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BIOMASS COMBUSTION OPTIMIZA-TION TO REDUCE PARTICULATE MATTER EMISSIONS

Relatore: Prof. Paolo Canu Correlatore: Gianfranco Gianfelice

Laureanda: ARIANNA LUCI

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Abstract

Nowadays it is very common to find fireplaces in our houses that allow heating or, simply, have the purpose of embellishing rooms. These equipments are usually fed by biomass. Yet, the thermal energy production derived from biomass shows some issues due to its physical characteristics, as the granulometry and the ash content. It has been observed that the combustion is generally incomplete, causing the release of harmful pollutants into the atmosphere, including particulate.

This work aims at analysing in some detail the combustion of biomass, focusing firstly on a single pellet, then moving on to several pellets. During tests, attention has been paid mostly on the particulate emission, both small and large particles, but a complete analysis of combustion is also carried out, studying the evolutions of temperature, the weight loss and the gas emission, such as CO, CO2, VOC, NO_x .

Riassunto

Al giorno d'oggi è comune trovare all'interno delle abitazioni apparecchiature per il riscaldamento o che semplicemente hanno come finalità l'abbellimento della stanza. Fino a qualche anno fa, stufe e camini venivano alimentate per lo più da combustibili fossili ma, per incoraggiare una decrescita nel loro utilizzo e nella loro conseguente dipendenza, da qualche anno si sta cercando di sostituirli con le biomasse. Tuttavia, la produzione di energia termica derivante da biomassa presenta alcune problematiche dovute alle caratteristiche fisiche di quest'ultima, come ad esempio la granulometria e la quantità di cenere presente all'interno. Si è visto che generalmente la combustione risulta essere incompleta, provocando rilascio in atmosfera di sostanze inquinanti dannose, tra le quali il particolato.

In merito a questo, il lavoro di tesi proposto cerca di analizzare nei dettagli la combustione di biomassa, concentrandosi prima su un singolo pellet per poi passare alla combustione di 2-3 pellet. Durante i test l'attenzione è rivolta soprattutto alle emissioni di particolato, sia fine che grosso, ma viene svolta anche un'analisi completa della combustione andando a studiare l'andamento della temperatura, della perdita di peso della biomassa e le emissioni dei gas principali quali CO, CO_2 , VOC.

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Introduction

Scopes and goals

The project developed in this thesis has the scope to analyse the biomass combustion in order to understand how to control it and reduce the emissions. In particular, the focus is on pellet, as biomass material, and on particulate matter that represents a considerable emission problem regarding domestic heating.

The interest in biomass as fuel is growing thanks to its nature as a renewable source and therefore to its carbon emissions neutrality. Currently, the combustion is the more traditional technology of biomass utilization, both for medium-large and small plants. However, wood-burning appliances show higher emissions than the ones with natural gas or diesel fuel of fine powders (PM₁₀, PM_{2.5}) and CO.

Biomass produces fine dust basically because of its physical characteristics: the solid form makes the combustion more difficult than the one of the other traditional liquid fuels.

From the particulate point of view, the emissions produced by biomass combustion show three different types of particles, divided according to their chemical composition: inorganic particles, carbonaceous particles (i.e. soot) and particles composed of organic matter. The proportion between these depends on the quality of combustion.

Numerous epidemiological studies [1] focus on this theme, showing a correlation between negative health effects and increased concentration of particulate matter in the ambient air. This is the reason why it is important to attempt in order to get the maximum control on the combustion and on the tool so that the biomass can burn in the optimal conditions.

In this context the present work is placed, to analyse the biomass combustion and the best conditions to reduce the particulate matter.

Thesis outline

In the first Chapter, basic on combustion, biomass and particulate matter are given, to better understand the discussion of the following chapters.

Chapter 2 analyses case studies to better understand the combustion conditions and to focus on which are the stoves functioning aspects which influence the emissions. The main factors that have to be taken in consideration are air feed, temperature combustion and the biomass chemical characteristics.

Chapter 3 describes the experimental set-up used to carry out tests presented in Chapter 5. Materials tested are pellets of type A1 that are characterized by thermogravimetric analysis in a tubular reactor. The first approach is the combustion of a single pellet, then tests with several pellets have been carried out. The particulate matter emissions have been analysed using an optical particles counter. Tests with different temperature and air feed conditions are performed.

In Chapter 4 are described validation tests for the tools used: OPC for the emissions of particulate matter and sensors for gases emission.

In Chapter 5 a discussion about the results obtained concludes this thesis work.

Chapter 1 Biomass combustion

1.1 Combustion

The combustion is a complex phenomenon involving simultaneous coupled heat and mass transfer with chemical reactions and fluid flow. In general, it is a high-temperature exothermic redox chemical reaction between a fuel which reacts with oxygen to release useful energy and presents as outputs: heat, some by-products and refuses [2]. In many cases the refuses have harmful characteristics and properties both for humans and for the environment.

In the combustion reaction, the chemical energy stored in the fuel is converted in thermal energy by oxidation: the carbon and the hydrogen contained in the biomass fuel are oxidized by the oxygen of the air (oxidizing agent) in carbon dioxide (CO_2) and water (H_2O) with heat production. Indeed, the process is much more complex and it is associated with a series of heterogeneous and homogeneous reactions. These lead to the formation of one multitude of by-products and intermediate compounds (Figure 1) [3].

 $\begin{array}{ll} \mathsf{CH}_{1.44}\mathsf{O}_{0.66} + \lambda \ 1.03 \ (\mathsf{O}_2 \ + \ 3.76 \ \mathsf{N}_2) & \rightarrow \mathsf{Intermediates} \ (\mathsf{C}, \ \mathsf{CO}, \ \mathsf{H}_2, \ \mathsf{CO}_2, \ \mathsf{C}_m\mathsf{H}_n \ \mathsf{etc.}) \\ \\ & \rightarrow \mathsf{CO}_2 + 0.72 \ \mathsf{H}_2\mathsf{O} \ \mathsf{+}(\lambda - 1) \ \mathsf{O}_2 + \lambda \ 3.87 \ \mathsf{N}_2 \ -439 \ \mathsf{kJ/kmol} \end{array}$

Figure 1 General combustion reaction. CH $_{1.44}O$ $_{0.66}$ typically represents the average composition of biomass

There are two main sources of particles from small-scale furnaces: an incomplete combustion and from volatilised ash. The domestic furnaces include uncontrolled open fireplaces as well as controlled devices, while all large-scale boilers are controlled. During batch-wise firing of wood logs, the combustion conditions vary between the different combustion phases [4]; indeed, the process of combustion can be divided in some phases depending on the increase of fuel temperature [5]:

- 1. Solid drying: the moisture is released.
- Devolatilization: the biomass liberates volatile components which constitute the 80-85% of the fuel by weight.
- 3. Combustion in gas phase: components released in gas phase are oxidized.
- 4. Char combustion.

The chemical composition of the particles emitted during combustion is closely connected to the combustion conditions and, thus, to the concentrations and size distributions, furthermore the quality of combustion is clearly affected by the type of appliance used.

1.2 Biomass

Due to continuous decrease in the amount and availability of conventional fossil fuels, it is becoming inevitable to search for new fuel sources. Biomass is not a mineral or fossil fuel, it is a biodegradable fraction of biological residue (vegetable or animal) coming from agriculture or from industrial or urban waste. Fossil fuels emit CO_2 absorbed millions of years ago, instead the biomass has a neutral CO_2 balance, because the one emitted is equalized by the one adsorbed during the biomass growth. Therefore, biomass can be considered a renewable source of energy and it is available constantly during the time and in the space, unlike the other renewable sources such as solar, photovoltaic, wind energy.

The biomass used can be divided in the following groups:

- Crops for energy purpose;
- Forest biomass;
- Residues from agricultural sector;
- Residues from zootechnic sector;
- Residues from agro-industrial sector.

Biomasses consisting of waste and residues are preferred to virgin materials, in order to avoid competition between the sector of food production and that for energy purposes.

Solid biomass, as the woody ones, are approved fuels, cheap and ecologically sustainable. It is necessary to evaluate some chemical properties for the biomass, as energy density, maximum mineral content and water content, since they influence the combustion performance. The energy density is the heat quantity that can be extract through the biomass combustion and it depends on the origin of the biomass. The water content is important too because it is inversely proportional to combustion energy yield and leads the decrease of maximum combustion temperature and the increase of the residence time useful to complete the chemical reactions. There are also some physical parameters as the melting point of the ashes, that can influence the choices of the combustion plant [6].

The main biomass fuel is wood chips that it is characterized qualitatively, following the normative EU CEN/TS 14961 of 2005, about the size and the moisture and dry matter content. The biomass used in this project is pellet. Pellet biomass fuels are compressed, homogenized and dried biomass fuels that possess several advantages during handling, storage and combustion when compared to unprocessed biomass fuels. Indeed, fuel pellets are especially well-suited for the residential biomass market, providing possibilities of more automated and optimized systems with higher combustion efficiency and less products of incomplete combustion (PIC), such as ash, smoke, CO, NO_x and SO_x [7].

Generally, pellets can be made from some different types of biomass, for example from industrial waste, food waste or agricultural residues. The most common one is wood pellets, made from compacted sawdust. Thanks to the lignin content, it is not necessary to add additives or some external chemical substances to obtain a compact product and, thanks to the pressing, the pellets' heating power is double respect to the same volume of wood.

