Universidade do Minho
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Combustion of alternative biomass fuels in a domestic boiler and in a large-scale furnace

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ABSTRACT

Biomass is a renewable source of energy, used in combustion on both domestic and industrial applications. Biomass combustion has a high impact in the environment due to the released products, which must be measured and analyzed. The main goal of this work was to study the viability of alternative biomass fuels, both for the economic valorization of these alternative materials and to ease the pressure on the demand of pine sawdust. This viability will depend on the characteristics of the combustion release products and the effects on the combustion equipments of using such materials. For achieving this goal, combustion test were performed with alternative biomass fuels in a domestic boiler and in a large-scale furnace. The raw materials examined were pine sawdust, furniture residues, cork residues and branches of vine, olive, kiwi and platanus. The combustion characteristics of these biomass fuels were studied by thermogravimetry, fouling and slagging indexes, chemical analysis of bottom and fly ashes, gaseous and particulate matter emissions and a scanning electron microscope for analysis of the particulate matter.

The characteristics of the traditional biomass fuel (pine sawdust) and alternative biomass fuels used were significantly different. The alternative biomass fuels presented higher heating value and lower nitrogen content. However, they contained more ashes, and the undesirable chemical composition of those ashes can constitute a problem. The thermogravimetric results showed that the alternative residues studied are good alternatives to the pine sawdust in terms of combustion parameters such as level of heat released and activation energy. The ashes indexes disclosed some problems related to slagging and fouling, due to the high levels of silica in pine sawdust and potassium in agriculture residues.

The combustion in the pellet-fired domestic boiler revealed some operational problems with the alternative biomass fuels. Accumulation of ashes in the grate by sintering mechanisms was observed and higher concentrations of CO were also measured, which was accompanied by the emission of soot particles, as detected by scanning electron microscope. The particulate matter emissions were also significantly higher (especially for vine and olive pellets) than those from the pine sawdust pellets, mainly for particles with very low diameter (0.32 and 0.76 μm). High levels of potassium were also found in the particulate matter from

the alternative biomass pellets. The presence of this element usually decreases the level of sintering of the ashes. However, the high presence of silicon in pine sawdust proved to be the biggest problem in terms of slag formation.

The combustion of pulverized biomass in the large scale furnace was performed for furniture and cork residues, and kiwi and platanus branches. The results showed that the cork residues are the most problematical regarding the particulate matter emissions, followed by the agricultural biomass fuels (kiwi and platanus). Particles with a diameter around 0.26 μm were those released in greater amounts for all biomass fuels tested, reaching a maximum of 137 mg/Nm^3@6%O_2 for cork residues. The scanning electron microscope analysis revealed high quantities of carbon in all samples of the particulate matter, especially for the lower diameters. Regarding the chemical composition of the particulate matter, the more representative inorganic element was potassium, followed by smaller quantities of chlorine and sulphur.

The pine sawdust and furniture residues, which are commercialized products, proved to be the best raw materials for combustion and originated less problematic products. The other biomass fuels studied can represent good alternatives when using equipment that does not require such high quality fuels, such as in industrial applications. However, the emissions of particulate matter with sizes below 2.5 μm, that are very harmful to human health by causing respiratory problems, need to be captured to prevent its release into the atmosphere.

Keywords: biomass combustion, pellets, pulverized biomass, domestic boiler, large-scale furnace, slagging, fouling, particulate matter.

RESUMO

A biomassa é uma fonte de energia renovável, usada em combustão para aplicações, quer domésticas quer industriais. A combustão de biomassa tem um elevado impacto no ambiente devido aos produtos libertados, que é necessário medir e analisar. O principal objetivo deste trabalho foi estudar a viabilidade de combustíveis de biomassa alternativos, quer para a valorização económica desses materiais, quer para aliviar a procura de serrim de pinho. Esta viabilidade dependerá das características dos produtos de combustão libertados e dos efeitos do uso desses materiais nos próprios equipamentos. Para alcançar este objetivo foram efetuados testes de combustão de biomassas alternativas numa caldeira doméstica e numa fornalha laboratorial de grandes dimensões. As matérias-primas analisadas foram o serrim de pinho, resíduos de mobiliário, resíduos de cortiça e ramos de videira, oliveira, kiwi e plátano. As características da combustão dessas biomassas foram examinadas recorrendo à termogravimetria, índices de *fouling* and *slagging*, análise química das cinzas residuais e volantes, emissões gasosas e de partículas e microscopia eletrónica do material particulado.

As características da biomassa tradicional (serrim de pinho) e das biomassas alternativas apresentaram diferenças significativas. As biomassas alternativas apresentaram um maior poder energético e baixos teores em azoto. No entanto, a presença de maiores teores de cinzas e uma composição química indesejável das mesmas podem constituir um problema nestas biomassas alternativas. Os resultados termogravimétricos mostraram que os resíduos estudados são boas alternativas ao serrim de pinho em termos de parâmetros de combustão, tais como o nível de calor libertado e a maior taxa de energia. No entanto, os índices das cinzas antecipam alguns problemas relacionados com *slagging* e *fouling*, devido a elevados níveis de silício no serrim de pinho e potássio nos resíduos agrícolas.

A combustão de *pellets* na caldeira doméstica revelou alguns problemas operacionais no caso das biomassas alternativas. Observou-se a acumulação de cinzas na grelha por mecanismos de sinterização e maiores concentrações de CO, acompanhadas por maior quantidade de partículas de fuligem emitidas, tal como observado nas análises por microscópio eletrónico de varrimento. A concentração de partículas em suspensão também foi significativamente maior do que no caso do serrim de pinho (especialmente para os *pellets* de videira e oliveira),

principalmente para partículas com pequenos diâmetros (0,32 e 0,76 µm). Foram encontrados elevados níveis de potássio resultantes da queima dos *pellets* alternativos. A presença deste elemento geralmente diminui o nível sinterização das cinzas. No entanto, a elevada presença de silício no serrim de pinho provou ser o aspeto mais problemático em termos de formação de escórias.

