Influence of combustion conditions on the genotoxic potential of fine particle emissions from small-scale wood combustion

Thomas Brunner 1, 2*, Joachim Kelz 1, Ingwald Obenberger 1, 2, Pasi I. Jalava 3, 4, Maija-Riitta Hirvonen 3, 4

2 Corresponding author: e-mail: thomas.brunner@bioenergy2020.eu
3 Institute for Process and Particle Engineering, Graz University of Technology, Inffeldgasse 21a, A-8010 Graz, Austria
4 Department of Environmental Health, National Institute for Health and Welfare, P.O. Box 95, FI-70701 Kuopio, Finland

Introduction and objectives
Due to increased efforts for CO2 emission mitigation, the energetic utilisation of biomass in small-scale (residential) heating systems for room heating and warm water supply has gained rising relevance all over Europe within the last decade. Old combustion systems show, due to their low technological level, not as good combustion conditions (burnout quality) as modern combustion systems and therefore significantly higher PM, CO, OGC as well as particle bound PAH emissions than modern systems. The differences regarding PM1 emissions of old and modern small-scale biomass combustion systems not only concern their magnitudes but also their chemical compositions [1, 2]. While PM1 emissions from modern systems have been found to contain mainly inorganic salts (alkaline metal salts) and a small amount of heavy metal oxides (mainly ZnO), PM1 emissions from old biomass combustion technologies are dominated by carbonaceous particles (organic compounds and soot). As scientific investigations indicate these inorganic salts are much less harmful for human health than organic particles and soot, however, systematic studies regarding this issue are still missing. Therefore, a project dedicated to the investigation of health risks caused by fine PM emissions from different old and modern small-scale biomass combustion technologies has been performed at the BIOENERGY 2020+ GmbH, Graz, Austria, in cooperation with the Institute for Process and Particle Engineering, Graz University of Technology, Austria, the Department of Environmental Health, National Institute for Health and Welfare, Kuopio, Finland, as well as the Department of Environmental Sciences, University of Eastern Finland, Kuopio, Finland. The objectives were to characterise PM emissions from the different biomass combustion systems concerning their concentration in the flue gas and chemical composition as well as to determine the health risks caused by these PM emissions by the performance of toxicological in-vitro studies. However, correlations between the performance of the combustion systems, the characteristics of their particulate emissions as well as the related health risks should be worked out. The overall aim of the project was to investigate the whole process chain starting at the definition of the performance of the combustion systems in terms of burnout and leading over an extensive chemical characterisation of the fine PM emissions to the investigation of the health risks caused by these emissions by toxicological in-vitro studies.

Methodology and test stand set-up applied
For the evaluation of the influence of combustion conditions on the toxicological potential of fine particulate emissions from small-scale wood combustion test stand measurements with a broad variety of residential biomass combustion systems have been tested covering automatically fed and automatically controlled boilers (pellet and wood chip boilers), manually fed and automatically controlled boilers (logwood boilers) as well as manually fed stoves (logwood fired chimney stoves and a tiled stove). The test stand setup is based on recommendations for particle sampling for toxicological tests, worked out within the ERA-NET Bioenergy project BIOMASS-PM [1]. It is important to mention that the test runs performed as well as PM1 emission sampling took place over whole day operation cycles and therefore, in contrast to other studies on PM emissions from residential biomass combustion, not only stable continuous operation phases but also transient operation phases have been investigated. Especially when operating old combustion systems and batch combustion systems based on natural draught but also during operation of modern boiler systems, phases with increased emissions of condensable hydrocarbons occur. In the real life situation these gaseous emissions condense later on in the atmosphere and form secondary aerosols which provide a substantial contribution to the ambient air PM concentrations. Therefore, the flue gas was diluted before the particle sampling in order to convert condensable organic species into particles. The dilution was performed with pre-cleaned particle free pressurised air and the dilution ratio was adjusted in a way that the diluted flue gas had a temperature of below 40°C.

The scheme of the test stand setup applied is presented in Figure 1. During the test runs the plant operation (flue gas temperature, combustion chamber temperature, boiler load for boiler systems, chimney draught etc.) was monitored, gaseous (CO, OGC, O2) as well as PM emissions were determined and PM1 emissions
were sampled and forwarded to subsequent chemical analyses and toxicological tests. Additionally, all relevant data (temperatures, mass flows) of the dilution air were controlled. For fine particulate emission measurements and particle sampling three different systems (ELPI – electric low-pressure impactor, BLPI – Berner-type low-pressure impactor, DGI – Dekati gravimetric impactor) were applied. Dilution of the flue gas was realised with porous tube diluters (DGI and BLPI) as well as ejector diluters (ELPI).