1.2.1 Principles of biomass combustion

A combustion plant for solid biomass has to control some parameters to achieve a good quality combustion, such as:

- Oxygen content and its distribution during the reaction; this parameter influences temperatures stability, the formation of carbon monoxide, the efficiency and the production of pollutants;
- Fuel content and the way it is feed into the chamber: this is important to allow a correct ignition and to stabilize the combustion regime;
- Temperature control, that can be applied by recycling fumes, decreasing so NO_x emissions.

It is important that conditions are optimal to avoid unburnt substance, as carbon monoxide or volatile organic compounds (VOC). If we are considering biomass, other pollutants can be derived from substances that are present in it, as sulphur and nitrogen oxides, or elements as Cu, Pb, Zn, Cd.

In general, combustion by-products and pollutants are divided in ashes, solid or condensable particles (powders) and gaseous compounds. Regarding the ashes, the management is regulated by the IV part of d.lgs. 152/2006 that classifies them as "special no-hazardous waste". As regards the powders, it will be further investigated. The main gases compounds, instead, are carbon monoxide, carbon dioxide and water vapor, then there are also acid gases as nitrogen and sulphur oxides [6].

The process of biomass combustion is complex because it involves many chemical-physical aspects and phenomena, to convert to heat the chemical energy contained in the fuel. Usually,

in optimal condition, this happens through complete oxidation reaction which lead to the expansion of heat and to water and carbon dioxide formation.

The devices feed with biomass are in general used to produce heat in small and medium size plants, but in some case also to produce hot water for hygienic and sanitary uses. The configuration and technical solution are not unique, they can vary for each type of plants. For example, the modern boilers are designed to obtain the combustion condition in several stages: there is the first zone, the gasification one, in which it occurs the first phase of oxidation with lower air respect to the stoichiometric amount. The fuel gas is developed and burnt in the secondary chamber, in which it is feed the secondary air to complete the reactions of oxidation.

The technology choice depends on the power of the plant and on the availability and the shape of the fuel. Ordinarily, the biomass devices work in better conditions only if there is a certain load and with high temperature.

The thermochemical processes that use biomass to produce energy are combustion, gasification and pyrolysis. Combustion is already analysed. Gasification is a partial oxidation with high temperature (about 800°C), which leads to the formation of a fuel gas by air, oxygen or water vapor with a sub-stoichiometric amount. Using oxygen, the product is a mixture of CO and H₂, called syngas, with a good thermal power. Pyrolysis, instead, is a thermal degradation process without oxidizing agents and involves the cracking phase, that is the splitting of chemical bounds. This process leads to the formation of a solid fraction as char, inert and ashes, liquid fraction as tar, and gaseous fraction formed by CO, H₂, CO₂, H₂O, CH₄.

1.2.2 Emissions

• Carbon monoxide: it is formed when the combustion air is lower than the stoichiometric value. The incomplete oxidation of carbon occurs according to the following reaction (exothermic), if the mechanism of the reaction is fast:

$$C + \frac{1}{2}O_2 \to CO$$

If CO has a residence time adequate to react with the oxygen, it produces CO_2 (endothermic reaction):

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

After that, the combustion goes on through the combustion bed, the oxygen is lower and the carbon dioxide is reduced, following the endothermic reaction:

$$CO_2 + C \rightarrow 2CO$$

The final concentration of CO becomes stable when the temperature decreases to a level in which the combustion velocity is negligible, so the equilibrium process stops (about 600-700 $^{\circ}$ C). If the concentration of air is in excess, the combustion chamber cools down decreasing the optimal temperature for the oxidation reaction and there is an increase in the CO concentration.

• Nitrogen oxides: nitric oxide (NO) and nitrogen dioxide (NO₂) are the two most important nitrogen oxide air pollutants, the second one is the more toxic and irritating compound. Nitric oxide is a principal by-products of combustion processes, arising from the high-temperature reaction between N₂ and O₂ in the combustion air, that occurs through two reactions, and from the oxidation of organically bound nitrogen. The two reaction are (Zeldovich mechanism):

$$N_2 + 0 \rightarrow NO + N$$

 $N + O_2 \rightarrow NO + O$

The first one has a high activation energy, due to the need to break the strong N₂ bound, and because of that it is the rate-limiting step to produce NO. It can say that the determining factors for the nitrogen oxides production are the concentration of nitrogen in the fuel, the oxygen concentration and the flame temperature. Instead, the fossil fuels do not present nitrogen in their composition and the NO_x formed depending on the reaction between nitrogen and oxygen that it is in the air for high temperature (about 1300° C).

- Sulphur oxides: biomass contain a high quantity of sulphur that it causes the formation of SO_x during the combustion. When the temperature goes down, SO₂ forms sulphates and it condenses on heat exchangers and on volatile ash particles. A huge amount of sulphur present in the biomass sticks on the fly ashes, while the remaining part it is issued in the chimney through the gases in the form of sulphur oxides.
- Total ashes.

1.2.3 Particulate Matter

Relevant attention must be paid to the issue of particulate matter (PM). The emissions of particulate air pollution are presently an intensely debated issue from the perspective of both global warming and human health. The emissions of carbonaceous aerosols are especially considered as an important contributor to the heating of the global atmosphere. Combustion process in the urban environment are major anthropogenic sources of fine PM pollution, and the present residential wood-log combustion is a significant reason for the deterioration of ambient air quality in residential areas.

Particulate matter refers to everything emitted in the form of a condensed, liquid or solid, phase. Its subdivision can be done based on the process that generates it or based on the particles dimension. The first approach subdivides particulate matter in primary, if it is formed by particles emitted as such and it represents principally the coarse fraction, or secondary, if it is originated by chemical-physical phenomena involving the transformation into particulate matter of substances emitted in gaseous form.

The second approach, instead, classifies PM in coarse mode (>1 μ m) and in fine mode (<1 μ m) particles. Fine-mode particles are formed by nucleation and/or condensation process of volatilized gas phase precursors, which subsequently coagulate and form agglomerates. The coarse mode can consist of a wide variety of mechanically generated particles, which are normally aggregates ashes that have been entrained with the flue gases from the fuel bed during combustion. Total suspended particulate (TSP) represents all particles present as well as PM₁, PM_{2.5}, PM₁₀, which involve the particle fractions with a diameter <10, 2.5, 1 μ m [8].

Coarse mode particles mainly come from mechanical processes such as abrasion and particle dispersion by traffic, industrial and agricultural processes, volcanic eruption and desert storms. Fine mode particles mainly originate from traffic, industry, agriculture and residential heating. The concentrations of organic carbon and soot increase with decreasing burnout quality and, consequently, the higher PM₁ emissions at low burnout quality are attributed to the formation of carbonaceous aerosols. The most efficient way to reduce health risks caused by residential biomass combustion is to optimise burnout, decreasing emission factor for PM₁, having lower concentrations of carbonaceous compounds in the PM emissions and less hazardous particles. The modern residential biomass combustion system, compared with the old ones, shows a significant improvement regarding this issue

PM emissions can be influenced by some factors, as the type of fuel and its moisture. Higher emissions of PM occur in incomplete combustion phases, in which the emission of matrix PM organic is very high, related to the presence of monoxide carbon and hydrocarbon. Indeed, incomplete combustion products have three negative effects: energy loss, impact on human health and impact on environmental pollution.

Particulate matter can be classified in three different categories: inorganic particulate, soot and semi volatile organic compounds (VOC). The inorganic part is formed for the most part by salt, as KCl, NaCl, K₂SO₄, and it is the prevalent component of the particulate emitted. Soot is the emission typical for bad combustion condition with high temperature and it is consisting of

elemental carbon in graphitic form (black carbon). VOC, instead, are caused by condition of insufficient temperature (during start-up and shut-down phase) in which the volatilized organic substance is not completely combusted [9].

1.3. Lockdown effect on PM10 emissions, during COVID-19 emergency. [10]

During the months of this project, there was sanitary emergency caused by worldwide spread of the virus COVID-19. Most people could not go out because of the lock down imposed by the government, therefore especially the traffic has decreased significantly. The quarantine months allowed to analyze the air pollution in an unusual situation, with more attention on the city of Padua, and the focus was on the PM₁₀ emissions.

In general, we would expect a decrease on the emissions due to the significant reduction in traffic, instead the data show a similar trend to that of past years in the same period. This is because, how it can be observed in Figure 2, the sector that has the greatest impact on emissions is the no-industrial combustion, i.e. home heating, with 10379 t/year.



The measures of PM_{10} follow the reference technical standard UNI EN 12341:2014, that is a reference gravimetric method to determine the mass concentration of PM_{10} suspended particulates. This method is based on the collection of the PM_{10} fraction on a special filter and subsequent determination of its mass by gravimetric way.