Foram realizados testes de combustão de biomassa pulverizada na fornalha laboratorial de grandes dimensões, com resíduos de mobiliário e cortiça, e ramos de kiwi e plátano. Os resultados mostraram que os resíduos de cortiça, seguido pelas biomassas agrícolas (kiwi e plátano) são os mais problemáticos relativamente a emissões de partículas. As partículas com um diâmetro em torno de 0,26 µm foram as libertadas em maior quantidade para todas as biomassas testadas, atingindo um máximo de 137 mg/Nm^3@6% de O_2 para os resíduos de cortiça. A análise das partículas com o microscópio eletrónico revelou grandes quantidades de carbono em todas as amostras, especialmente nas de menor diâmetro. Em relação à composição química, o elemento inorgânico mais representativo foi o potássio, seguido de menores quantidades de cloro e enxofre.

O serrim de pinho e os resíduos de mobiliário, produtos atualmente já comerciados, provaram ser a melhor matéria-prima para combustão, com produtos menos problemáticos. As outras biomassas estudadas podem representar boas alternativas para utilizar em equipamentos que não exijam combustíveis tão nobres, nomeadamente em aplicações industriais. No entanto, é necessário capturar as emissões de partículas com diâmetros inferiores a 2,5 µm para que não sejam libertadas para a atmosfera, pois são muito prejudiciais para a saúde humana causando problemas respiratórios.

Palavras-chave: Combustão de biomassa, *pellets*, biomassa pulverizada, caldeira doméstica, fornalha laboratorial de grandes dimensões, escórias, depósitos, partículas em suspensão.

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LIST OF ABBREVIATIONS

APS – Aerodynamic particle sizer

a.r. – As received

CO – Carbon monoxide

CO_2 – Carbon dioxide

CR – Cork residues

d.a.f. – Dry and ash free

d.b. – Dry basis

DSC – Differential scanning calorimetry

DTG – Derivative thermogravimetric curve

EDS – Energy-dispersive x-ray spectroscopy

FR – Furniture residues

GHG – Greenhouse gases

HC – Hydrocarbons

HHV – Higher heating value

KB – Kiwi branches

LHV – Lower heating value

LPI – Low pressure impactor

MMD – Mass median aerodynamic diameter

NG – Natural gas

NMVOC – non-methane volatile organic compounds

NO_x – Nitrogen oxides

O_2 – Oxygen

OB – Olive branches

PAH – Polyaromatic hydrocarbons

PB – Platanus branches

PM – Particulate matter

SD – Pine sawdust

SEM – Scanning electron microscope

SO_2 – Sulfur dioxide

SOA – secondary organic aerosols

Soot – Mass of impure carbon particles resulting from the incomplete combustion of hydrocarbons

TGA – Thermogravimetric analysis

VB – Vine branches

w.b. – Wet basis

VOC – Volatile organic compounds

wt.% – Weight percentage

1. INTRODUCTION

The aim of this chapter is to highlight the motivation and objectives of the work, and to present the organization and structure of this thesis entitled "combustion of alternative biomass fuels in a pellet domestic boiler and in a large-scale furnace". The motivation and goals are the starting point to understand the importance of this scientific work and the reasoning behind the proposed tasks. Lastly, the organization of the thesis is described, with a small summary of each chapter.

The biomass is the greatest renewable energy source available for heating. Heating with biomass represents more than 93% of all renewable heat production in Europe and 12.9% of the total heat demand in Europe is covered with biomass [1]. The potential of biomass energy in avoiding the use of fossil fuels and release of greenhouse gases (GHG) to the atmosphere can be controversial. In fact, collecting live biomass to burn and release more GHG may not have great advantages in solving this problem. Instead, one of the most attractive solutions can be the use of residues, or sub-products, from industry, forestry and agriculture, that do not have other noble applications, to produce biofuels. Regarding industry processes, furniture and carpentry, sawdust and other resulting wood products can be used. Forest activities, such as cleaning bushes and trees, fire prevention and land management, also give origin to wood products. In the agriculture activities, pruning generates a lot of residues that are normally burned directly on the fields. The application of these residues to produce biomass fuels can be a green solution and a biomass energy valorization method. Furniture industry, wood processing, forestry and agriculture activities are some of the main activity sectors, economically sustainable, in the regions where the residues considered in this work were collected (Minho and Algarve regions of Portugal). The incorporation of residues in traditional wood biomass, as sawdust pellets, is not new and some non-organic residues have been successfully exploited for this purpose [2-4]. However, when incorporating these non-traditional residues, some ash formation mechanisms of bottom and fly ashes can induce key technological problems (e.g., slagging and fouling) and environmental risks (e.g., particulate matter emissions and spreading of hazardous elements) [5].

