NANOPARTICLES EMISSION FROM SMALL OUTPUT COAL-FIRING FURNACES

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Abstract
Solid fuel combustion systems produce smoke emission, which are of health and environment concern to authorities and public. The particles in emission have long residence time in the atmosphere and may be associated with adverse health effects due to their penetration and deposition in the lower respiratory tract and their enrichment in potentially harmful components (e.g. heavy metals, POPs). The production of engineered nanoparticles has become an important sector of nanotechnology and both number of types and quantity of production increased significantly. Consequently, the investigation of possible health effects of nanoparticles started and nowadays it is a concern of several research projects.

The measurement of nanoparticles creation during combustion in small output automatic boiler was realized. Distribution of particles was measured in the range 5 nm to 250 nm by FMPS spectrometer. It results from the experiment that during the combustion of coal, mainly larger nanoparticles (60 to 200 nm) are produced, and second, narrow maximum is at very fine fraction. The most represented fraction totally are nanoparticles with the size of about 6 nm. On the cross profile of the sampling places the nanoparticles are not distributed proportionally. It results from comparing the concentration of nanoparticles taken from two different places in the dilution tunnel, that at the end of the dilution tunnel the concentration of particles is approximately half that of behind the boiler. The active supply of fuel does not influence the total concentration of originating particles but the concentration of the smallest fraction under 6 nm is increased.

Keywords: nanoparticles, emission, combustion, small output furnaces

1. INTRODUCTION
At present, there is frequent discussion about problems related to nanotechnologies, nanoparticles, nanotoxicity, etc., concerning the areas of variances in the dimensions and concentrations of particles. Laws of conventional physics are in nano-scale combined with laws of the micro-world which leads to the behaviour of nanomaterials which may differ from the behaviour of the same materials in macro-scales. In professional literature, there are discussions about nanoparticles as particles where at least one dimension is smaller than one hundred nanometres [1]. These small particles are used for the development of materials and equipment with new properties. The greatest development of modern nanotechnologies has been reported during the last 15 years and their positive contribution to society is undisputed. However, possible risks brought by “nano” issues are not often mentioned, including risks for the environment and for people’s health.

However, it is necessary to take into consideration the fact that nanoparticles are also part of most natural processes and they have been present for a long time. Particles with microscopic dimensions originate during fire, the erosion of earth, the eruption of volcanoes and other natural phenomena. In addition to intentionally produced and naturally occurred nanoparticles, it is possible to define the third area of the creation of nanoparticles as the undesired creation of small particles from anthropogenic activities (combustion, braking processes, friction, abrasion and degradation of materials, etc.). One potentially important source of nanoparticles are combustion processes using
solid fuel, mainly combustion of coal in thermal power plants and the combustion of solid fuel in local combustion facilities. This ratio is supported by the existing economic situation because people have started to return to solid fuels with increased ash material content. From the viewpoint of the environment, the combustion of coal is a significant source of pollution and the history of industrial development is joint with the issue of contamination of the environment caused by the combustion of coal. Ensuing is the relationship between measuring methods and the level of knowledge about the harmful effects of emissions. In the past the monitoring of air pollution was limited to the measurement of the content of sulphur dioxide and solid particles, followed by the measurement of nitrogen oxide, and later a series of research studies have dealt with emissions of other pollutants. At present, during the monitoring of emissions from combustion, attention is paid to the following groups of substances: SO$_2$, NO$_x$, solid particles, volatile organic compounds (VOC), polyaromatic hydrocarbons (PAH) and other persistent organic pollutants (POPs) and toxic heavy metals. An interesting category is the solid particles when in emissions we ascertain their total content, but in emissions, only fine fractions of particulate matter (indicated as PM$_{10}$a PM$_{2.5}$) are measured. Some studies also show that the existing trend, based on the continuously increasing importance of fine fractions, will continue and will probably extend into the area of nanoparticles.

