

# Particle size distribution during thermal decomposition of the wood sample in oxidizing and inert atmosphere

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*Abstract:* This paper presents a laboratory procedure that combines the thermogravimetric analysis during thermal decomposition of wood sample with detailed monitoring of the size distribution of fine particles produced. Thermogravimetric analysis (TGA) allows monitoring the exact temperature influence of a small fuel sample (wood) according to the desired schedule. TGA also influences the composition of the atmosphere flowing around the sample. Two types of atmosphere on the thermal decomposition of wood sample were compared: oxidizing (21% O<sub>2</sub>) and inert (100% N<sub>2</sub>). The cool aerosol stream leaving TGA enters a Scanning Mobility Particle Sizer (SMPS) where the particle size fractions are separated. A number of particles in the particles size fractions are identified by the condensation particle counter (CPC). The parametrical study was carried out to assess the influence of oxidizing and inert atmosphere and thermal decomposition of the wood on the production and size distribution of ultrafine particles.

*Key-Words:* Particulate matter, size distribution, fine particles, combustion process

## 1 Introduction

Increasing of the particulate matter (PM) concentration level in cities stimulates an intensive research focused on better understanding of particles formation and particle behaviour during their lifetime period in urban areas. The highest concentrations of PM are generally present in the inner parts of urban areas. The main sources emitting fine particles in urban areas are automobile combustion engines and local combustion of solid fuels. Fine particles dispersed in the ground level of the atmosphere pose a significant health risk to the population. However, attention is increasingly drawn to smaller fractions, namely PM<sub>10</sub> and PM<sub>2.5</sub>. Most of the particles produced by the combustion process are PM<sub>1</sub> (particles with a diameter of less than 1 μm). These fractions have a considerable impact on the health of the population. They are easily breathable (inhalable) and can penetrate deep into the human respiratory system. In addition, compared to larger particles, they have a much greater active surface at the same weight; and therefore, have a high ability to bind other harmful substances [1, 2].

Fireplaces and biomass boilers have become the main source of fine particles in urban areas in recent years. The fine particles entrained in the flue gas stream are generated in the combustion equipment

by condensation of vapours released from the biomass during its heating. In the case of ideal combustion, these vapours are converted to products that do not condense above 100 °C. In the case of incomplete combustion, certain components are condensing in fine droplets during the cooling of the flue gas. Depending on the actual conditions, droplets drifting with flue gases may either increase in size or dry out. These processes are difficult to identify within a real biomass boiler because of the variety of processes and reactions occurring in the combustion chamber. Detailed identification of particle formation is possible only under laboratory conditions [3].

Real combustion of biomass is always associated with the formation of fine particles in the flue gas. Their production depends on the properties of the fuel (humidity, granulometry, etc.), the type of combustion equipment, but mainly it depends on temperature, reaction time and content of oxygen in the atmosphere.

Wood can be separated into three fractions: extractable, cell wall components, and ash. The extractable are, generally, present in amounts of 4% to 20% on a dry basis, consisting of materials derived from the living cell. The cell wall components, representing the bulk of wood, are principally the lignin fraction and the total

carbohydrate fraction (cellulose and hemicellulose), termed holocellulose. Lignin, the cementing agent for the cellulose fibres, is a complex polymer of phenyl propane. Cellulose is a polymer formed from d(t) glucose, while the hemicellulose polymer is composed of other hexose and pentose sugars. The cell wall fraction of most woody material contains lignin and holocellulose in the ratio of 43:57. Residues from woody plants, such as bark and sawdust, have differing compositions.

This article presents a result of laboratory research of particle production during the burning of redwood sample. The redwood belongs to the group of softwoods with composition: Ash (0,21%), Extractables (17,13%), Lignin (34,21%) and Holocellulose (48,45%) [4].

## 2 Thermal Decomposition of Wood and Particle Formation

The solid phase of woods affected by heat flux can be divided into three layers. These are: the char layer, pyrolysis layer and virgin wood. Char front is defined as the transition between the char layer and the pyrolysis layer. It is the zone where thermal degradation of wood and char formation occurs. This transition is usually considered to take place at the 300 °C isotherm, called the char-line [5]. Decomposition processes of woods under external heat flux are shown in Fig. 1.