Fine particulate samples for the toxicological studies were collected with DGI and for chemical analyses (inorganic elements, organic carbon (OC), elemental carbon (EC) and inorganic carbon (IC)) with BLPI. Furthermore, the concentration of aerosols in the diluted flue gas was determined continuously with an ELPI. From the test runs performed with each combustion system, PM$_1$ samples from 2 representative tests were forwarded to chemical analyses and toxicological tests.

![Scheme of the measurement and particle sampling system](image)

**Biomass combustion systems investigated**

The combustion systems investigated represent a cross section of residential heating technologies presently applied in Europe. Since the stock of applications in most countries is dominated by old combustion systems (sometimes older than 20 years) not only state-of-the-art technologies but also old technologies have been investigated. A modern pellet boiler, a modern wood chip boiler, a modern and an old logwood boiler, a modern and an old logwood fired chimney stove as well as a modern logwood fired tiled stove have been tested. The nominal boiler capacities were between 15 and 30 kW and the nominal heat output for the natural draught systems between 4.2 and 6.5 kW. With this selection of combustion technologies the major share of applications which are usually operated in Europe could be covered. For the test runs wood pellets according to ÖNORM M 7135, wood chips according to ÖNORM M 7133 as well as logwood according to ÖNORM M 7132 and ÖNORM CEN/TS 14961 were used as fuels. As comparisons with database values show, the fuels applied during the test runs are representative for the respective fuel category.

**Gaseous and particulate emission trends over whole day operation determined**

During the test runs with the modern pellet boiler with the exception of some very short periods (some seconds) acceptable burnout conditions prevailed. Only during the initial start-up phase as well as the shut down and restart phases of the boiler larger CO, OGC and PM$_1$ emission peaks occurred. Especially partial load operation resulted in slightly increased PM$_1$ emissions which are mainly due to the, compared with full load operation, lower combustion chamber temperatures during these phases which lead to the formation of organic aerosols and soot emissions. However, also during partial load operation good gas phase burnout could be achieved. The wood chip boiler was operated under the same load programme and showed a comparable behaviour regarding emissions, however, the emission levels were slightly higher.

Also during most time of the operation of the modern logwood boiler good burnout conditions and consequently comparably low CO, OGC and PM$_1$ emissions prevailed. Compared with the pellet boiler, the emission peak during the start-up phase occurs over a significantly longer period (about 30 minutes compared to about 10 minutes) which is typical for logwood boilers [3]. This period is followed by stable operation characterised by very low emissions. During the burnout phase an increase of CO and PM$_1$ emissions can be recognised. As the operation cycle of the modern logwood boiler consisted of two batches some short emission peaks can be identified during the re-charging process. After some minutes stable combustion conditions are reached again and also the gaseous and particulate emissions are reduced to the same low level as during the first batch. At the end of the second batch again the increase of CO and PM$_1$ emissions as reported can be recognised. During the operation of the old technology logwood boiler
significantly higher emissions have been measured due to higher excess air ratios and consequently lower combustion temperatures. In Figure 2 process data and emission trends recorded during test runs with the modern pellet boiler and the modern logwood are presented.

Figure 2: Operation parameters as well as gaseous and particulate emissions during test runs with the modern pellet boiler and the modern logwood boiler

Explanations: concentrations related to dry flue gas; TSP, PM, CO, OGC emissions related to 13 vol% O₂; TCC ... combustion chamber temperature; TFG ... flue gas temperature; TFeed ... feed temperature; Load ... boiler load; BLPI and TSP lines indicate the measured PM concentration over the respective sampling period, vertical lines indicate the start respectively endpoint of the batches.
The combustion process of natural draught systems is characterised by three combustion phases, namely the ignition phase, the main combustion phase and the burnout phase and is illustrated in Figure 3. At the beginning of a combustion cycle, during the ignition phase, the $O_2$-content of the flue gas decreases while the furnace temperatures increase. As long as the $O_2$-concentrations are too high and the furnace temperatures are too low to achieve appropriate burnout conditions, high CO, OGC and PM$_1$ emissions are detected. As soon as stable combustion conditions have been reached the main combustion phase begins which is characterised by quite stable $O_2$-concentrations in the flue gas and sufficiently high temperatures in the furnace to provide acceptable burnout conditions. During this phase the gaseous and particulate emissions are significantly lower than during the ignition phase. At the end of the combustion cycle charcoal burnout takes place, the burnout quality decreases and the CO emissions increase. The OGC and the PM$_1$ emissions however stay on a rather low level which is due to the fact, that the main amount of volatiles has been released from the fuel during the ignition and the main combustion phase. The major part of the emissions generated during one combustion cycle is related to the ignition phase. Only during the first combustion batch this behaviour is not very pronounced since the stove is still heating up to operation temperature and therefore, generally higher emissions are measured due to the too low combustion temperatures. This behaviour has been determined for both the modern and old technology stove. However, the emissions from the old technology stove were in general about doubled. The combustion process in tiled stoves is comparable with the one in stoves, but it consists of only one batch.