1.1 Motivation

This work focuses on the study of the combustion of alternative biomass fuels in two specific kinds of technology (in grate and suspension). Pellets represent a higher quality biomass fuel, in comparison to the traditional biomass in the form of wood logs. The domestic use of pellet-fed boilers (i.e, combustion in grate technology) has been growing exponentially. Due to this reality, the equipments have become more user-friendly, with automatic feeding systems and features to promote combustion efficiency. On what industrial applications are concerned, the use of pulverized biomass fuels in large-scale furnaces (in suspension) allows higher levels of efficiency, as it resembles the burning of a fluid given the reduced dimensions of the fuel. The use of alternative biomass fuels in combustion, for heating purposes, whether in domestic or industrial applications, is the major motivation of this study, given the high demand for certain common biomass solid fuels for combustion, such as the pine wood. Besides decreasing the demand for pine sawdust, the use of alternative materials could also lead to the economic valorization of these residues. The use of these alternative fuels can, however, generate several major obstacles regarding emissions (dust, gas and aerosols), deposit formation (slagging, fouling) and equipment corrosion. The content of nitrogen, sulphur, chlorine and potassium is increased by the use of chemicals, fertilizers and pesticides/herbicides in agricultural and industrial residues. Hence, it becomes important to understand the problems caused by the ashes and particulate matter, and to promote a rational utilization of these alternative biomass fuels, as sources of renewable energy, in heating equipments. When ashes react at typical combustion temperatures, they can severely impair the operation of heating equipments, due to the agglomeration and deposits formed. The gaseous emissions, particulate matter and the fly ashes are harmful pollutants to the environment and for human health. The presence of some element combinations leads to significant emissions of NO_x, SO_x, and HCl, as compared to standard wood biomass. The high levels of potassium influence both particulate matter emissions and slagging (by lowering the softening temperature of the fuel) of an increased ash volume (5% for some agriculture residues to 0.5% for sawdust). Finally, biomass fuels with high chlorine content may result both in corrosion problem on boiler's surfaces and in formation of dioxins. In order to evaluate the viability of using alternative biomass for combustion, all these

aforementioned factors must be assessed and studied. The alternative fuels studied were chosen from a number of available materials existing in Portugal.

1.2 Objectives

One of the main objectives of this study is to evaluate the combustion of a number of alternative residues in comparison with the traditional pine wood used in Portugal. Such study can serve as a preliminary assessment of the viability of these residues as alternative biomass fuels. These alternative residues have significant differences in terms of ash content and problematic elements, compared to traditional used wood, which presents a relatively high "purity" and homogeneity. For this evaluation, some wood residues from industry sub-products and agricultural residues (fine branches) from pruning activities were analyzed. The performance of these residues on the different combustion technologies is a good indicator to analyze the combustion behavior and the best application for them. The gaseous and particulate matter emissions are also important parameters to access the possible environmental problems and human health effects.

Chemical analysis of the biomass fuels is essential to predict some behaviors during combustion, especially from the agricultural residues studied. For example, the ashes that have comparatively low levels of calcium, but high levels of potassium and silica, begin to be sintered and melt at low temperatures during combustion [6]. The study of these biomass fuels in different technologies (grate and suspension, most applied for domestic and industrial applications, respectively) is essential to verify which of the different fuels can be applied successfully in each market.

One of the goals of this study is to evaluate the potential for biomass combustion of some easily available residues of agriculture (branches from vine, kiwi, plane tree and olive) and furniture and cork residues from industry, and compare them with the reference biomass material used in Portugal – pine wood. The biomass physical and chemical analysis and its combustion behavior, evaluated through thermogravimetric analysis (TGA), can be used to predict the combustion phases, ignition and burnout temperatures and maximum combustion rate [7-10]. Ash analyses are also indicative of the tendency for slagging and fouling phenomena that can occur in the combustion equipment [11–15]. Particulate matter emissions were also analyzed to verify the tendency of these biomass fuels to release particles

into the atmosphere [16–18]. These experiments were accomplished with combustion tests in two different technologies (grate and suspension).

1.3 Organization of the thesis

The present thesis is divided in 7 chapters. In the present chapter all the introductory issues for the proposed work were discussed, concerning specifically the biomass fuels used, combustion products analyzed and technologies employed.

In chapter 2 a literature review is carried out on biomass in general, addressing its composition and combustion behavior, with a focus on pellets and pulverized fuel. The state of the art is based in the existing biomass combustion equipments and description of the different types of problems caused by the combustion products. Lastly, a critical review of the previous works carried out in combustion equipments (grate and suspension) is presented.

Chapter 3 comprises the description of the materials (the different biomass fuels and equipments used) and methods (the different types of analyses performed) used for the experimental tests with the domestic boiler and the large-scale furnace. The experimental techniques used for the biomass fuels preparation, thermogravimetry, gaseous and particulate matter emissions, and ash characterization are also described here.

Chapter 4 is dedicated to the thermogravimetric analysis and ash characterization results of the biomass fuels used. The results for industrial woody and agricultural combustion are discussed. In this chapter the physical and chemical analyses results of the biomass fuels collected are presented. The thermogravimetric results allowed identifying the reaction kinetics of the biomass fuels examined. The fouling and slagging indexes, based on the chemical composition of the ashes, helped to predict the problems generated during combustion.

Chapter 5 is dedicated to results and discussion of the particulate matter emissions and ash characteristics in a domestic boiler fired with alternative biomass pellets. The pellet production with the pine sawdust, cork residues, and branches of vine, olive, kiwi and platanus is characterized. The operating conditions of the pellet boiler are described. The bottom and fly ashes were collected and the results of the chemical analysis are discussed.

The particulate matter emissions were analyzed based on its size distribution and chemical analysis.

Chapter 6 features the discussion of the results regarding the particulate matter emissions and fly ash characteristics in the pulverized biomass fired laboratory large-scale furnace. The pulverized biomass fuels (pine sawdust, furniture residues, cork residues, and branches of vine, olive, kiwi and platanus) characteristics are also described, and the operating conditions of the large-scale furnace are presented.

Finally, chapter 7 summarizes the main conclusions of this work and presents some suggestions for future work.

2. LITERATURE SURVEY

In this chapter the previous studies concerning fuel characterization, combustion of biomass and its products (ashes, particulate matter and gaseous emissions) are reviewed, with focus on the technologies and equipments of combustion of biomass in grate and suspension, such as those used in this thesis. The analysis of residues used as biomass fuels and technologies applied to the biomass combustion are also important for understanding the following chapters. The review of the biomass combustion is focused on the study of its products: ashes, and gaseous and particulate matter emissions occurring in the combustion process.