The determination of fine particulate in the atmosphere is executed by samplers or analyzers. The first one consists of a pump that sucks in the ambient air through a sampling head, the geometry of which has been internationally regulated and is able to select the powders with an aerodynamic diameter of less than 10 μ m, with an efficiency of 50%. The particulate component selected by the head is then passed through a filter membrane of suitable porosity and made up of different materials (quartz, glass fiber, Teflon, cellulose esters, etc.), depending on the type of analysis required on the filter. The membrane is then weighed in the laboratory and by difference with the tare (white filter) there is the mass of the particulates. The sampler also contains a volumetric meter capable of recording the volume of sucked air, corrected continuously by various internal and external temperature and pressure sensors, to bring it back to environmental conditions. From the knowledge of the volume of air sampled and the mass of the particulates, the concentration of PM₁₀ in μ g / m³ is calculated.

About the analyzers, like samplers, they record a volume of air passed through a filter membrane. However, they are also able to determine the mass of the particulates, using the principle of attenuation of the beta rays emitted by a small radioactive source. These analyzers can have a sampling system based on single filters (such as samplers) or have a tape that runs at selectable and regular time intervals, on whose sections the particulate is deposited. By combining the volume and mass data, these instruments directly provide the PM₁₀ concentration value.

March and April were the months in which there was the lock down, so it was analyzed this period comparing with the same months of the year 2019. Trends of 2019 is showed in Figure 3, together with temperature and humidity trends.



Figure 3 Trend of PM10 in March and April 2019

It is already possible to note from these two graphs the influence of weather conditions, in particular of humidity. The trend of this factor and of PM_{10} emissions is similar, an increase of humidity value may cause an increase of emissions.



In Figure 4 it is showed the PM₁₀ trends during March and April of this year.

Figure 4 Trend of PM10 in March and April 2020

Natural sources also contribute to the emission of fine particles, including for example deserts with their sand and volcanoes. In fact, at the end of March 2020 it can see a peak that is linked to advection phenomenon of desert dust from Caspian Sea, due to strong winds from the eastern quadrants, and an accumulation episode between 7 and 14 of March.

As it possible to observe in Figure 5, the daily concentration of PM_{10} in March 2020 shows a slight decrease compared to the average over the years 2016-2019.



Figure 5 Trends of PM10 in March 2020 comparing with the average of 2016-2019

As already mentioned, the road traffic is just one of the sources of particulate matter. The main one is the domestic heating and during the lockdown the emissions deriving from this source have not decreased, on the contrary, they could be increased because of the longer stay of the population in their homes following the measured issued. Therefore, the reduction of particulate concentrations determined by the stop of road traffic, may have been offset by the increase in the use of home heating.

So, it can be concluded for the PM_{10} emissions, of which the main source is biomass combustion, the effect of the lockdown is negligible.

Chapter 2

State of art of biomass combustion

Residential wood combustion (RWC) has claimed to be a major source of fine particle mass emissions, particulate polyaromatic hydrocarbons (PAHs) and gaseous pollutants such as VOCs. Poor operational practices increase clearly fine particle emissions, so the use of smallscale appliances has the advantage that is easier to improve the combustion technology and with that to decrease emissions. The chemical composition of the particles emitted during domestic combustion is closely connected to the combustion conditions, and thus to the concentrations and size distributions.

The combustion conditions are affected by the combustion temperature, the mixing in the combustion chamber and the level of excess air. This last parameter seems to affect the number concentration of particle emitted. These factors are strictly correlated, indeed good mixing reduces the amount of air needed, providing lower excess air ratios and higher combustion temperature. On the contrary, inadequate mixing in the combustion chamber may lead to either high emissions of incomplete combustion or low combustion temperatures due to high excess air ratios.

The conditions required for complete combustion, assuming air to be the oxidizing media, can be affected by:

- Supply of air;
- High temperature for chemical reaction kinetics;
- Long residence time at high temperature;
- Mixing (turbulence) of fuel components and air.

In almost all practical combustion situations, these conditions are not simultaneously performed, and products of incomplete combustion are formed as solid or gaseous by-products. These products can be pyrolysis products, VOC, polycyclic aromatic hydrocarbons and soot particles.

Many studies have been done to compare different appliances, with different technology, to analyse the better conditions.

The studies [12] [13] show the positive effect of supplying a secondary air, which became an established technique for modern wood combustion appliances.



Figure 6 Schematic illustration of Modern (MMH) and Conventional Masonry Heater (CMH). 1, Primary air supply; 2, Window flushing air supply; 3, Secondary air supply; A, Upper combustion chamber; B, Secondary combustion zone; C, Flue gas ducts; D, Secondary air flow between ceramic plates; E, Primary combustion zone; F, Rift grate; G, Ash box; H, Flue gas exhaust to chimney (behind the heater) [12].

The Figure 6 illustrates the different two types of heaters analysed in [12]: the one on the left is a modern masonry heater and the on the left is a conventional masonry heaters. The MMH has a secondary air preheated in the interstitial space of the wall element before the supply into the combustion chamber and it is distributed to envelop the fuel batch through the panels with small rifts in the firebox wall. The air supplied as secondary air is about 45% and it generate a secondary combustion zone.

In these studies, gas emissions are continuously measured by a gas analysers system and the sample is taken from the stack gas through an insulated and externally heated (180° C) line. Usually these analysers are for carbon monoxide (CO), carbon dioxide (CO₂) and oxygen (O₂).

The particle number emissions, the number size distributions and the particle mass size distributions are measured using an impactor and a particle sizer. While PM samples are collected on membrane filters for gravimetric and elemental analyses; a cascade impactor is used to remove particles with different aerodynamic diameter. A mass spectrometry is used to perform elemental analyses. Thermocouples are used to monitor the temperature of the flue gas, particle sample and laboratory room air.

Analysing the study [12], the feed is a birch wood, it is the same for both appliances and it is divided into three equal batches. The experiments are done also with different quantity of total mass.

The results are, as expected, affected by the combustion technology: the emissions in modern appliances are lower, indeed the reduction of CO is between 33% and 81% depending on the total mass fed. The amount of volatile organic compounds is the one most influenced by the air staging, for CMH the VOC emission is 332 mg MJ⁻¹, instead for MMH it is only 82 mg MJ⁻¹.

An important observation can be done about the three different batches: it is relevant that gaseous emissions increased from batch to batch without air staging whereas they decrease from batch to batch with the new technology appliances. This is because the air staging affected particularly the emissions during devolatilization of fuel.

About PM emissions, PM_1 is analysed and it is observed that decreases using modern technology appliances. Considering the whole combustion period, the reduction is between 21% and 53%. Also in this case the emission is the highest during the first batch, so it should take care with the operation during this phase.

These analyses are reported in Figure 7 and Table 1:



Figure 7 Average fine particle mass (PM1), elemental carbon (i.e. soot, EC) organic carbon (OC) and fine ash emissions

Table 1 Comparable emission factors of total suspended particles (TSP), fine particle mass (PM1), particle composition, and gaseous emissions (mg MJL1) and relation of TSP/PM1 during combustion of second batch. OC, organic carbon; EC, elemental carbon; Fine as h, sum of anions and cations analysed; CO, carbon monoxide; OGC, organic gaseous substances.

	TSP	PM ₁	OC	EC	Fine ash	CO	OGC	TSP/PM ₁
1 tnCMH	15	62	48	15	1.2	1880	450	0.24
2.7 tnCMH	20	89	32	47	2.8	5260	420	0.23
1 tnMMH	26	39	15	25	3.2	720	92	0.65
2.7 tnMMH	10	32	10	18	3.0	490	69	0.31
1.2 tnMMH	18	46	22	18	1.4	1590	360	0.39
1.85 tnMMH	21	43	13	30	1.7	640	66	0.49
1 tnMMH2	33	37	9	23	2.5	630	81	0.88

Generally, it can be observed that gas and particle emissions are reduced in modern appliance, mostly the organic ones.

To confirm this study, another analysis has been done [13].

In this case a modern appliance is used for three different fuels: birch, beech and spruce wood. It has a massive soap stone for slow heat release, an upright enclosed firebox, where the secondary air is supplied in the upper combustion chamber, and a double glass window door. The secondary air is to generate a secondary combustion zone. The total feed is divided in six batches and every 35 minutes one batch is put in the combustion chamber, with the residues of the previous one. Subsequent to the sixth batch, remaining ember is stoked and the secondary air supply is blocked.

This appliance is compared with an automatically fired top-feed pellet boiler, that works in continuous with a nominal power of 25 kW. The pellet boiler was operated with commercial softwood pellets under stable conditions over 4 h and connected to heat exchanger. Those boilers are usually connected to a reservoir of water for warm water supply and therefore have to constantly produce heat in contrast to pellet stoves.

In this study the PM analysed are the $PM_{2.5}$ using a filter. The emitted aerosol is iso-kinetically sampled from the stack, diluted by using a porous-tube/ejector dilutor and cooled to room temperature to enable condensation of semi-volatile species. Then, particles are segregated to an aerodynamic diameter smaller than 2.5 μ m and iso-kinetically sampled on quartz fibre filters. The analysis of $PM_{2.5}$ are carried out by mass spectrometric techniques.

Comparing the logwood combustions in masonry heaters and the pellet in boiler, the emission of organic carbon and elemental carbon are higher in the first type of technology. Generally, carbonaceous particulate emissions are substantially lower compared to wood combustion appliances without secondary air.

About results, in the pellet boiler, which has a more controlled and continuous combustion, presents about one order of magnitude lower emissions of CO and VOC. Inorganic emissions are affected by the content of the respective element in the fuel, the fuel bed temperature, the volatility of the element and concentrations of possible binding partners. Birch wood and pellet combustion show the highest emissions of alkali, alkaline earth and transient metals.