Nanoparticles, thanks to their small size, are present in the air for a long time, and with small size of nanoparticles there can be sedimentation only after their mutual coagulation or catching on other particles or solid surfaces. Many studies prove that some toxic metals and organic pollutants are concentrated on small particles [6] and this trend will probably continue to nanoparticles. Then, they could have a significant impact on human health (negative influence on cardio-vascular and respiratory systems of human body). The respiratory system represents the easiest way for nanoparticles to enter the human body where, after concentration, they may have a toxic and fibrogenous effect, and also other ways of exposure cannot be ignored. Moreover, in recent times, in relation to emissions and the production of nanoparticles, it is possible to observe discussions about the possible mutual interaction of such small particles with DNA, RNA and proteins [2,3]. Many studies, sometimes with controversial results, deal with the extend at which nanoparticles are toxic. Nevertheless, it is possible to state now that nanoparticles can represent a serious risk for the human body [4], and even if nanoparticles from combustion remain in the environment for a long time, their combination by intentionally prepared nanoparticles may result in a synergic effect. For the above-mentioned reasons, the importance increases for control of small sources without the advanced technology for the cleaning of emissions. For these reasons, described experiments were performed.

The objective of the work was a pilot study containing measurements of emissions of nanoparticles from the automatic boiler C-100 (Benekov, CZ) combusting brown coal.

2. EXPERIMENTAL

The measurement of nanoparticles from the combustion process does not represent an easy task because it is the procedure demanding for instrument equipment, and because the overall approach and performing of measurements requires both an overview and a sense for detail. For small combustion sources this is twice as valid, because complications related to the measurement of nanoparticles are combined with difficulties of measurement of small boilers. This is caused by the character of such small particles, including the possibility of their mutual influence and their behaviour which differs from common particulate matter; their high concentrations in combustion gases from the boiler and the consequent necessity to use series dilution of emissions. Other complications arise from the complex composition of matrix (emissions), including risk of condensing of the liquid phase and the necessity to recalculate emissions to standard conditions (content of oxygen).

For measurement of nanoparticles in the ambient air and waste gas, highly sensitive devices are used which, due to used principles of measurement, can be used for the measurement of emissions of
nanoparticles from small combustion sources only in combination with the diluting system. The most used procedure is the dilution by pre-filtered atmospheric air [5], which is, due to the great difference between measured values and the background (concentration of nanoparticles in the filtered air), an acceptable procedure. The problem is the homogeneity of the diluted mixture and the issue of the separation of nanoparticles by coagulation or by absorption on walls of the sampling train.

In realized experiment we focused on finding the distribution of nanoparticles originated from coal burning after optimising of the combustion in the automatic boiler C-100 with the output 100 kW. Brown coal was used as fuel (North Bohemian mines, Bilina mine), size nut #2, and during the combustion process the boiler was set for the output of 90 kW. The dosing frequency of the fuel was set for period 15 seconds (15 s fuel dosing, 15 s timeout). The measurement was performed with the reference content of oxygen 10 %. Fig. 1 shows the arrangement of the experiment. One of the objectives was to evaluate whether the concentration of nanoparticles is influenced by the sampling train and to what extent. For this reason, a complex measuring system with two distant sampling points was used (see Fig. 1), with one point in front of the dilution tunnel and the second point at its end.

Measurement in front of the tunnel: The first sampling place was located about 2 m behind the boiler. The measurement was performed in a tunnel with the diameter of 180 mm.

Measurement in the tunnel: The second sampling place was at the end of the diluting tunnel with a diameter of 150 mm. Due to the dilution, in the tunnel is a lower concentration of solid particles and because of the controlled output of exhaust ventilator the emissions are at a stable velocity. The velocity of the combustion gases was set within the range 5 to 6.5 m/s according to the required under-pressure and dilution. During the sampling the air velocity in the dilution tunnel was almost constant. In the dilution tunnel the concentrations of CO₂ and CO, TOC, NOₓ, SO₂, O₂ were measured as well.