The raw materials employed in this study consist of woody biomass residues produced in Portugal from different activities (forestry, agricultural and industrial). There is a large variety of equipments suitable for the combustion of these fuels, developed for domestic or industrial applications. However, this literature review focuses on equipments used for combustion in grate and in suspension. The combustion problems analyzed in this work are related to the combustion products – ashes, and gaseous and particulate matter emissions. The fouling and slagging formed during the biomass combustion cause serious damages to the internal components of the equipments, decrease the combustion efficiency, increase the particulate matter released into the environment and can originate emissions that are harmful to the human health. The state of the art also comprises previous works featuring biomass characteristics and combustion of traditional and alternative residues, in grate and suspension, where the effects on its products are observed.

2.1 Biomass characterization

In this section, the biomass is characterized according to its classification and composition. The biomass as fuel was also analyzed regarding its availability and potential, according to its main sources (forestry, agriculture and industry).

Biomass classification

The wide range of biomass sources that can be used for combustion creates the need for a classification system through which they can be identified and distinguished. However, according to Vassilev *et al*. [19, 20], there is a lack of generally accepted terminology, classification systems and worldwide standards for biomass and biofuels, which leads to some serious misunderstandings during investigations.

Biomass residues for solid fuel production have been classified according to its origin. According to literature [21, 22], biomass can be classified as primary wastes (by-products from food crops and forestry products), secondary wastes (by-products of biomass processing for the manufacture of food or other products), tertiary wastes (have been used for some function but have reached the end of its useful life), and energy crops (i.e., crops grown for energy production purposes).

Jenkins *et al*. [15] also refer that the properties of biomass is another criterion used for its classification. A more complete division of biomass by its properties can be established as follows: wood and woody fuels (newly harvested hard and softwoods); agricultural biomass (straw, grass, stalks, etc.), aquatic biomass (algae, etc.), animal and human wastes (bones, manure, etc.), contaminated biomass and industrial biomass (solid municipal wastes, waste-water treatment sludge, refuse-derived fuel, etc.), and energy crops and biomass mixtures [22]. With a similar classification Williams *et al.* [23] separate the major groups into different classifications based on the general assessment of their source as follows: woody biomasses (pine chips or energy crop, as the willow), herbaceous (miscanthus and switch grass), agricultural residues (wheat straw, rice husks, palm kernel expeller, bagasse and olive residue). Animal wastes, such as cow dung, can form another category although these are not strictly related to biomass.

Biomass composition

The biomass composition is highly important to identify its value as a fuel, to provide an estimate of the burning characteristics and to predict problems associated to the quality and quantity of their ashes.

According to García *et al.* [24] the values of the moisture, volatile, fixed carbon and ash contents of the biomass fuels are very distinct. The moisture content can vary between ~ 10% for pre-dried biomass to as high as ~ 50% for collected field/forest residues. The moisture content depends on a combination of harvesting method, climatic condition, time of year when harvesting takes place, and the length and method of storage. Moisture content has a negative effect on combustion efficiency and at high values (> 10%) fuel pre-treatment may be necessary by drying processes. However, biomass with moisture level below 50% is effectively used in combustion.

Generally, biomass presents high volatile and low fixed carbon contents and the combustion of such highly volatile biomass requires specialized combustor designs to manage the rapid gas evolution when heated. Fuels with low volatile matter contents need to be burnt on a grate as they take a long time to burn out unless they are pulverized to a very small size. The biomass composition also helps to determine the optimal settings of the primary and secondary air supplies during combustion. The volatile matter content is in the range 65% to 85% for general biomass, and from 76% to 86% for woody biomass. Fixed carbon levels are generally between 7% and 20% [24].

The ash content (inorganic mineral) provides information on ash behavior. The ash elemental analysis and fusion temperatures can help to predict the problems of slagging, fouling and clinker formation. The expected values of ash content are close to 0.3% for wood without bark, but general values for alternative biomass fuels may be in between 5% and 21% [24]. Concerning the ash elements, the concentration and behavior of elements such as chlorine, potassium, sodium, phosphorus, sulphur, silicon and heavy metals are mostly responsible for many technological and environmental problems during biomass processing [19].

According to Vargas-Moreno *et al.* [22], the elemental composition of biomass consists of 30%-60% of carbon content, 5%-6% of hydrogen, and 30%-45% of oxygen (wt.%, on dry basis). The amounts of nitrogen, sulphur and chlorine, are generally small, accounting for less than 1% of the weight in dry basis (d.b.). The ultimate analysis is also used to predict the heat content of the fuel instead of using a calorimeter.

Table 2.1 presents some biomass physical and chemical characteristics and related possibly problematic effects that may occur when using biomass as fuel.

Table 2.1. Physical and chemical characteristics to their effects on biomass fuels [25].

Parameter	Effects
Physical characteristics	
Bulk density	Transport and storage expenditures, logistical planning
Unit density	Combustion properties (specific heat conductivity, rate of gasification)
Particle size distribution	Bridge-building tendency, operational safety during fuel conveying, drying properties, dust formation
Share of fines	Bulk density, transportation losses, dust formation
Durability	Quality changes during transshipment, disintegration, fuel losses
Chemical characteristics	
Water content	Storability, calorific value, losses, self-ignition
Calorific value	Fuel utilization, plant design
Element content	
Cl	HCl emission, dioxin/furan emissions, corrosion in super heaters
N	NO_x, HCN and N_2O emissions
S	SO_x emissions, decreased corrosion
K	Corrosion in super heaters, reduction of ash melting point (favors slagging), aerosol formation, ash utilization (plant nutrient)
Na	Corrosion in super heaters, reduction of ash melting point (favors slagging), aerosol formation
Mg, Ca	Raising of ash melting point, ash utilization (plant nutrient)
P	Ash utilization (plant nutrient)
Heavy metals	Pollutant emissions, aerosol formation, use / disposal of ashes
Ash content	Particle emissions, costs for use or disposal of ashes
Ash softening behavior	Operational safety, level of pollutant emissions
Fungi spores	Health risks during fuel handling