Figure 3: Operation parameters as well as gaseous and particulate emissions during test runs with the modern logwood fired chimney stove

Explanations: concentrations related to dry flue gas; TSP, PM$_1$, CO, OGC emissions related to 13 vol% $O_2$; TCC … combustion chamber temperature; TFG … flue gas temperature; TFeed … feed temperature; BLPI and TSP lines indicate the measured PM$_1$ concentration over the respective sampling period, vertical lines indicate the start respectively endpoint of the batches

Average gaseous and particulate emission over whole day operation

A summary of the mean values of the gaseous and PM$_1$ emissions determined during the test runs is presented in Table 1. It has to be pointed out that the ELPI measurement provides particle number related data. Therefore, the mass related data have to be calculated by applying a correction factor considering the density and the particle size of the different particle fractions. Due to the heterogeneity of the particle collective it is not possible to calculate a reliable correction factor based on theoretical considerations and therefore, the number related ELPI results have been correlated with the in parallel performed gravimetric BLPI measurements in order to gain an average correction factor over a test run. In Table 1 these corrected mass related ELPI data are presented.

The average PM$_1$ emissions over the test runs increase from the modern automated boiler systems (pellet boiler: 6.0 resp. 6.2 mg/MJ, wood chip boiler: 13.6 resp. 15.3 mg/MJ, logwood boiler: 14.2 resp. 17.6 mg/MJ) over modern natural draught systems (modern tiled stove: 31.3 resp. 28.0 mg/MJ, modern stove: 47.2 resp. 46.1 mg/MJ) to old combustion technologies (old technology stove: 74.2 resp. 55.5 mg/MJ, old technology logwood boiler: 106.1 resp. 98.6 mg/MJ).
Table 1: Mean values for gaseous and PM\textsubscript{1} emissions over the whole test runs for the different biomass combustion systems investigated

<table>
<thead>
<tr>
<th>Combustion system</th>
<th>Test run</th>
<th>O\textsubscript{3} [vol. % d.b.]</th>
<th>CO [mg/MJ]</th>
<th>OGC [mg/MJ]</th>
<th>PM\textsubscript{1} [mg/MJ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pe-m</td>
<td>1</td>
<td>12.6</td>
<td>47.1</td>
<td>2.5</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.5</td>
<td>45.4</td>
<td>1.7</td>
<td>6.0</td>
</tr>
<tr>
<td>Wc-m</td>
<td>1</td>
<td>12.2</td>
<td>168.1</td>
<td>3.0</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.1</td>
<td>182.2</td>
<td>5.4</td>
<td>13.6</td>
</tr>
<tr>
<td>Lw-m</td>
<td>1</td>
<td>8.6</td>
<td>700.4</td>
<td>78.7</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.6</td>
<td>793.1</td>
<td>62.4</td>
<td>17.6</td>
</tr>
<tr>
<td>TST-m</td>
<td>1</td>
<td>15.4</td>
<td>1,207.3</td>
<td>52.4</td>
<td>31.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>15.3</td>
<td>1,007.5</td>
<td>69.2</td>
<td>28.0</td>
</tr>
<tr>
<td>ST-m</td>
<td>1</td>
<td>12.5</td>
<td>1,048.2</td>
<td>94.2</td>
<td>47.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.1</td>
<td>1,035.6</td>
<td>95.5</td>
<td>46.1</td>
</tr>
<tr>
<td>ST-o</td>
<td>1</td>
<td>10.8</td>
<td>2,355.4</td>
<td>223.9</td>
<td>74.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11.1</td>
<td>2,084.6</td>
<td>185.7</td>
<td>55.5</td>
</tr>
<tr>
<td>Lw-o</td>
<td>1</td>
<td>11.3</td>
<td>12,632.3</td>
<td>1,143.8</td>
<td>106.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11.0</td>
<td>8,969.4</td>
<td>650.8</td>
<td>98.6</td>
</tr>
</tbody>
</table>