Alkali and alkaline earth metals, in combination with other fuel elements such as silica and sulphur, and facilitated by the presence of chlorine, are responsible for many undesirable reactions in combustion appliance.

Figure 8 shows the mass fractions of alkali compounds, found in a pellet combustion.



Figure 8 Mass fractions of alkali compounds in a particle fraction from combustion of wood pellets in the pellet.

Mechanism of alkali release is explained in [14]:

- 1. For woody fuel with relatively low alkali and chlorine contents, alkali is primarily released through vaporisation or decomposition of alkali sulphate.
- 2. During combustion of fuel with high concentration of alkali and chlorine, alkali chlorides are the primary species released.
- 3. For fuels with high concentration of alkali and low chlorine content, most of the alkali leaves the fuel as alkali hydroxide.

Adding steam to the combustion environment shifted the release of alkali from alkali chloride to alkali hydroxide.

The chlorine and sulphur content in the fuel may influence particle formation. The chlorine increases volatilization of alkali metals and their enrichment in the fly ash.

The behaviour of the alkali elements is important for the ash transformation processes and formation of fine particles during combustion. Therefore, alkali elements are analysed in different articles, as in [15], in which six different typical pellet fuels are combusted in three different commercial pellet burners with nominal heat outputs of 10-15 kW installed in a reference boiler. The behaviour of those elements is of vital importance for particle formation and characteristics. Sodium and potassium are captured to a varying degree in the bottom ash as silicates and/or salt mixtures, while the remainder volatilizes and condenses as fine particles. The degree of volatilization for these elements determines the emissions of inorganic fine PM.



Figure 9 Chemical equilibrium diagram during cooling of the volatilized potassium calculated for stored sawdust.

The Figure 9 shows the theoretical distribution of the volatilized potassium in a range of temperature between 50 °C and 950 °C. The main consideration is about KCl, which is the dominant inorganic phase with a homogenous condensation gas-to-particle when temperature is around 600 °C, together with K_2SO_4 .

An important factor that influences the emissions is the type of fuels and in this case the type of wood used. Each wood has a different ash content, which influences the combustion conditions. With higher fuel ash content, the air/fuel ratios are higher and the fire chamber outlet temperatures are lower, indicating a slower combustion process for high ash content fuels.

These analyses are observed in [16] and the properties of the fuels used in this study are showed in Table 2.

pellet fuel	commercial	birch bark	birch stem	spruce bark	spruce stem	alder bark	alder stem	pine bark	pine stem	willow	willow
moisture (%)	5.9	6.1	7.0	6.8	5.8	5.4	3.4	6.9	5.8	6.7	7.5
ash (%)	0.3	1.5	0.4	4.0	0.5	3.0	0.5	1.6	0.4	3.9	0.6
LHV (MJ/kg)	17.7	23.6	16.9	17.8	17.5	19.8	17.6	18.2	17.6	17.9	17.1
Na	< 5.6	20.2	112	8.5	< 5.4	< 5.3	< 5.3	8.1	< 5.4	76.6	44.2
Mg	164	426	171	704	228	582	208	464	267	727	183
P	49.1	459	110	463	170	577	165	375	232	1200	396
S	52.7	342	81.5	393	117	567	167	309	135	891	169
CI	41.2	300	199	213	28.7	97.7	41.0	82.6	50.8	81.9	43.3
K	409	1250	626	2025	606	2695	986	1580	661	3875	1245
Ca	752	3900	758	13 500	829	7590	1115	4340	792	11 700	1110
Zn	9.32	127	18.0	143	12.3	103	24.6	25.8	10.1	211	17.3
Cd	0.13	0.21	0.20	< 0.1	< 0.1	< 0.1	< 0.1	0.27	< 0.1	3.88	1.04

Table 2	Properties	of the	fuels	used
---------	------------	--------	-------	------

The PM and CO concentrations also are correlated linearly with the total ash content of the fuel (showed in Figure 10 for PM concentration).

nat final



Figure 10 PM1.0 concentration as a function of the fuel ash content.

The trend is the same for CO even if the temperature remains constant, so CO emissions are fuel-dependent and temperature-dependent. Indeed, if the chamber temperature is low, the CO emissions are higher, as showed in Figure 11.



Figure 11 CO and O2 concentrations as a function of the fire chamber

To conclude it can be said that in general all the emission values increase with the increase of the fuel ash content. This is because of the increase of inorganic matter release and of incomplete combustion. Moreover, the major part of the fine-particle emissions consists of fly ash, independent of the fuel wood species used.

As it is showed, PM emissions are different depending on the combustion condition, however, in general, fine PM is mainly composed of organic matter, elemental carbon (as soot) and fine ash, which is inorganic compounds. The organic matter and the soot result from incomplete combustion while the fine ash particles result from the inorganic material in the fuel ashes. Figure 12 describes the physicochemical properties of these three classes of particulate.

	Spherical organic carbon particles	Soot (elemental carbon aggregates)	Inorganic ash particles
Schematic			
drawing		₩¥	•
Diameter measured by electron microscopy*	50-600 nm	20-50 nm - ``	50-125 nm ¹
Mobility diameter	100-300 nm (50-300 nm (50-125 nm
Internal turbostratic microstructure	No **	Yes / No for a la	No
Solubility (H ₂ O)	Depends on ageing	Insoluble	Soluble
Main chemical characteristic	Organic carbon ((Most abundant organic compounds: metoxyphenols and monosaccaride anhydrides)	Elemental carbon with variable amounts of organics condensed on the surface (Most abundant organic compounds: hydrocarbons and polycyclic aromatic hydrocarbons)	Alkali salts (mainly KCl and K ₂ SO ₄ with small amounts of trace elements (e.g. Zn))
Combustion conditions	Low-temperature, incomplete combustion	High-temperature, incomplete combustion	High-temperature, complete combustion • •
Possible sources	Air starved combustion or start-up phase of batch wise combustion in conventional stoves, open fireplaces	Combustion in conventional stoves, open fireplaces, boilers for wood, wood chips and pellets	Combustion in pellets stoves, boilers for wood, wood chips and pellets

Figure 12 The physicochemical characteristics of the three classes of wood combustion particles. [9]

In real combustion situations, especially during transient cycles, the particle classes may coexist and interact. Since the combustion conditions in an appliance change during a burn cycle, the emissions contain several of the defined particle classes. The formation of these particles is illustrated clearly in the scheme in Figure 13, that shows the basic steps during thermal conversion of the fuel and the formation of different by-products:



Figure 13 Schematic illustration of the different stages during combustion of a biomass fuel particle. [17]

Previously it is analysed the correlation between PM emissions and the amount of ash in the fuel, but some studies show that this correlation is stronger with the *sooting* tendency of the

fuel. This tendency is a measurement of the incipient soot particle formation rate: the higher is its value, the easier is the soot formation from the considered hydrocarbon. Soot is a carbonaceous solid produced in pyrolysis and combustion systems when conditions are such as to allow gas-phase condensation reactions of the fuel and its decomposition products. Usually, during biomass combustion soot particles occurred in two forms: as individual particles that can join in short chains or as branched clusters of these chains (aggregates). It appears possible that the higher temperatures stimulated the sooting tendency, by intensifying biomass pyrolysis and the rate of conversion of the gas precursors to soot.



Figure 14 Influence of maximum combustion temperature on soot formation. [18]

The temperature affects:

- pre-particle chemistry responsible for the formation of incipient soot particles: the lower the temperature, the lower the particle number density;
- soot surface-mass growth mechanism during biomass combustion: the higher the temperature, the higher the soot mass concentration.

For large emissions of soot and other hydrocarbons, the colour of the filter is either black or black-brown. After heating the filters (about 550 °C) in an oxygen rich atmosphere, the colour of the filters changed to white, indicating that the major weight loss of this heating step comes from oxidation of organic compounds and soot. Soot and hydrocarbons emissions are affected by some physical parameters as residence time, temperature and turbulence in the combustion chamber: to ensure a complete oxidation of soot and hydrocarbons are necessary high temperatures for more time with good mixing between fuel and air [19].

The purpose of [20] is to analyse the emission of PM from a domestic pellet-fired boiler, for different boiler thermal inputs. The pellets are manually loaded into a hopper with a capacity

of 45 kg and are fed to the burner through a screw feeder. The consumption rate of pellets is controlled and measured by a weighbridge located under the boiler.

The instrumentations used for analysis are a low pressure three-stage cascade impactor to quantify PM size fractions, a total filter holder for the total mass concentration, analytical instrumentation to measure flue-gas concentrations of oxygen, carbon monoxide and dioxide, nitrogen oxides and hydrocarbons and a SEM (scanning electron microscope) to characterize PM. The impactor is covered by a heating jacket to avoid condensation and it can collect three particulate sizes during each sampling:

- PM with diameters above 10 µm;
- PM with diameters between 2.5 µm and 10 µm;
- PM with diameter below 2.5 µm.

PM is then collected on quartz microfiber filters. After each test, the filters are dried to eliminate moisture and weighted to determine the quantity of PM captured. The morphology of the PM is, subsequently, examined in a SEM.