There are other parameters in the biomass composition that have huge impact on its quality as source of fuel. These include cellulose, hemicellulose, lignin, lipids, simple sugars and starch [22]. The structural components cellulose, hemicellulose and lignin may appear in biomass in six different orders (regarding relative quantity):

- cellulose > hemicellulose > lignin – biomass belonging mostly to groups and sub-groups of wood stems, herbaceous and agricultural biomass (grasses, straws, stalks, fibers, husks, residues) and contaminated biomass (semi-biomass);

- cellulose > lignin > hemicellulose – commonly the sub-groups of wood stems and agricultural husks;
- hemicellulose > lignin > cellulose – biomass belonging normally to sub-groups of wood barks, twigs and leaves;
- hemicellulose > cellulose > lignin – that include mostly the sub-groups of tree leaves and grasses;
- lignin > cellulose > hemicellulose – that belong commonly to groups and sub-groups of some herbaceous and agricultural biomass (shells/husks, pits, residues) and animal biomass (only a cattle manure);
- lignin > hemicellulose > cellulose – for wood bark and hazelnut shells.

Hemicellulose is abundant in annual and fast-growing plants or plant parts and this constituent plays a role of conducting and concentrating tissue for mineralized solutions abundant in sulphates, chlorides, nitrates and silicic acid in plants [20]. According to Al-Shemmeri *et al.* [26], cellulose is a primary structural component of the cell walls of biomass material. This long chain structured polymer is usually represented by the generic chemical formula $(C_6H_{10}O_5)_n$. Hemicellulose is another component of the cell walls of the plant, it is made up of random amorphous structures and it can be represented by the generic formula $(C_5H_8O_4)_n$. The binding agent present in the secondary cell walls, which acts like a cement between the cellulose fibers, is called lignin. Hemicellulose has closer characteristics to cellulose. Lignin has three-dimensional structures and is generally represented by $(C_{11}H_{12}O_4)_n$.

Biomass as solid fuels

Solid biomass fuels are available in a variety of forms to meet the requirements of heating equipments. These include the traditionally available logs and processed products such as chips, pellets and pulverized fuels mainly from wood, straw and a range of agricultural residues. The traded biomass need to fulfill the standards with respect to dimensions, moisture content, ash and nitrogen. In the case of the pellets, they are made from small particles (1 mm to 6 mm) of the biomass, with the lignin acting as a binding agent. However, alternatively, a binder may be added to the pellet producer [23]. The pellets have been

successfully implemented in the market as a solid biofuel to use in the domestic boilers. Its production consists of a few basic sub-processes: trituration of the raw material, drying, pelletizing and cooling.

In a common way, in the pellet production of biomass, the raw material is first grinded in a hammer mill or a chipping machine. The particle size is adjusted to a uniform maximum dimension, which is approximately 85% or less of the minimum thickness of the pellet to be produced. If necessary the next step is drying the high moisture content that the raw material can have, in some cases, 50%. For this, the residue from the hammer mill is transported to a dryer (generally a rotary drum) where the moisture content of the uniformly dimensioned particles is reduced to about 10%. After the raw material been dried and triturated, is moved to a pellet mill, where the pellets are extruded through the action of rollers acting on a perforated matrix. On the outer side of the matrix, a knife cuts off the pellets at the desired length. The residual moisture in the feedstock turns to steam during compression and helps lubricate the compression die. After the extrusion, the pellets are very hot (90 °C - 100 °C) and are immediately air quenched down to 25 °C. This sets up the lignin and hardens the product, and contributes to maintain its quality during storage and handling. Finally, it is screened in order to separate the residual fines that are generally re-used in the process. Dust free pellets are ready for storage or packing [25].

García-Maraver *et al.* [27] made a comparative study on the quality of biomass fuels, specially focused on the pellets. The pellets quality is directly related to their physical, chemical, and mechanical properties. Certain European countries have developed standards specifying control parameters and guidelines with a view to guarantee the effective and environmentally-friendly combustion of pellets to prevent operating problems in the equipments and turn the market more reliable. The application of a common standardization could be beneficial for Europe since it will remove an important barrier to the further development of European pellet and combustion technology market in general and will increase international pellet trade in particular.

The use of biomass fuels with fossil fuels, like in co-combustion processes with coal, is one of the most advantageous ways of utilizing biomass and waste for replacement of fossil fuels

for stationary energy conversion [28]. Table 2.2 compares the properties of coal and biomass [29].

Table 2.2. Comparative properties of biomass and coal.

Property	Observation
Pyrolysis	Starts earlier for biomass fuels compared to coal fuels and releases CO, CO_2 and H_2O.
Volatile matter	Higher in biomass compared to that of coal.
Heating value volatiles	Specific heating value of volatiles is lower for biomass fuels compared to those from coal fuel.
Heat contribution by volatiles	The fractional heat contribution by volatiles in biomass is of the order of 70% compared to 36% for coal.
Oxygen contents	Biomass char has more oxygen compared to coal.
Ash contents	Biomass fuels have ashes that is more alkaline than those from coal.

The use of biomass fuels has some positive and negative aspects. The advantages associated with the use of natural biomass are [19, 29]:

- It is a safer fuel to use because it does not have the high explosion risks or flammability of the fossil fuels;
- The waste from other activities (by-products) as biomass translates into energy recovery;
- The use waste reduction and the use of renewable energy reduces the dependence on external fuel supply;
- Usually low contents of ash, carbon, sulphur, nitrogen, and trace elements
- Normally high concentrations of volatile matter, calcium, hydrogen, magnesium, oxygen, and phosphorus;
- Great reactivity during conversion;
- Mitigation of hazardous emissions (CH_4, CO_2, NO_X, SO_X, trace elements);
- Capture of some hazardous components by ash during combustion;
- Huge availability and relatively cheap resource;
- Diversification of fuel supply;

- Rural revitalization with creation of new jobs;
- Potential use of oceans and low-quality soils, and restoration of degraded lands;
- Reduction of biomass-containing wastes;
- Cheap resource for production of sorbents, fertilizers, liming and neutralizing agents, building materials, and for some synthesis or recovery of certain elements and compounds.