Explanations: Pe-m ... modern pellet boiler; Wc-m ... modern wood chip boiler; Lw-m ... modern logwood boiler; Lw-o ... old logwood boiler; ST-m ... modern logwood stove; ST-o ... old logwood stove; TST-m ... modern tiled stove

The mean values of the emissions over the test runs also clearly show the interdependencies between burnout quality and formation of gaseous and particulate emissions. A clear and statistically significant correlation between the CO and OGC emissions exists ($R^2=0.9809$, statistical evaluation: significance $p<0.05$). Moreover, the results underline that with decreasing burnout quality (increasing CO emissions) also the PM\textsubscript{1} emissions significantly increase. Again, a direct statistically significant correlation prevails ($R^2=0.7538$, statistical evaluation: significance $p<0.05$).

**Chemical composition of the PM samples**

Based on the elemental composition of the samples their composition with respect to different chemical compounds has been estimated. Therefore, the following approach was applied. Since it is known that alkaline metals (K and Na) in aerosols are usually bound as sulphates, chlorides and carbonates firstly the alkaline sulphate concentration was calculated based on the assumption that all sulphur is bound by the alkaline metals. The same assumption was made for chlorine. The remaining alkaline metals, left over after the formation of chlorides and sulphates, where estimated to be bound as carbonates. All other elements detected (mainly Ca, Mg, Si and Zn) are assumed to be bound as oxides.

The inorganic fraction of the PM\textsubscript{1} emissions mainly consists of alkaline metal compounds. With the exception of the old logwood boiler and the modern stove, where higher shares of alkaline carbonates respectively other oxides are found, alkali metal sulphates clearly dominate the aerosol composition. For all samples with exception of the one from the modern stove (60%) alkaline metal compounds account to more than 80% of the total inorganic particle mass.

Regarding the analyses of the overall compositions of the particle samples, element recovery rates of more than 90% could be achieved. With increasing aerosol emissions the concentrations of carbonaceous compounds clearly rise. While for the aerosols from the pellet boiler the concentrations of elemental and organic carbon were below the detection limit, they slightly increased for the wood chip boiler and the modern logwood boiler. Higher concentrations were determined for the stoves and the highest ones for the old logwood boiler. While for the stoves the elemental carbon emissions dominate the carbonaceous aerosol fraction, organic carbon is higher concentrated in the particles from the old logwood boiler. These results confirm that a basic PM\textsubscript{1} emission level is provided by the formation of inorganic aerosols (which is comparable for all the systems tested) and that the further increase of the emissions is caused by the formation of organic aerosols as well as soot emissions due to decreasing burnout quality.

Special attention was paid to the determination of the PAH concentrations in the particle samples since PAHs are known to be of significant health relevance. A fraction of the pooled, extracted DGI samples which have also been used for the toxicological tests has been analysed regarding in total 30 different PAHs.

A clear correlation between the total PAH emissions and the total of the 13 genotoxic PAHs defined by the WHO [4] exists ($R^2=0.9813$, statistical evaluation: trend $p<0.1$). About the same correlation was found for the total emissions of the 30 PAHs and the 6 genotoxic PAHs according to the directive 2004/107/EC [5]. Also between the average OGC emissions determined during the test runs and the particle bound PAH emissions a clear correlation could be found (see Figure 4). As expected, these parameters show a good correlation ($R^2=0.9035$, statistical evaluation: trend $p<0.1$) which is mainly due to the fact that both are a result of incomplete combustion and confirm that the burnout quality achieved plays a relevant role in the formation of PAHs [6].
Figure 4: Average OGC emissions over the whole test runs vs. condensed PAH emissions

Explanations: data in µg/Nm³ related to dry flue gas and 13 vol% O₂

Toxicological in-vitro tests of PM samples investigated

The size-segregated particulate samples were prepared for the toxicological studies using previously validated procedures [7, 8]. Mouse RAW264.7 macrophages were separately exposed to four doses (15, 50, 150 and 300 µg/ml) of each PM₁ sample for 24 hours. The specific aims of the toxicological in-vitro tests were to investigate cell death and to study the inflammatory responses caused by PM as well as to assess the PM induced genotoxicity as measures for possible health effects caused by these emissions. Inflammatory parameters, proinflammatory cytokine TNFα and chemokine MIP-2 were analysed from the cell culture medium. Cytotoxicity was analyzed with MTT assay and flow cytometric methods. Genotoxicity was determined with comet assay. Generally, there is a good agreement concerning the results for the 2 samples of each combustion system tested. Moreover, it has to be pointed out that for all parameters investigated dose dependent responses were gained, which means that with increasing dosage of PM₁ the reactions of the cells increase.