The analysis carried out show a similar trend about PM and CO emissions (Figure 15). The maximum CO emissions coincides with the maximum PM mass concentration and their evolutions with the thermal input are rather similar. So, CO emissions can be an indicator of the performance regarding the PM emissions. In this case NO_x emissions are very low in all cases.



Figure 15 PM, NOx and CO emissions as a function of the boiler thermal input.

Considering the size fraction of PM emissions, it is showed in Figure 16 that the quantity of PM is relevant for diameters lower than $2.5 \,\mu m$ and higher than $10 \,\mu m$.



Figure 16 Size fraction PM emissions as a function of the boiler thermal input.

This trend is observed also in [21], in which there is a comparison between two similar stoves with different load. It is show that the PM is in all cases dominated by fine particles and the fraction of coarse PM is higher during low load compared to high load.

Going back to the previous article, the SEM analysis identify three different structures of PM:

- 1. Ultra-fine particles, with diameter lower than $10 \,\mu m$;
- 2. Sub-micrometer and micrometer sized particles/agglomerates;
- 3. Isolated spherical and irregularly shaped large particles.

These structures are correlated with the size fraction of PM emissions, indeed particles with a diameter lower than 2.5 μ m include sub-micrometer sized particles/agglomerates and the first structure type; fraction between 2.5 μ m and 10 μ m comprises micrometer sized particles/ag-glomerates and some particles with the third structure type; above 10 μ m the only structure observed is the third one.

The elemental composition of ultra-fine particle is showed in Figure 17 and it can be observed that this structure is composed mainly of O, K, Cl, Na and S.



Figure 17 Elemental composition of ultra-fine particles collected on the quartz microfiber filters.

In [22] the origin of these ultra-fine particles is after the soot formation process, when the temperature decreases because of condensation of alkali sulphate and alkali chloride vapours.

Instead the main elemental of sub-micrometer sized particles/agglomerates are C, O, Ca, Mg, K and P (showed in Figure 18) and, because of the huge amount of carbon presents in it, they are produced from soot.



Figure 18 Elemental composition of sub-micrometer sized particles/agglomerates collected on the quartz microfiber filters.

The isolated spherical and irregularly shaped large particles, instead, are released from the fuel bed during combustion and they consist mostly of carbon and oxygen, with minor amount of Ca and Mg.

This consideration about elemental composition of PM emissions are the same also in [15], introduced previously. The fuels are fresh and stored (for six months) material from softwood sawdust (S0/S6), logging residues (L0/L6) and bark (B0/B6).



Figure 19 Elemental composition of the fine PM for the different fuels combusted.

The trend of elemental composition of the fine PM is the same of the one observed in the previously analysis and it is similar for each burner used. The mainly elements are carbon, that can be derived from unburned material or carbonates as alkali carbon, oxygen from organic material or from inorganic compounds, potassium, sodium, sulphur, chlorine and zinc. As in Figure 17, for fine particles potassium and chloride are the dominating elements. In [21] too, the fine inorganic PM emissions are dominated by potassium, sulphur and chlorine in the form of K_2SO_4 , $K_3Na(SO_4)_2$ and KCl.

Developments

Considering what has been analysed in the literature, a targeted experimental campaign has been designed to obtain reliable correlations between emissions and operating conditions. In particular, the focus is on the influences of air feed and temperature reactor on emissions, especially on particulate matter emissions.

Chapter 3 Experimental methods

To carry out the experimental campaign, a series of tests were produced at the K-INNLab Laboratory at the University of Padua. In this chapter, analytical instruments and experimental set-up are presented.

The tests are performed in a lab-scale flow reactor.

3.1. Macro-TGA applied on flow reactor

Thermogravimetric analysis (TGA) is an analytical technique used to determine the material's thermal stability and its fraction of volatile components by monitoring the weight change which occurs as a sample is heated at a constant rate. This measurement provides information about physical phenomena, such as phase transitions, absorption and desorption; as well as chemical phenomena including thermal decomposition, and solid-gas reactions. Results can be plotted as a thermogram where x-axis represents or the temperature or the time depending on the speed of change. In general, the thermo-balance allows to analyze quantities of material in the order of milligrams.

It has been used this type of method with a balance of grams' order to allow analysis of a greater mass.

The tests performed are listed in Table 3 and the main operating conditions are reported.

# test	Number of pellets	Pellet weight	Temperature	Air flow
		[g]	[°C]	[L/min]
1	1	0.76	450	1
2	1	0.75	450	2
3	1	0.72	450	5
4	1	0.81	450	10
5	1	0.73	550	1
6	1	0.82	550	2
7	1	0.72	550	5
8	1	0.74	550	10
9	3	2.03	450	2
10	3	2.20	450	5

Table 3 Tests performed with different operational conditions

11	2 (vertical)	1.35	550	5
12	2 (horizontal)	1.22	550	5

Each test was repeated 3 times to verify reproducibility.

3.1.1 Single pellet

The set-up used for tests with a single pellet (Figure 20) is a tubular reactor, with an inner diameter of 40 mm and height 360 mm. External heating is provided close wall reactor. The biomass is settled in the middle of the reactor and it is connected to a balance with a dynamometer, in order to control the weight loss. Furthermore, a multipoint thermocouple is inserted from the bottom along the reactor wall to analyze the temperature profile inside the tool with five equidistant point (the colored dots in Figure 20). A second thermocouple is located inside the biomass to measure its temperature during the combustion reaction. The air flow is measured with a flowmeter and then it is fed in the reactor from the bottom. Two probes suck the gases produced from the top of the reactor, one connected to the sensor for particulate and the other to gas sensors.



Figure 20 Set-up used for single pellet

During all these tests, the software CX-Thermo is connected to a temperature controller thermoregulator used to apply and control the heat on the tool. Two thermocouples are presented on the tubular reactor and connected to the software. Each test is carried out with the reactor pre-heated, so the biomass is inserted when the reactor has achieved the set-point temperature applied with the software.

The weight is monitored using the balance RADWAG (model PS 2100.R2) which is connected to the PC. It has two decimal places, so it is not completely accurate when the biomass weight loss is almost total. The balance program acquires data continuously and it returns the values

recorded by the instrument associating them with a time counter expressed as progressive seconds.

Tests are carried out using a single pellet per time, changing the reactor set point and the air feed.

3.1.2 Several pellets

Experiments with several pellets are carried out. The set-up used is the same of one pellet, but a small basket with pellets is connected to the thermocouple (Figure 21). This one is no longer inserted inside the biomass; it is placed in the center of the pellets bed.



Figure 21 Set-up used for several pellets (vertical and horizontal)

The procedure is the same applied in the case of a single pellet. A flux of air is fed from the bottom, the reactor is pre-heated with a set-point value of temperature and on the top there are two probes to suck the emissions: one connected to the gas sensors, the other one to collect the particulate matter that are analysed from the optical particle counter. A multipoint thermocouple is inserted from the bottom to control the temperature inside the reactor, a single point thermo-couple is inserted from the top and linked to the balance with a dynamometer. Pellets are introduced in a basket connects to the thermocouple, so it is able to read during the time the temperature of the pellets bed.

3.2. Pellet used

The biomass is a single pellet and the analysis have been carried out for pellet of class A1. Pellets of type A1 has an excellent quality, instead other types of pellet as A2 have a medium quality in fact the ash concentration is higher (<0.7% for A1, <1.5% for A2). So, pellet of class
A1 is used for laboratory analysis and the A2 for common use, since it is cheaper. Table 4 shows the elementary analysis of pellet A1 (U.M is unit of measure, I.M is detection limit and L.R. is measurement uncertainty).

Parameters	U.M.	Results	I.M.	L.R.
Calorific value	-			
Upper calorific value	KJ/Kg	18666	±568	700
Lower calorific value	KJ/Kg	17334	±498	700
Moisture at 105°C	%	5,0	±0,4	0,1
Ash	% s.s.	0,2	±0,1	0,1
Carbon	%	47,2	±5,7	0,01
Oxygen	%	41,1	±4,9	0,01
Hydrogen	%	6,28	±0,75	0,01
Sulphur	%	<0,001		0,001
Nitrogen	%	0,20	±0,02	0,01

Table 4 Chemical-physical properties of pellet A1 (Fonte: Gruppo C.S.A.)

Pellets are mainly minced, with variable lengths. The samples were chosen in order to fit in the specified dimension range (D=6mm; L= $25 \div 30$ mm), so that physical manipulation of the pellet could be avoided. In order to insert the thermocouple inside the pellet, they are been pierced with drill press. The dimensions of the hole are d=1.75mm and h=L/2.



Figure 22 Pellet used for the tests

3.3. Optical particle counter, OPC

To analyse the combustion pollution, it is used an OPC sensor that count and size particles suspended in both air and liquids; this instrument is based on the principle of light scattering from particles. Its operation consists in (illustrated also in Figure 23): the size of the particle is determined using light, which illuminate the sensitive volume of the detector chamber with

uniform intensity, due to the availment of the focusing optics. Each particle, when enters the sensitive volume, is detected and the light scattered towards the detector increase proportionally to the size of the particle. This process allows the electronic to process the signal, that interprets the intensity of scattered light and assigns a particle count to the appropriate particle-size channel [23].