![Fig. 1 Experiment – nanoparticles analysis](image-url)
Because the dilution ratio of combustion gases/air behind the boiler (Sampling point 1) and in the dilution tunnel (Sampling point 2) was not sufficient, the combustion gases were further diluted by means of the diluting device (see Fig 2). The resulting dilution factor was adjusted by the flow rate of the filtered diluting air and the flow rate from the dilution tunnel. The dilution in the dilution tunnel was set for 1.7 by using the concentration of carbon dioxide as reference value and in the dilution device the dilution ratio was 1:123 (realized on the basis of measurement of passed volumes). A spectrometer FPMS 3091 (TSI) was used for the analysis of nanoparticles distribution. The characteristic data of particles are given in the form of the mode diameter (MD) as the most frequent size of a particle population and the total number concentration (TNC) as the total amount of particles over the overall measured range. The particle distribution graphs is organized by following way: the channel width, which is the represented particle diameter (dp) range, is plotted on a logarithmic scale against the total number concentration that is calculated from the measured number of particles (dN) divided by the logarithm of channel width (dlog(dp), where dp is the mobility diameter). After ignition of the boiler and the achievement of the set output, the dilution equipment was set for the suitable dilution ratio whereby the concentration of measured nano particles was within the range of measurement of the device.

![Fig. 2 Dilution equipment](image)

The automatic boiler was tested on site. The lab infrastructure allows repeatable test conditions by use of an accurate platform scale to measure the burn cycle. The experiment lasted several hours. Samples were taken over stabilized cycles. On both sampling places a cross profile was measured – off-take of a sample of combustion gases on the sides and in the middle of the tunnel. Silicone rubber tubes were used (inside diameter 5 mm) to take the samples. Various lengths of sampling tubes were tested, as well as the influence of the length of the tube on the file concentration and distribution of particles. In addition, the influence of the switching of the worm (supply of fuel) on the change of distribution and concentration of nanoparticles was monitored.

3. RESULTS

First of all combustion gases were taken from the sampling point No. 2. On the basis of the comparison of the concentration cross profile in the dilution tunnel it was found that the concentration of nanoparticles is not constant in the cross, and gradually increased from one side to the other. This phenomenon is more significant for the sampling point No.1 which can be explained by better mixing of combustion gases with the air in the dilution tunnel. The overall concentration of nanoparticles recalculated on the standard content of the oxygen and normal conditions varies within the range 5.06x10⁵ to 6.25x10⁶ particles per cm³. The detailed allocation of combustion gases was ascertained
also at the sampling point No. 1. The total concentration of nanoparticles in combustion gases in this location varied within the range $9.13 \times 10^6$ to $1.32 \times 10^7$ particles per cm$^3$ (Tab. 1). The concentration of nanoparticles in combustion gases was significantly influenced also by the length of the silicone rubber tube. In the sampling point No.2 samples were taken by a shorter silicone rubber tube (1.5 m) (DT s1a, DT s2a, DT s3a), which was followed by the approximately three times higher loss of particles on the inner surface of the tube. Modus remained in both cases approximately the same.