However, the use of biomass as solid fuel also presents some disadvantages [19, 30]:

- The biomass-derived fuels have a lower energy density compared to fossil fuels (heating value: 50 MJ/kg of natural gas > 40 MJ/kg of diesel> 30 MJ/kg of coal> 18 MJ/kg of solid biomass);
- High investment cost;
- The raw material also has a low density, so it occupies a large volume, which makes difficult the transport and storage activities;
- High collection, transportation, storage and pre-treatment costs;
- Incomplete renewable energy resource for biomass fuel with respect to the complete life cycle assessment;
- Lack of accepted terminology, classification systems and standards worldwide;
- Insufficient knowledge and variability of composition, properties and quality;
- Commonly high contents of moisture, chlorine, potassium, sodium, manganese, and some trace elements;
- Potential competition with food and feed production;
- Possible soil damage and loss of biodiversity;
- Odor, potential emission and leaching of hazardous components during disposal;
- Possible hazardous emissions during heat treatment;
- Potential technological problems during heat treatment (agglomeration, deposit formation, slagging, fouling, corrosion, erosion);
- Regional and seasonal availability.

Portugal has a high potential as a solid biofuels producer [3]. With more than one third of its area covered by forest, there is great potential for reducing its dependence on fossil fuels. In 2010 Portugal imported 75.45% of the primary energy consumed [31]. The Portuguese wood

pellet production reached 700 kton in 2012 [32]. The Eurostat data from 2010 showed a significant volume of exports: around at 695 kton of pellets, mainly to the United Kingdom (291 kton), Denmark (246 kton) and Sweden (105 kton) [1]. In the study of Esteban *et al.* [33] the potential, availability and average annual production of agricultural and forest biomass was calculated for the Portuguese territory, as presented in Table 2.3.

Table 2.3. Biomass resources estimated in Portugal [33].

Residues	Potential (kton/year)	Availability (kton/year)	Average annual production (ton/ha/year)
Forest	2230	640	0.29
Agricultural	2380	1700	0.96

Although there is a large biomass potential through all Portuguese territory, its exploitation as an energy resource has not been quantified. The Portuguese territory is mainly occupied by 35% forest area and 24% agriculture [34]. The rest of the territory consists of woods and pastures (32%), unproductive (2%), inland waters and wetlands (2%) and urban area (5%). The different crops and forest species dispersed in these regions can be sources of biomass residues, either permanent or seasonal.

As a final product for combustion, the biomass can be presented in various forms: logs, chips, briquettes, pellets or pulverized, from higher to smallest size fuel. Depending on the fuel type, the combustion technology required differs. In the last 10 years the pellet market has grown considerably. The technology applied to pellet boilers allows the final costumer to have efficient equipment, obtaining the convenience of using biomass instead of fossil fuels. In terms of the European situation, Portugal has, currently, a high production of pellets (see Figure 2.1).

In this work, the woody biomass considered was essentially forest, agriculture and industrial residues so that the herbaceous residues were excluded due to its lower carbon content, higher ash content and problematic alkali elements [35].

2.1.1 Forest residues

The forest is the main source of biomass solid fuels and the *Pinus pinaster* is the most common tree species used in Portugal [32]. *Pinus pinaster* is the second most common species in the Portuguese forests (23%), after *Eucalyptus globulus* (largely used by the paper industry) [34]. These species are mostly used by the wood industry in Portugal as the main raw material used by the furniture industry. Thus, pine sawdust is the most common residue to produce the pellets. It presents low levels of moisture, the granulometry is close to the desired levels and favorable to produce the wood pellets. The wood comes mainly from the trunk of trees, without bark (where the major minerals and noncombustible material are located). The identification of biomass resources in Portugal has major importance in understanding its energy potential. Viana *et al.* [36] used a GIS (Geographic Information System) analysis to calculate the quantities of residues from *Eucalyptus globulus* and *Pinus pinaster*. According to this study, the forest area has more than 1.355 million hectares of these species with more than 600 kton/year of dry biomass available.

