                           | 62          |
| VOC (Org.-C, FID) | 115                                         | 27                                            | 77          |

Table 7: Emission values during the course of the aging experiments with MMO/α-Al₂O₃ catalyst.

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