Figure 23 On the left OPC sensor by Alphasense used during the thesis; on the right the representation of how the sensor works

The OPC used in this project is OPC-N3 from Alphasense Company and it works as the conventional optical particle counters explained before. The object of this tool is to determine the particle size and the particle number concentration, assuming a particle density (about 1.65 g/ml) and refractive index (about 1.5+i0). These two factors are necessary to convert from the optical size of each particle. The OPC classifies each particle size, at rates up to ~10,000 particles per second, recording the particle size to one of 24 "bins" covering the size range from 0.35 to 40 μ m. The OPC detects ~100% of particles at 0.35 um and ~50% at 0.3 um. PM₁, PM_{2.5} and PM₁₀, data are recorded by the OPC and showed them through histograms and plots. On the side of the tool there is a fan that with its speed determines the sample air flow rate, but this speed can vary therefore the variations are monitored and corrected by the sensor so that the particle concentrations and derived PM values are unaffected by flow variations.

As it is analysed in literature, the particulate matter study is done by impactor or filter, but these tools do not allow to observe the emission during the time. Only the final result is obtained. Instead, using a tool as the OPC the analysis are more accurate and it can be analysed the emissions profile from the beginning to the end of the test, to understand better the phases linked to the greater emissions. So, it is an innovative procedure.

3.4 Gas sensors

A sensor is a device that responds to a physical stimulus, such as heat, light, sound, pressure, magnetism or movement, and transmits a resulting electrical impulse as a means of measuring the change of any intrinsic property of the constituent material.

The sensors used to analyse gas emissions from pellet combustion are the ones from Alphasense. This type of sensors converts the information associated with electrochemical reactions into an applicable quantitative voltammetric signal.

The sensors available were: SO₂, NO₂, H₂, CO, O₂, CO₂, NO, VOC, NH₃, HCN.



Figure 24 Gas sensors

3.5 Wi-Fi temperature data logger

A thermocouple is inserted inside the pellet in order to control and analyse the biomass temperature. This thermocouple is connected to a data logger, that collects temperature values during the test with an interval of 0,10 s.



Figure 25 Temperature data logger

Chapter 4 Experimental validation

This chapter is focus on instruments calibration and validation of the experiments.

4.1. OPC

4.1.1. Comparison with filter

To verify the performance of OPC, it is carried out a single pellet test with two probes: one connected to the tool, the other one to a cylinder with a white filter inside. The reactor temperature is about 550°C, with air feed about 5 L/min. The initial weight of the filter is 0.0.495 g and at the end of the test is 0.0513 g, so there is an increase of weight about 0.0018 g because of the particulate emissions, and the filter is no longer white as show in Figure 26.



Figure 26 Filter at the end of test

The formula used to calculate the concentrations of particulate matter read by OPC is:

$$M = \frac{\rho * W}{100 * SFR * t} \sum_{i=0}^{B} c_i * V_i * R_i$$

M= total mass density $[\mu g/m^3]$;

 ρ = density [g/cm³]; it is used 1.86 [g/cm³] [18]

c= counts (cumulative over sampling time)

V = particle volume $[\mu m^3]$

W = sample volume weighting [dimensionless]

R = respirable convention (at 1 micron) [dimensionless]

SFR = sample flow rate [ml/s]

t = sample time [s]

B = final bin number [dimensionless]

The comparison between OPC values and the emission weight catch by the filter is carried out integrating the PM_{10} curve as a function of time and this value is multiplied for the suction volumetric flow, that in this case is about 0.5 L/min. So, the equation is:

$$\int_{t=1min}^{t=5min} PM10 \ dt * \dot{V} = Mass$$

The curve of particulate emission is showed in Figure 27:



Figure 27 Trend of particulate matter analysed by OPC

The result obtained from the curve integration is about 0.0017 g, comparable to the value obtained from the weight of the filter. In conclusion, the gravimetric test for the OPC can be validated.

4.1.2. Comparison with another OPC

The validation of this tool is also be done comparing with another OPC. Both were located halfway up of a column and they sucked a flow composed by aerosol, which was fed inside. The acquired data were compared, and the results were approximately the same, as showed in the graphics in Figure 28. All dimension classes are considered, i.e. from 0.3 to 40 μ m.



4.1.3. Test with a cigarette

A test with a cigarette is carried out to compare the acquired data from OPC to the ones one literature. A cigarette is inserted in a quartz tube after ignition, so it can be observed the combustion over time. The OPC is connected directly to the tube and with its to suck the fumes. Figure 29 shows the set-up.



Figure 29 Set-up used for cigarette combustion

The cigarette, thanks to the suction, is able to be completely consumed in the axial direction (Figure 30).



Figure 30 Phases of combustion cigarette

Some articles were analysed to verify the reliability of the data collected.

A report [24] has analysed ultrafine particle emission by electronic and normal cigarettes, in a confined space of 50 m^3 in which inside a volunteer smoked. The particles emitted was measured using a pre-calibrated particle counter. The results obtained are showed in Table 1Table 5.

Table 5 Particulate matter production by e-cigarette and normal cigarette

Micrograms per m ³ (±SD)	PM1.0	PM2.5	PM7.0	PM10.0	TSP
e-cig without nic	3.5±7.3	7.2±9.6	8.7±9.9	9.9±10.3	11.6±15.5
e-cig with nic	0.0±0.3	0.5±1.1	-0.3±3.1	-0.6±4.4	1.2±10.1
normal cig	76±18	139±32	155±36	158±37	160±37

The acquired data are analysed referring to the data found in the literature



The trend of PM_{10} in the test carried out is:

In the graph above all data are considered, instead in the one below the concentration range is the one found in literature. It can be observed that the cigarette emission from the tests are in line with the results found in the article.

About diameter size, the main distribution is in the range of $0.3 \div 5 \mu m$, as it shows in Figure 32.



Figure 32 Diameter for cigarette emissions

4.2. Gas sensors

Before tests, it was necessary to calibrate the sensors. Mixtures with known concentrations are sent to sensors, thanks to certified tank and flow mixing, monitoring their response.

For each sensor, the volumetric flow used is about 300 ml/min.

OXYGEN

Alphasense oxygen sensors generate a current, which is proportional to the rate of oxygen consumption, following Faraday's law. There is a load resistor, which value is typically 10-100 Ω , between the cathode and the anode that measures the current and the resultant voltage drop.



Figure 33 Calibration of O2 sensor

The ordinate axis represents the percentage of oxygen in the feed, while in the abscissa axis there are the value of the resistor.

The values are linear and R^2 is near to 1, so the calibration is excellent.

CARBON DIOXIDE

The carbon dioxide sensor uses the principle of Non-Dispersive Infra-Red (NDIR) to determine gas concentration. It consists of an infrared source, optical cavity, dual channel detector and internal thermistor. Light from the infrared source passes through the optical cavity when it interacts with the gas before impinging on the detector. The active channel is fitted with a filter such that the only light with a wavelength that corresponds to an absorption band of the target gas is allowed to pass through.



Figure 34 Calibration of CO2 sensor

The ordinate axis represents the percentage of carbon dioxide in the feed, while in the abscissa axis there are the value of the resistor.

The values are linear and R^2 is near to 1, so the calibration is excellent.

The other sensors used are electrochemical. They generate a current that is linearly proportional to the fractional volume of the gas. There are three metal strips that connect each electrode to the three pins outside of the sensor body. The working electrode is the surface where the electrochemical oxidation or reduction occurs and its current changes when the applied potential is varied.

CARBON MONOXIDE

The CO sensor is powered with constant voltage equal to 10 V and it can return a signal in Volt, between 0.5 and 2.5 V.



Figure 35 Calibration of CO sensor

• NITROGEN MONOXIDE



Figure 36 Calibration of NO sensor



HYDROGEN



For all of them the values are linear and R2 is near to 1, so the calibration is excellent.

Chapter 5 Results and discussion

In this Chapter, results obtained from experiments are showed and analysed. The first analysis is about the combustion of single pellet. Profile of temperature, weight loss, gases and particulate emissions are analysed. After that, test with several pellets are carried out.

5.1. Single pellet

Tests are performed using the tubular reactor pre-heated, but the air feed influences in a strong way the isothermal control of the reactor since the feed is at ambient temperature. Figure 38 shows this effect considering a value of set-point of reactor temperature about 450°C with air flow of 10 L/min. Temperature inside the reactor is lower than the set point in each point of the thermocouple considered (referring to the set-up analysed in § 3.1.1) and this effect is more evident in the lower zone of reactor because it is the one reached first by the air.



Figure 38 Temperature trend inside the reactor in absence of biomass, with air feed of 10 L/min and set point of 450°C

Because of this analysis, it is decided to use a smaller feed to avoid a significant decrease in temperature inside the reactor.

In Figure 39 it is reported the different trends of temperature for each point of the thermocouple. It can be observed that the one more influenced by the combustion is the second one starting from the bottom ('25' in the graph). So, in the following plots the reactor temperature refers to this point.



Figure 39 Temperature trend inside the reactor for each multipoint of thermocouple

Figure 40 shows the trend of temperature, during combustion, feeding a different air flow rate. With the same conditions, profiles are reproducible: tests are carried out over again with the same conditions and the results are the same. As expected, with lower air feed the temperature is able to remain around the set point (dashed line). For all graphics, the thermocouple sensor taken into consideration is the one in correspondence of the biomass.