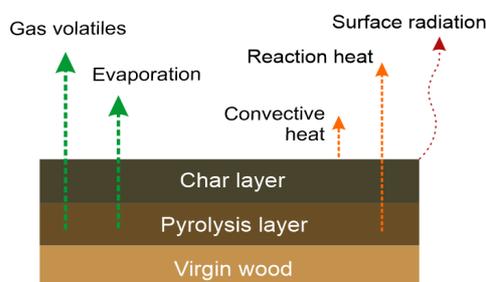


Fig.1 Decomposition processes of woods under external heat flux

When external heat flux affects the wood surface, part of heat is reflected from the surface. This radiation heat is dependent on surface emissivity of woods and ambient temperatures. Part of the heat goes straight into wood slab which can be expressed by thermal conductivity. Convective heat transfer between surrounding gases and wood surface also occurs.

In the pyrolysis layer, water evaporation occurs together with pyrolysis reactions and production of gas volatiles. Bound water changes into free water first, after absorbing heat. The water vapor is then produced by vaporization of free water. Vapor and

gas volatiles penetrate through pores and leave the wood.

### Under 100 °C

Wood may begin to lose strength depending on the type, chemical composition, humidity, type of thermal stress and the time length of exposure and temperature.

### Between 100 °C ÷ 200 °C

Over 100 °C the chemical bonds in the wood starts to break and first weight losses can be observed. Wood is being dehydrated and water vapor and other non-combustible gases, like carbon dioxide, formic acid and acetic acid, are released. With a prolonged exposure to these temperatures the wood can be oxidized with defunding oxygen a create charcoal.

### Low-temperature pyrolysis (200 °C ÷ 300 °C)

At these temperatures an intensive pyrolysis of some of the wood components takes place and a high volume of volatiles is released in the form of carbon monoxide and tars. Hemicellulose undergoes pyrolysis at the temperatures between 200 °C to 300 °C and lignin between 225 °C to 450 °C. Cellulose does not take part in the pyrolysis at these temperatures, but its decomposition can be accelerated by the presence of water, acids and oxygen. Acids are formed mostly during the pyrolysis of hemicellulose and the presence of water is result of lignin dehydration. Overall, the pyrolysis reactions are endothermic and the heat is provided by combustion of the volatiles.

### High-temperature pyrolysis (300 °C ÷ 450 °C)

At these temperatures start a quick depolymerization of cellulose and a significant release of volatiles. Generally, this process occurs between 300 °C and 350 °C. Combustion of volatiles helps to raise the temperature further. Between 370 °C and 400 °C the carbon bonds in lignin are broken. That represents exothermic reactions and these raise the temperature even further.

### Above 450 °C

Over 450 °C the release of volatiles from each wood component ends and only charcoal remains, Charcoal further oxidizes and forms carbon dioxide and water. This process continues until only ashes remain. These values are only indicative, because the water and mineral contents blur the start of the pyrolysis process.

Released volatile components have different values of partial pressure. After reaching the saturation point, the formation of a new phase begins. We call it the nucleation process. The molecules are clustered into ultrafine particles up to 0.1 µm in size.

The resulting particles can be further enhanced by coagulation mechanisms (aggregation of colloidal and macromolecular organic particles into larger aggregates), by agglomeration (bonding based on the adhesion of the surfaces), and by oxidation reactions or condensation on the particle surface [6,7].

Particles that are formed in the combustion chamber are called primary particles. Secondary particles are formed in the flue gas duct and in the atmosphere. According to volatility, the resulting organic compounds are divided into volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) [8, 9].

### 3 Experimental Procedure and Device

The laboratory procedure which was developed combines the advantages of thermogravimetric analysis with the detailed monitoring of the size distribution of produced fine particles. Thermogravimetric analysis (TGA) allows to monitor the exact temperature influence of a small fuel sample according to the desired schedule. TGA also influences the composition of the atmosphere flowing around the sample. During the test, the TGA monitors the weight of the heat-affected sample and identifies its loss. From the analysis of the development of temperature rise, it further identifies the presence of endothermic and exothermic reactions.

The measurement was carried out with utilizing the TGA device NETZCH – Jupiter F3. The base component of the STA-449 Jupiter analyser is a very precise digital weighting system with vertical design. The weighting system is connected to a shielded ceramic module (TG-module) into which the analysed samples are placed. During the measurement, the entire module is inserted into a gas-tight laboratory furnace with controlled heating rate. The result of the measurement is a TGA curve showing the weight change in dependence on the temperature of the sample.