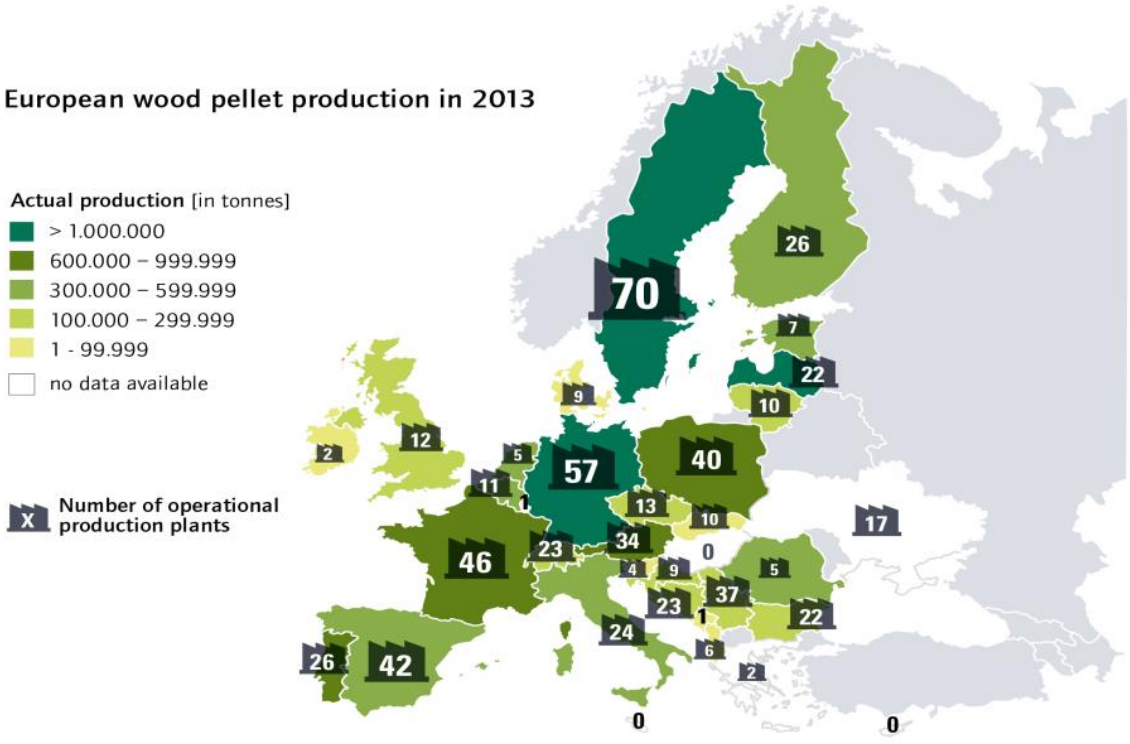


Figure 2.1. Power plants and actual production in European countries [37].

According to a study carried out by Telmo *et al*. [38], several Portuguese and tropical woody biomass species used in the Portuguese market have great potential to be used as biomass fuel, with heating value for energy recovery. Its lower heating value (LHV) varies between 15 MJ/kg and 18 MJ/kg and the higher heating value (HHV) varies between 18 MJ/kg and 21 MJ/kg. *Pinus pinaster*, as the reference woody biomass used for combustion, has an HHV of 20.2 MJ/kg and an LHV of 16.9 MJ/kg, with a moisture content of 10.3%.

2.1.2 Agriculture residues

Agriculture produces around 1.7 Mtons of residues in Portugal [33]. These cultures are usually used for food production and the herbaceous residues for animal foods. However, the woody residues from pruning activities are not used in Portugal as a resource. A study carried out by Voivontas *et al.* [39] characterized the woody and herbaceous residues in terms of potential availability, moisture content and energy recovery from each crop. These values show that the woody cultures have higher potential to produce residues and higher energy can be recovered from this biomass in comparison to herbaceous cultures.

According to the data provided by Portuguese statistics [40], the most cultivated agriculture crops are cereals and industrial crops, followed by the fruit cultures of vineyard, fresh fruits and olive grove. The latter are the suitable to obtain residues to produce biomass fuels. Olive groves and vineyards are two cultures widely produced in Portugal. Esteban *et al.* [33] studied the productivity of residues that can be used as energy, for different crops species, and calculated that vineyard yields 0.3 kg residue/kg and olive yields 0.5 kg residue/kg.

The agricultural residues can be obtained through straw, fruit stone, dry fruit waste, cork, grain, cotton, malt and tobacco waste, with obviously, woody residues. In this work, the residues studied resulted from pruning activities, consisting of leaves and branches. Usually, these residues are burned in the fields by the farmers (Figure 2.2), but these residues that can be used as solid biofuel in various heating equipments. The availability of the agricultural residues resulting from pruning activities discussed so far was considered for the selection of the woody biomass sources used in this work.

The agricultural residues selected in this work were residues of vine, olive, kiwi and platanus. Vine branches are the largest source of agricultural residues in Portugal. Vine crops require a pruning season from December to January every year, a few months after the harvest vintage (September and October). The branches collected from pruning may yield as much as 4.97 ton/ha of residues, with a 45% moisture content, an HHV of 18.9 MJ/kg in dry basis and 90% of energy recovered from biomass [39].



Figure 2.2. Farmer burning agricultural biomass in the field.

Olive cultures are one of the most common agricultural productions. Olive production prevails in Mediterranean countries, such as Spain, Portugal, Italy, Greece, Turkey, Tunisia and Morocco, where 90% of the world's production takes place [41]. Olive oil has a large impact in the economy of rural regions. The potential of pruning residues for heating is high. Yet unexplored, the olive groves, used to produce olive oil as principal product, also produce olive stones and bagasse that can be used as source of biofuel. This has already been studied and used. The pruning of the olive groves, however, also produces high quantities of branches that have not been explored. The branches collected from pruning have potential to produce 2.82 ton/ha, with 35% moisture content, an HHV of 18.1 MJ/kg and 90% of energy recovered from biomass [39].

Kiwi and *platanus* residues have not been yet considered for combustion. However, due the high production of these residues from the pruning activities they can be an interesting biomass fuels. Portugal produces annually about 23 kton of kiwi in 1581 ha of plantation [40]. The production of kiwi is growing in the north of Portugal (where more than 75% of national production is located) due to its favorable climatic conditions. The cultivation of kiwi requires a winter pruning operation between December through mid-February. The *Platanus* tree genus is very common in Portugal. Currently it is widely used as ornamental, flanking the urban roads and decorating parks and gardens, or as support piling of hanging vineyards in the sub region of *Alto Minho*.

2.1.3 Industrial residues

Industrial residues of carpentry, sawmill, panels and veneers and furniture industries are the main applications for the species *Pinus pinaster* and *Eucalyptus globulus*, and high quantities of residues are produced by these industries (~ 600.2 dry kton/year) [42]. Furniture wastes have several applications in the market, as medium-density fiberboard (MDF) or particleboard. These residues contain small concentrations of formaldehyde and other compounds that can cause problems to human health. This has been studied in respect to combustion gaseous emissions and chemical composition [43]. The furniture waste combustion was studied by Rabaçal *et al.* [44] in a domestic pellet boiler (22 kW), revealing high levels of NO_x emissions. No other problems were detected by this study in furniture wastes pellets. Previous studies carried out by Dias *et al.* [45] have shown this problem regarding the NO_x emissions, and also concluded that increasing excess air contributes to raise these emissions. Yorulmaz *et al.* [43], focusing on pellets obtained by furniture waste such as MDF, revealed that treatment of wood with additives and glues, appears to change the oxidation mechanisms.