Figure 40 Temperature trend inside the reactor during combustion with different air feeds

Each curve displays an initial decrease due to the insertion of the pellet which is at ambient temperature and then an increment which matches with the initial combustion. This increment is lower as the air feed increases, and the combustion condition are not optimal. If the temperature is too low, the combustion is partial and it can be observed visually only the phenomenon of smouldering, without flame.

This situation can be observed in case of high air feed or low temperature value of set point. The set-up in these figures is different from the one introduced in Chapter 3, just to be able to photograph the combustion during time. The single pellet has been freely inserted into the reactor and only one probe is located on the top.



Figure 41 Smouldering phases at 450°C

Smouldering effect, showed in Figure 41, is the slow and flameless form of combustion, sustained by the heat evolved when oxygen directly reacts on the surface of a condensed phase fuel [25]. Smouldering is the leading cause of death in residential fires [26]. The fundamental difference between smouldering and flaming combustion is that, in the former, the oxidation reaction and the heat release occur on the solid surface of the fuel or porous matrix, instead in the latter it occurs in the gas phase surrounding the fuel. Because of its low temperature, this effect is characteristically an incomplete oxidation reaction and thus emits a mixture of toxic, asphyxiant and irritant gases and particulates at a higher yield than flaming fires [27].

Otherwise, if the conditions are optimal for combustion, the flame can be observed as in Figure 42. It stars at the sides of pellet and then spreads gradually towards the centre.



Figure 42 Flame phases at 550°C

5.1.1. Temperature set point of 450°C

Tests carried out at temperature of 450°C are analysed, inserting the single pellet in the thermocouple. Temperature is set and the air feed has been changed (1-2-5-10 L/min). For each test trends of reactor and biomass temperature, and CO, VOC, O₂, CO₂ emission and weight loss are showed. No flame was seen in any test with this temperature of set point.



Figure 43 Temperature, weight loss, and CO, O2, CO2, VOC profiles for test at 450°C, with 1 L/min of air



Figure 44 Temperature, weight loss, and CO, O2, CO2, VOC profiles for test at 450°C, with 2 L/min of air



Figure 45 Temperature, weight loss, and CO, O2, CO2, VOC profiles for test at 450°C, with 5 L/min of air



Figure 46 Temperature, weight loss, and CO, O2, CO2, VOC profiles for test at 450°C, with 10 L/min of air

In general, the biomass temperature is not heavily influenced by the different air flow and in each test the combustion is able to reach more or less 700 °C. Instead, different trends can be observed for weight loss. With a small air flow (1-2 L/min) the pellet lost more than 50% of his weight in a range of time of 3 minutes; increasing the air feed the weight loss is smoother and at 6 minutes it is still 50%.

About gases emission, the most relevant trends are of CO and CO_2 : increasing the air flow, the emission decreases. They show the same trend and in each test the increment of these two gases is observed while the biomass temperature is increasing. So, as soon as the pellet starts burning, it releases the first emissions.

To represent the acquired data by the OPC, we consider all the bins, except the first one because its respirable convection value is around 100%. So, even if the particles count is low, its influence becomes relevant, as it can be observed in the graph in which the contribute of the others bin seems to be negligible (coloured tracks around zero).



So, the attention is focused on the particulate emissions. For each single test profiles of particles counts and PM_{10} concentrations are plotted in parallel to the reactor and biomass temperature and the CO trend.



Figure 48 Profiles of particulate emissions at 450°C, with 1 L/min of air



Figure 49 Profiles of particulate emissions at 450°C, with 2 L/min of air



Figure 50 Profiles of particulate emissions at 450°C, with 5 L/min of air



Figure 51 Profiles of particulate emissions at 450°C, with 10 L/min of air

Just in the tests with lower air feed, it can be observed a peak for the PM_{10} concentration.



To understand better which type of particles are emitted, 3-D plot are used to represent the diameter of the particles.

Figure 52 Diameter distribution for test at 450°C, with 1 L/min of air



Figure 53 Diameter distribution for test at 450°C, with 2 L/min of air



Figure 54 Diameter distribution for test at 450°C, with 5 L/min of air



Figure 55 Diameter distribution for test at 450°C, with 10 L/min of air

Increasing the air feed, the particles emission increases and the size is more in the range of 0.5-2 μ m; instead in the test with 1-2 L/min of air it can be observed emissions of particles with diameter between 4 μ m and 10 μ m, meaning that the combustion conditions are worst. Bins connected to diameter above 14 μ m are not considered, because no particles with that size is observed during the test.

5.1.2. Temperature set point of 550°C

Following the previous observations, the focus has been shifted to lower air feed and the temperature reactor has been set to 550°C. The effect of these assumption can be immediately observed, analysing again the trends of temperature inside the reactor (Figure 51).



Figure 56 Temperature trend inside the reactor at 550°C, with different air feeds

At lower air feed, the reactor temperature profile is above the value of set point and, during the ignition, combustion is able to reach high temperatures.

In any case, the pellet reaches the flame around the first minute of the test and the flame duration is around 40 seconds.

The combustion with higher air feed starts later than the others, in fact the increases in CO and CO_2 is delayed in comparison to the curves for test with less air flow, as it shows in Figure 57.



Figure 57 Gases concentrations with different air feeds and set point of 550°C

As said before, if the combustion is not optimal and only smouldering is observed, the gases emissions are higher. This fact is showed in VOC profile which is more marked during test with 5 L/min of air. Part of these volatile compounds contributes to the formation of particulates, specially in a cold atmosphere. Applying secondary air, above the combustion zone, could be useful to decrease these emissions: the flow would be heated, limiting condensation and particle formation.

During combustion, the biomass reaches temperature in a range of 700-800°C, losing 80% of the total weight. As the pellet temperature increases, the reactor temperature profile shows a peak meaning that the pellet consumption occurs from the surface to the inside, where the thermocouple is located. In fact, it can be observed that the high level of pellet temperature is after the peak, when the flame appears.



Figure 58 Temperature, weight loss and CO profiles for test at 550°C, with 1 L/min of air



Figure 59 Temperature, weight loss and CO profiles for test at 550°C, with 2 L/min of air



Figure 60 Temperature, weight loss and CO profiles for test at 550°C, with 5 L/min of air

Comparing to the tests with T=450°C, the trend of weight loss is more pronounced: the pellet burns faster and after the flame, the weight is trifling. Only char remains. In this case, the weight loss does not show influence from the air flow. At this temperature, the results about weight loss reproduce trends find in literature [3]:



Figure 61 Thermogravimetric analysis of biomass combustion

The total oxidation of biomass organic fraction (complete combustion) is possible only if the basic combustion requirements are met:

- the comburent air must be supplied in sufficient quantity to allow the complete oxidation of the fuel;
- the temperatures generated must be high enough to guarantee and support the chemical reactions with a certain kinetics;

- the residence time at high temperatures must be long enough in order that the heat exchange and oxidation can take place;
- sufficient turbulence must ensure adequate mixing between fuel and comburent in order to avoid local areas with oxygen deficiency

Going back to the test results, CO concentration is similar in each test despite the variation of incoming air. A common feature in the emissions of this gas is the presence of two different increments: an initial one at the flame, during which char is formed; a second one which is attributable to the char oxidation.

About particle emissions, high concentration values are observed only during the flame phase and, increasing the air flow, this value is lower. In the same time range, concentration of PM_{10} shows a relevant peak, but in this case the value is slightly lower with lower air flow.



Figure 62 Profiles of particulate emissions at 550°C, with 1 L/min of air



Figure 63 Profiles of particulate emissions at 550°C, with 2 L/min of air



Figure 64 Profiles of particulate emissions at 550°C, with 5 L/min of air

For each air feed, tests seem to be reproducible. In fact, the mean counts in the time, doing the mean of the particles emitted in each bin, show a similar trend. The profiles consist in a initial double peak, that are more consistent with lower air feed. An unexpected third peak can be observed towards the end of tests, mostly with 2 and 5 L/min of air.



Figure 65 Profile of mean of particles count considering all bins with 1 L/min of air



Figure 66 Profile of mean of particles count considering all bins with 2 L/min of air



Figure 67 Profile of mean of particles count considering all bins with 5 L/min of air

An analysis of diameter size is carried out using 3-D plots, to try to understand the reason why a third peak is showed in particles counts profile. The focus is on the most interesting time range.

In each test the bins considered are from 2 to 7, because it is observed that in the other bins the concentration of particles emitted is irrelevant. So, the diameter range is from 0.46 μ m to 2.3 μ m.

In the case of 1 L/min of air feed, concentrations peaks are only in the first two minutes of tests, during the flame. As it showed in the graph, the emissions are composed by fine particle, mostly with diameter less than 1 μ m. The particles concentration is higher at the ignition of the flame

and a lower peak is observed at the end the flame. Between these two peaks, the concentration is composed by particles with diameter higher than 1 μ m (around 1.5 μ m).

In the plots all these peaks are showed: on the left the peak at the beginning of test, on the right the one at the end.



Figure 68 Diameter distribution for test at 550°C, with 1 L/min of air



Figure 69 Diameter distribution for test at 550°C, with 2 L/min of air



Figure 70 Diameter distribution for test at 550°C, with 5 L/min of air

In general, the trend is similar to the one analysed for the test with 1 L/min: the main concentration is formed by particles of 1 μ m. The difference is that, increasing the air feed, the total particles count decreases, showing a better combustion. However, in the case with higher air flow, the peak at the end of the test displays also particles with diameter between 1 μ m and 2 μ m.