The gaseous components released from the fuel sample during the TGA are scattered in the test atmosphere and removed from the device. Subsequent flow through the connecting pipeline cools the stream to the ambient temperature. The cool aerosol stream enters a Scanning Mobility Particle Sizer (SMPS) where the particle size fractions are separated.

Nearly every particle has some level of electric charge. Electrostatic classifier requires aerosol to achieve a steady state of charge distribution.

This is achieved by Aerosol Neutralizer device, which provides discharging and charge neutralization process. After this process, particles pass through a bipolar charger and reach equilibrium charge level on the particles. Then, aerosol flows into the electrostatic classifier (DMA) where sizing occurs (Fig. 2).

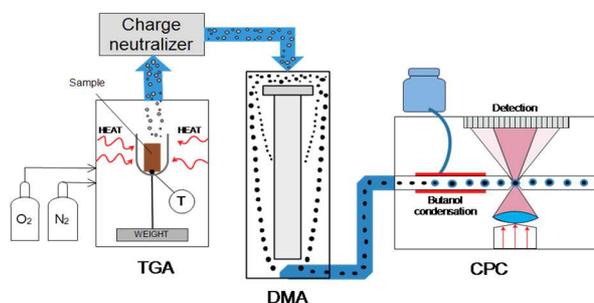


Fig.2 Scheme of the Measuring equipment and the particle flow: TGA - Thermogravimetric analysis; DMA - differential mobility analyser; CPC - Condensation Particle Counter

In a particle sizing system, the Electrostatic Classifier separates particles by size for high resolution measurements of particle size distribution. Scanning Mobility Particle Sizer (SMPS) allows classifying particles in the range from 10 to 1000 nanometres in diameter. Differential mobility analyser (DMA) selects flowing particles of specific size from a polydisperse aerosol. Particles are separated according to their electrical mobility. As a result, there is a highly monodisperse aerosol containing particles of a certain size. Monodisperse particles leaving the electrostatic classifier continue to a Condensation Particle Counter (CPC). This device measures particle number concentration. A number of particles in the particle-size fractions are identified by the condensation particle counter (CPC).

### 4 Measurement and Results

The parametrical study was carried out to assess the influence of temperature and the composition of the atmosphere on the production and size distribution of ultrafine particles during a heating of solid fuel. The samples of redwood were used as the tested material. The heating sequence started at 20 °C and the temperature rise was set to 10 °C/min. The sample was heated continuously until its temperature reached 600 °C.

Two different composition of the surrounding atmosphere was tested:

- a) oxidizing 21 % O<sub>2</sub> + 79 % N<sub>2</sub>,
- b) inert 100 % N<sub>2</sub>

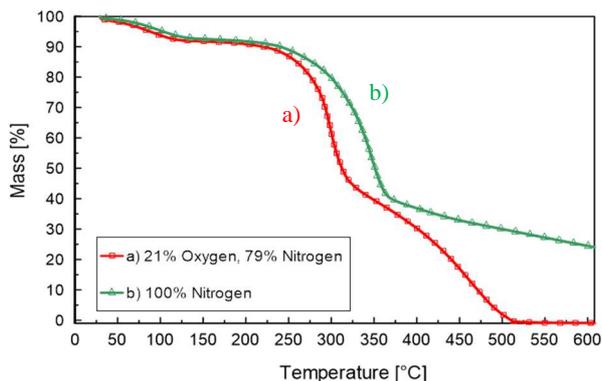


Fig.3 Thermogravimetric curves of the wood sample in oxidizing (a) and inert (b) atmosphere

Thermogravimetric curves of the wood sample in oxidizing and inert atmosphere are shown in Fig. 3. The difference in weight corresponds to the intensity dependence of the oxidation reactions. It can be assumed that the oxidation reaction ends in the products of complete combustion. Using the known elemental composition of the fuel (wood sample), it is then possible to determine the amount of CO<sub>2</sub>, H<sub>2</sub>O produced.

At 250 °C there is a noticeable acceleration of weight loss, respectively, on the onset of oxidation reactions as compared to thermal decomposition in an inert atmosphere. This intensity is significantly reduced at a temperature of 325 °C. Another increase of weight loss due to oxidation reactions occur by the temperature level of 400 °C. In the case of a sample with an oxidizing atmosphere, a complete burnout of the sample is evident. Upon thermal decomposition in nitrogen, the final sample weight was 23.75%.