The old technology logwood boiler was in its own class to cause both inflammatory and cytotoxic responses in the macrophages. It caused also disturbance of the normal cell cycle and markedly increased genotoxicity. By the results of the toxicological tests, it is obvious that the incomplete combustion is associated with larger toxic potential when compared to almost complete combustion. This effect was seen also less dramatically by comparing the old and modern technology stoves. On the other hand, wood chip and pellet boiler derived samples caused consistently the lowest response levels among the samples, except for cytotoxicity detected with MTT-test. Also the samples of the modern technology logwood boiler and both tiled stove samples showed low response levels, except for the cell cycle analysis where the samples caused increased apoptosis. The lower response levels were also associated with the small-scale biomass combustion appliances that showed smaller CO, OGC and PM₁ emissions in many cases.

Most likely the cytotoxic responses of pellet boiler and wood chip boiler derived samples are associated with the inorganic composition of the samples. Overall, present results suggest that combustion technology, respectively the burnout quality achieved as well as type of combustion (batch vs. continuous combustion) affects the relative harmfulness of the particulate emissions. Detailed information regarding the toxicological tests is given within the lecture Health related toxicological effects of aerosols from small-scale biomass combustion systems by Maija-Riitta Hirvonen.

Figure 5 illustrate a clear and statistically significant correlation between the average CO emissions detected over the whole test runs and the genotoxicity (olive tail moment) of the samples measured with Comet assay after exposure to PM₁ samples from different combustion appliances with a dose of 150 µg/ml (R²=0.9616, statistical evaluation: significance p<0.05). The result further widens the gap between modern and old technology appliances, respectively almost complete and incomplete burnout quality.
Summary and conclusion

Combustion tests with 7 different old and modern residential biomass combustion systems have been conducted simulating real life whole day operation cycles. During these test runs the gaseous and particulate emissions have been measured and PM$_1$ samples have been taken and forwarded to chemical analyses and toxicological tests. Therefore, for the first time, comprehensive data concerning gaseous and PM emissions of different old and modern residential biomass combustion systems, the chemical characterisation of their PM$_1$ emissions as well as the potential of these PM$_1$ emissions for causing health risks are available.

From the emission data it could be derived that the burnout quality significantly decreases from modern automated residential biomass combustion systems (pellet, wood chips and logwood boilers) over modern natural draught systems (stoves and tiled stoves) to old technology stoves and logwood boilers. As an example the average CO emissions over the whole operation cycle increased from the pellet boiler (45.4 resp. 47.1 mg/MJ) over the modern logwood stove and the tiled stove (1,000 to 1,200 mg/MJ) and the old technology logwood stove (2,100 resp. 2,350 mg/MJ) to the old technology logwood boiler, which showed exceptionally high emissions of up to 12,600 mg/MJ. A pronounced correlation between the average CO and OGC emissions could be detected. Moreover, also the average PM$_1$ emissions ranging from around 6 mg/MJ for the pellet boiler to about 106 mg/MJ for the old technology logwood boiler correlated well with the OGC and CO emissions. As chemical analyses of PM$_1$ samples taken during the test runs have shown, the concentrations of organic carbon and soot increase with decreasing burnout quality and consequently, the higher PM$_1$ emissions at low burnout quality are attributed to the formation of carbonaceous aerosols. Moreover, it has been shown, that the particle bound PAH emissions also correlate with the OGC emissions and consequently with the burnout quality.

Overall, the composition from incomplete combustion seems to induce stronger toxicological effects than the composition from more complete combustion. The particulate samples from old technology appliances can be considered significantly more harmful due to their large genotoxic potential. Finally, the present data also demonstrated clearly that the combustion technology, respectively the burnout quality achieved affect both the emissions and their toxicological responses. Furthermore, it has been revealed that toxicological methods can support the development of modern combustion technologies and utilised when planning strategies for less harmful emissions from residential heating with biomass and thus, cleaner ambient air.

Based on the data presented in this paper it can be concluded that the most efficient way to reduce health risks caused by residential biomass combustion is to optimise burnout. This leads (i) to decreased emission factors for PM$_1$, (ii) lower concentrations of carbonaceous compounds in the PM emissions and consequently (iii) less hazardous particles. Therefore, comprehensive efforts should be made in order to substitute old residential biomass heating systems by modern state-of-the-art technologies. Moreover, additional efforts should be made to further develop modern residential biomass combustion systems in order to optimise burnout and minimise PM emissions, especially during partial load operation and under transient combustion conditions.

References