<table>
<thead>
<tr>
<th>Output</th>
<th>CO</th>
<th>NOx</th>
<th>SO2</th>
<th>TOC</th>
<th>CO2</th>
<th>Total concentration (dN/dlog Dp)</th>
<th>Modus (the most frequent fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[kW]</td>
<td>[mg/m3N]</td>
<td>[mg/m3N]</td>
<td>[mg/m3N]</td>
<td>[g/m3N]</td>
<td>[#/cm3]</td>
<td>[nm]</td>
<td></td>
</tr>
<tr>
<td>BS4</td>
<td>87</td>
<td>77.95</td>
<td>0.46</td>
<td>7.11</td>
<td>0.73</td>
<td>1.37E+07</td>
<td>6 : 124</td>
</tr>
<tr>
<td>BS5</td>
<td>86</td>
<td>80.21</td>
<td>0.52</td>
<td>8.38</td>
<td>0.84</td>
<td>1.32E+07</td>
<td>6 : 143</td>
</tr>
<tr>
<td>BS6</td>
<td>85</td>
<td>76.15</td>
<td>0.57</td>
<td>7.71</td>
<td>0.84</td>
<td>9.13E+06</td>
<td>6 : 130</td>
</tr>
<tr>
<td>DTs1a</td>
<td>91</td>
<td>15.03</td>
<td>0.81</td>
<td>6.9</td>
<td>0.6</td>
<td>1.57E+07</td>
<td>6 : 93</td>
</tr>
<tr>
<td>DTs2a</td>
<td>89</td>
<td>30.85</td>
<td>0.66</td>
<td>7.34</td>
<td>0.89</td>
<td>1.75E+07</td>
<td>6 : 107</td>
</tr>
<tr>
<td>DTs3a</td>
<td>89</td>
<td>50.95</td>
<td>0.61</td>
<td>7.87</td>
<td>0.88</td>
<td>1.84E+07</td>
<td>6 : 107</td>
</tr>
<tr>
<td>DTs1</td>
<td>71</td>
<td>18.65</td>
<td>1.49</td>
<td>13.2</td>
<td>0.17</td>
<td>5.06E+06</td>
<td>6 : 102</td>
</tr>
<tr>
<td>DTs2</td>
<td>84</td>
<td>11.16</td>
<td>1.74</td>
<td>6.2</td>
<td>0.28</td>
<td>6.25E+06</td>
<td>6 : 102</td>
</tr>
<tr>
<td>DTs3</td>
<td>84</td>
<td>63.99</td>
<td>0.49</td>
<td>7.66</td>
<td>2.34</td>
<td>5.95E+06</td>
<td>6 : 100</td>
</tr>
</tbody>
</table>

In sampling point 1 (before dilution tunnel) and sampling point 2 (in the end of dilution tunnel) were measured the cross profile in 3 points (Bs4 – Bs5 and DTs1 – DTs3). Values from DTs1a – DTs3a were measured with shorter (1.5 m) tube. The histograms have two the most frequent fractions which are expressed by modus.

During measurement we met the problem of condensing of burnt gases in the silicone rubber tube on the output of the dilution tunnel. This problem will be resolved in the future. Within the analysis of the distribution of particles and the total concentration, the influence of the switching of the dosing equipment of the fuel was monitored. The dosing equipment of the fuel was switching at 15 second intervals and approximately at these intervals a change in the size of the most frequently occurring fraction was monitored (modus). During the dosing of the fuel the allocation of nanoparticles and their concentration remained similar, only the concentration of the smaller fractions significantly increased. It is not yet possible to explain the reason for this phenomenon (Fig. 3). It resulted from the histogram that the most represented nanoparticles are with the size under 6 nm and within the range 60 to 200 nm.

**Fig. 3** Histogram of nanoparticles distribution from sampling point 1 (Bs5) during switch on fuel dispenser (left) and switch off fuel dispenser (right)
4. CONCLUSIONS

It results from the experiments that during the combustion of coal in automatic boiler mainly larger nanoparticles (60 to 200 nm) are produced, but the most represented narrow fraction are nanoparticles with the size of about 6 nm. On the cross profile of the sampling places the nanoparticles are not allocated proportionally, even at the second sampling place where a sufficient dilution and mixing with air and the proportional allocation of nanoparticles was expected. It results from comparing the concentration of nanoparticles taken from two different places that at the end of the dilution tunnel the concentration of particles recalculated to CO$_2$ content is approximately half that of directly behind the boiler, i.e. particles are probably caught on the walls of the dilution tunnel or are separated by coagulation. The active supply of fuel does not influence the concentration of originating particles but the concentration of the smallest fraction under 6 nm is increased. It is necessary to consider the measured values are relative due to possible losses in the measuring and dilution route.

It was found that after passing through the dilution tunnel, there was a decrease in the measured concentrations of nanoparticles approximately by half, however, the distribution profile remained practically unchanged. Similarly, the distribution profile remained unchanged in the case of passing through a longer tube (8 m), but compared with the short tube (1.5 m) the concentration of nanoparticles decreased by three times. So, it seems that even if the existing level of measurement enables the performing of qualitative measurements (relative distribution of particles), the determination of absolute concentrations is still at most semi-quantitative only.

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LITERATURE