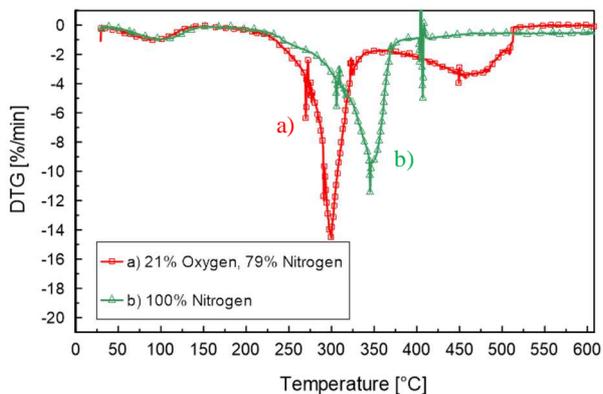


Fig.4 Derivate curve of TG signal the wood sample in oxidizing (a) and inert (b) atmosphere

Fig. 4 shows first derivatives of thermogravimetric curves for oxidation and inert atmospheres, where

individual phases of thermal decomposition can be observed.

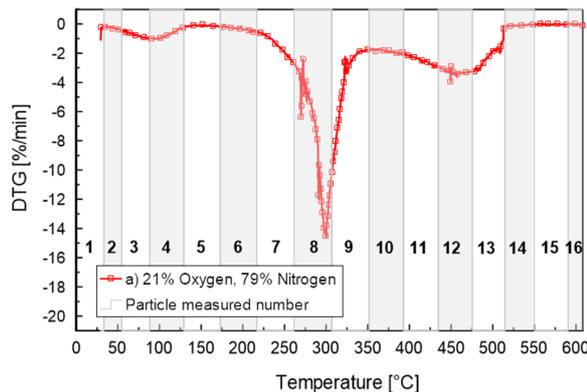


Fig.5 Derivate curve of TG signal the wood sample in oxidizing atmosphere with TSI particle measurement bands (1-16)

Based on the principle of measurement, the size concentration is identified discontinuously. The measuring cycle lasts 240 s. For this reason, particle analysis was performed by 16 continuous measurements continuously (vertical bands 1-16 in Fig.5). Using the introduced label (1-16), a detailed concentration field of particle distribution for the oxidation atmosphere (Fig. 6) is presented.

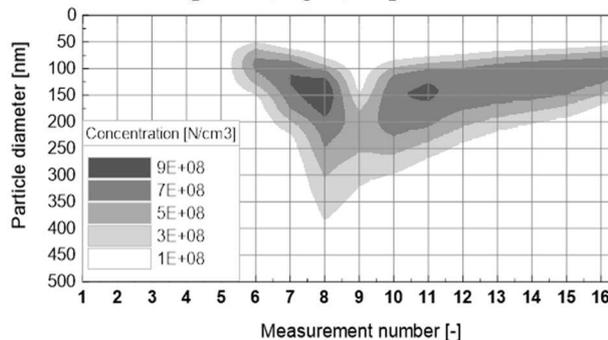


Fig.6 Particle concentration field of the wood sample in oxidizing atmosphere for the analysis bands 1-16.

The concentration field depicted in Fig. 6 present a common representation of the observed particle size distribution and concentration in the flue gas stream leaving the TGA. Fields are characterized by two maximum peak concentrations for temperatures of about 300 °C and 400 °C.

The highest concentrations are identified for particle size of 150 nm. The observed trend is the increase in particle size at temperatures considered in the interval 1-8. The opposite trend is evident in the interval 10-16.

Fig. 7 shows the curve of the first derivative of the TG signal for the thermal decomposition of the wood sample in an inert atmosphere, where

the evaluated cycles of particle analysis are indicated with vertical bands 1-16.