5.2. Several pellets

After analysis of a single pellet combustion, tests with several pellets are carried out. The conditions applied are the same of previous tests.

The combustion never reaches the flame at temperature set point of 450° C and it presents only the smouldering effects, as analysed before. Instead, at temperature of 550° C it is observed the flame with a high about $20\div25$ cm, which in some cases it came out of the top of reactor, as in Figure .



Figure 71 Flame during combustion of three pellets

Results from tests with the two different temperature have been compared, to analyse the performances.

The tests at 450°C are about the combustion of three pellets with air feed of 2 and 5 L/min.

The discussion starts analysing the trends of temperature, gases emission and relative weight for the two different air feed, respectively in Figure 72 and Figure 73.



Figure 72 Trends of gases emission and relative weight of pellet for test at 450°C and with 2 L/min of air



Figure 73 Trends of gases emission and relative weight of pellet for test at 450 $^\circ\rm C$ and with 5 L/min of air

Despite the temperature inside the reactor is more influenced in the test with 5 L/min of air and it is lower than the test with 2 L/min, the biomass is able to reach higher temperatures during the combustion. Moreover, the pellets weight loss is faster but the difference in CO emissions is not so relevant.

Comparing these tests with the ones analysed before for a single pellet, it can be observed that the weight loss trend is different increasing the air feed. For single pellet, at 450 °C and with 5 L/min of air, the weight loss is very slow, indeed at the six minute of the test, the percentage was still 50%; in the case with three pellets, with same conditions, in 5 minutes the weight loss is more or less complete. Also, the emissions of CO are more consistent during combustion of more pellets despite the increase in air flow which previously positively influenced the emission.

The focus now is shifted on particulate emissions. The particles concentration is almost the same, instead the PM_{10} concentration shows a slightly different trend between the two tests.

In test with 2 L/min of air, two relevant peaks of PM concentration are easily identifiable with a maximum duration of 30 seconds, and another smaller is present at the beginning of combustion.

In the second test, there is only one relevant peak of concentration, but the duration time is about 2 minutes and also the range is 10 times bigger than the previous one.



Figure 74 Trends of gas and particulate emission for test at 450°C and with 2 L/min of air



Figure 75 Trends of gas and particulate emission for test at 450°C and with 5 L/min of

At 550°C, tests are carried out for two pellets, as already with a single pellet it was possible to observe the flame. Two different tests are carried out with the same conditions of temperature and air flow, but the pellets were insert in one test in vertical and in the second one in horizontal.



Figure 76 Pellets inside the basket in vertical and horizontal positions

The disposition of the pellets influences the combustion. In vertical position, the biomass is able to reach higher temperature but the CO emissions are also higher than test with pellets in horizontal position. In both cases, the CO peaks correspond to the moment in which the flame is present (between 1'30" and 2'30"). The biomass temperature in this range is from 508°C to 670°C in the first test, while in the second is from 389°C to 607°C. Despite the lower temperature, pellets in horizontal position are able to burn and to produce flame as the ones in vertical position. Moreover, the weight loss during flame phase is a little bit higher in the second test and it is slower comparing with single pellet tests.



Figure 77 Trends of gases emission and relative weight of pellet



Figure 78 Trends of gases emission and relative weight of pellet

About particles emission, the peaks observed correspond to the time range in which the flame occurs.



Figure 79 Trends of gas and particulate emission for test at 550°C and with 5 L/min of air (pellets in vertical position)



Figure 80 Trends of gas and particulate emission for test at 550°C and with 5 L/min of air (pellets in horizontal position)

In the case of pellets positioned horizontally, the concentration of particles is around 1500 (counts/ml), compared to the one with vertical pellets in which the maximum concentration is 600 (counts/ml).

The behaviour of emissions in these two tests is similar to the ones of single pellet test but with lower values, both for particulate matter and particles concentrations, meaning a better combustion.

Comparing the tests with different set point of temperature, it can be observed that with T=450°C the emissions are relevant for diameter between 2.5 μ m and 10 μ m. Instead, in tests with higher temperature, the range of diameter is 0.4÷3 μ m.



Figure 81 Mean diameter for tests at 450°C and 550°C

As analysed from literature in Chapter 2, with high temperature the particles formed derive from the soot and organic compounds, which make the filter black, as seen during validation.

3-D plots are reported to understand better the particles size distribution. It is already showed that in test at 450°C the particles emitted have larger diameters. Indeed, in both tests it is necessary to consider also bins correlated to large diameter.

In the case of 2 L/min of air, the main particulate emissions are in the second half of the test (from minutes 8) and the size of diameter is mostly less than 1 μ m. Instead, in the previous minutes all bins have been considered because the slight emissions found are made up of particle with larger diameter, between 4 μ m and 37 μ m.



Figure 82 Particles size distribution for test at 450°C of 3 pellets and with 2 L/min of air



Observing the test with 5 L/min, particles show a greater diameter, mostly in the second part of the test. All bins are necessary to consider.

Figure 83 Particles size distribution for test at 450°C of 3 pellets with 5 L/min of air

The tests with temperature set-point of 550°C show only emission of fine particle, both in the case with pellets in vertical and horizontal position, meaning a better combustion.



Figure 84 Particles size distribution for test at 550°C of 2 pellets in vertical position with 5 L/min of air


Figure 85 Particles size distribution for a test at 550°C of 2 pellets in horizontal position with 5 L/min of air

Particles show mostly diameter of 0.46 µm.

After that, at 550°C it is done a comparison of biomass temperature profiles considering the combustion of two and three pellets with different values of air flow (2 and 5 L/min).



Figure 86 Temperature profiles of biomass in cases of several pellets with different air feed

As it can be observed from the graph, the test that show a slower combustion is the one with 3 pellets and 2 L/min of air. Instead, the increase on the amount of pellet is compensate by the higher air feed. Indeed, the test with 3 pellets and 5 L/min of air shows a similar profile of the test with only 2 pellets and with 2 L/min of air.

This fact can be associated to the oxygen demand: three pellets require more air to burn and a air feed of 2 L/min is not enough to facilitate the combustion. Indeed, the graph below shows



higher particulate emissions for the test with 3 pellets and lower air feed than the one with 5 L/Min.

Figure 87 PM10 profile for different test with several pellets, with different air feed

So, oxygen deficiency leads to greater pyrolysis and a consequent increase in particulate matter.

Conclusions

The purpose of this thesis was to analyze in detail the biomass combustion, in particular focusing on pellet. The main problem of this process is the possibility not to reach a complete combustion with a consequent increase of noxious emissions. Therefore, it is important to meet the basic combustion requirements:

- the combustion air must be supplied in sufficient quantity to allow the complete oxidation of the fuel;
- the temperatures generated must be high enough to guarantee and support the chemical reactions, with the given kinetics;
- the residence time at high temperatures must be long enough in order that the heat exchange and oxidation can take place;
- sufficient turbulence must ensure adequate mixing between fuel and oxidant, to avoid local spots with oxygen deficiency.

For all the tests performed in the laboratory for this thesis work, all these requirements have been taken into consideration, trying to achieve the best combustion conditions.

The attention was payed mainly to gas emissions with a particular focus on the particulate matter. The analysis of the particulate has been carried out using an optical particle counter which allows to collect data during the entire test and to analyse profiles during the time. This is an innovative procedure because in the literature studies only impactors and filters have been used to collect the particulate during the test, at the end of the pipe, but without giving information on data over time.

Performing the tests, it has been observed that the air flow negatively influenced the temperature inside the reactor, if not properly pre-heated; therefore, lower flow rates (in the range of 1-5 L/min) has been used in the reactor during tests to avoid false temperature data.

The tests performed was firstly focused on a single pellet, with set-point of temperature reactor about 450°C and 550°C. For both set points, the air flow has been varied to analyze the optimal condition for the combustion.

At 450°C the combustion is unable to create a flame, in each case of different air flow rate. Only smoldering has been observed, which do not represent an optimal condition because in this case the emissions are higher and the particles show large diameter, being an incomplete combustion. The weight loss is very slow, specifically with higher air flow. Considering the second set point, at 550°C the pellet can burn with flame with air fed of 1-2-5 L/min and, during this phase, the biomass loses most of its weight. In this range of time relevant peaks of particulate emissions can be observed and they show a distribution of particles diameter mostly under 1 μ m. With the higher air flow, the concentration of particles emitted is lower.

After the analysis of a single pellets, tests with several pellets have been carried out.

At 450°C, also with more pellets the combustion shows only the smouldering effect, concluding that this temperature is not enough to guarantee a good process.

Instead, at 550°C the flame is always visible. It has been observed that the pellets arrangement in the crucible can influence the combustion: pellets in horizontal position are able to make flame at lower temperature with lower particles concentration.

In the future, some other tests can be performed to continue the study to achieve the best combustion conditions. Firstly, the feed of pre-heated air can improve the performance and the addition of a second air flow from the top of the reactor can help to complete the combustion of the gases emitted. After that, analysis on a real stove can be performed to check if the conditions observed in the small reactor can be reproduced in a larger scale.

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