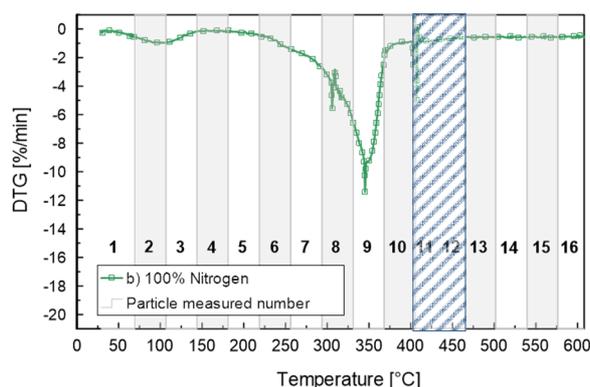


Fig.7 Derivate curve of TG signal the wood sample in inert atmosphere with TSI particle measurement bands (1-16).

When measured in an inert atmosphere, a larger particle concentration is achieved over the entire observed measurement range. The hatched area in Fig.7 and Fig.8. Identifies the time interval when the particle concentration exceeds the measuring range of the measuring apparatus and the data in that area is not available.

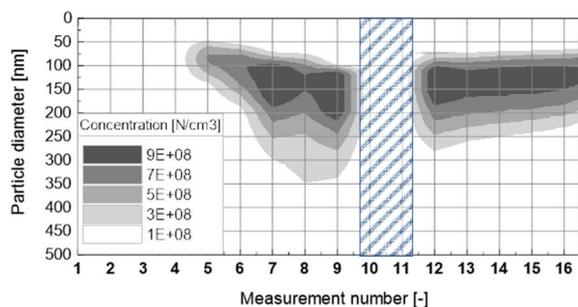


Fig.8 Particle concentration field of the wood sample in inert atmosphere for the analysis bands 1-16.

It is clear from the concentration maps that no significant peak concentrations of particle size close to 150 nm are present, and that high particle concentrations are maintained within these significant magnitude of thermal decomposition in these sizes. It is clear from the concentration maps that no significant peak concentrations of particle size close to 150 nm are present. High concentrations of particles of these sizes are maintained throughout a significant range of thermal decomposition.

However, there remains a clear trend of increasing particle size for temperatures in the interval 1-8. The opposite trend of decreasing particle size is also noticeable for the interval 12-16.

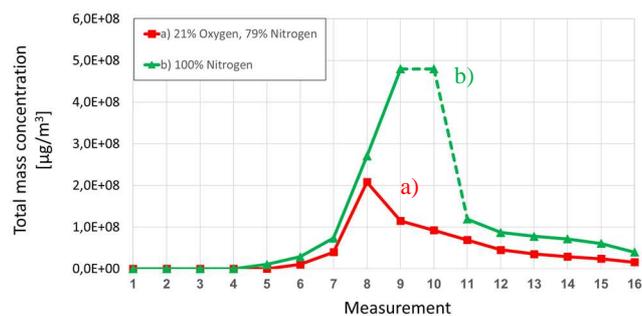


Fig.9 The mass concentration of ultrafine particles in oxidizing (a) and inert (b) atmosphere for the particle analysis bands 1-16.

The mass concentration of ultrafine particles in the observed time periods is shown in Fig. 9. The dependence significantly differs at a temperature that corresponds to the intense onset of oxidation reactions in an oxidation atmosphere. The dependence obtained from measurements performed for the inert environment (100% N<sub>2</sub>) presents the maximum possible mass concentration of the particles. The corresponding dependence is depicted in Fig. 9 by a continuous line in time periods when correct measurements were performed. The dotted line supplements the predicted course of dependence in time periods with a high particle concentration which could not be affected by the used measuring device.

From the onset of oxidation reactions in the oxygen atmosphere, there is a constant lower mass concentration of the particles in the oxygen atmosphere in the flue gas stream up to a temperature of 600 °C. The inert atmosphere over the entire measuring range of thermal decomposition exhibits higher mass concentrations. From the trend observed in the concentration fields, it is clear, that the increasing temperature in the interval 400-600 °C is a decrease in the mass concentration of PM close to the linear dependence.

## 5 Conclusion

The paper presents a successful connection of the thermogravimetric analysis of the wood samples with detailed monitoring of the size distribution of fine particles in the flue gas. From the carried-out study it is clear, that the dependence of mass concentration on thermal decomposition in oxidation and inert atmosphere differs significantly. The mass concentration of ultrafine particles significantly differs at a temperature that corresponds to the intense onset of oxidation reactions in an oxidation atmosphere. The inert atmosphere over the entire measuring range of thermal decomposition exhibits higher

mass concentrations. The size of emitted particles is very strongly related to the temperature of the wood sample and composition of the atmosphere.

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