In addition to the traditional use of sawdust as sole raw material, there has been a growing interest in the incorporation of residues from the processing industry, such as the cork sector, with the black granulated cork as the main residue. This material corresponds to the outer bark of a tree of cork oak (*Quercus suber).* The cork granulated can result from various

operations including grinding, cleaning, particle size separation of granulated and finished panels/boards clusters.

2.2 Biomass combustion

The biomass combustion is a complex process that consists in various consecutive homogeneous and heterogeneous reactions [46]. In a simple way, the biomass combustion includes the following steps: heating-up, drying, devolatilisation to produce char and volatiles (tars and gases), combustion of the volatiles, and combustion of the char [23]. In combustion, the heating, drying and thermal decomposition of biomass fuels are endothermal processes and the volatiles and char oxidation are exothermal processes [47]. These reactions consist of three distinct stages. The first is the preheating phase (1st stage), the second process is the distillation phase or gaseous phase (2nd stage), and the third process is the charcoal phase or solid phase (3rd stage). In the 3rd stage, after the volatile matter being released, the oxidation of the carbon originates CO and CO_2, as shown in Figure 2.3.

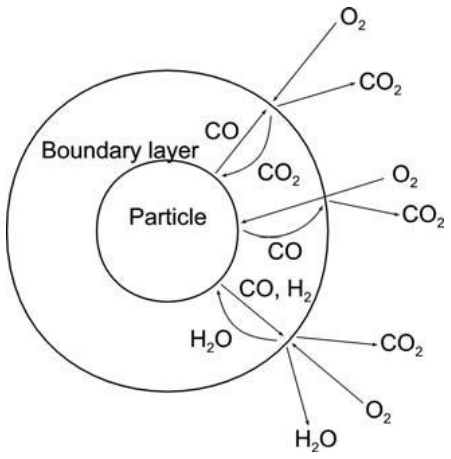


Figure 2.3. Oxidation of a carbonous particles [48].

To understand these phenomena, the thermogravimetric analysis (TGA) is essential. The results of a TGA analysis depend on fuel type, heating rate and oxidizer composition, among others. The different stages can be distinguished in a TGA curve (see Figure 2.4). For instance, for biomass fuels it can be observed that the fractional heat contribution from the

devolatilization is approximately 70%, which is significantly higher than that for coal (30%-40%) owing to the lower volatile matter of the coal [49].

According to the study of Vamvuka *et al.* [50], the ignition and burnout temperatures increase with particle size and moisture content of the fuels and decrease with oxygen concentration in the oxidizer. The temperature at which the biomass exhibits maximum combustion rate, the ignition and the burnout of the fuel are parameters important to establish the residence time desired for the biomass in the combustion chamber. These parameters can be obtained by the derivative of the TGA curve (DTG). Moreover, the thermogravimetric analysis is very useful to study the kinetics of the combustion processes and it has been used extensively in biomass combustion and co-combustion studies [47, 51–53]. According to Williams *et al.* [23] the rates chosen for the regimes of drying, pyrolysis and char combustion depend on particle size and can be defined as thermally thin, or thermally thick with thermal wave regimes. In the first case, the temperature is constant across the particle and this is normally assumed in the heating up step for small particles in the drying and pyrolysis steps, as in pulverized combustion. For larger particles, as in fluidized or fixed beds, a thermal wave is assumed to pass through the particle, causing sequential drying, pyrolysis, char formation and then combustion. In this case all the regimes coexist. The thermally thick case is assumed when there are large sized material involved and considerable thermal gradients.

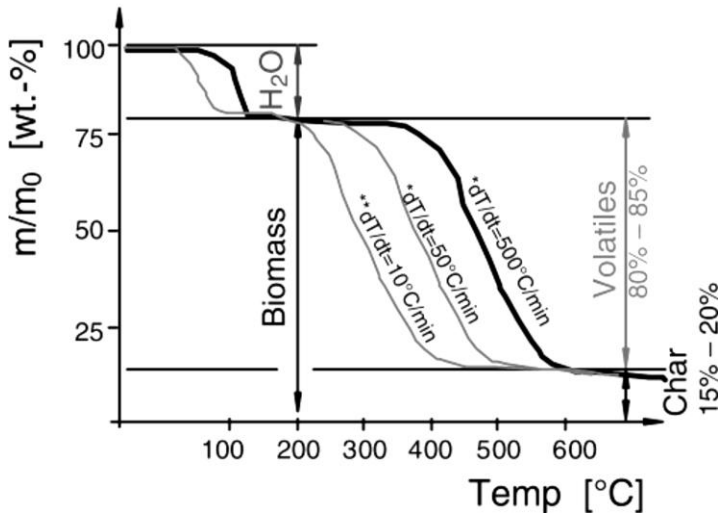


Figure 2.4. Decrease of initial mass during combustion of biomass in different combustion stages [46].

Combustion reaction

Knowledge of the biomass composition is essential to predict the combustion products that can be formed. Biomass wood is generally composed by volatiles (76%), fixed carbon (21%) and ash (3%), in dry basis [29]. Besides the ashes, biomass is composed by different quantities of carbon, hydrogen, nitrogen, oxygen, sulphur and chlorine. These elements have a high impact in the formation of the gaseous emissions. The combustion process evolves through several steps (which as mentioned before can be distinguished in a TGA curve) that transform the fuel in the combustion products, and specific products can be released at specific stages.

Formation of gaseous products in a typical biomass combustion process is described by Equation (2.1). In this case the constituents of the fuel, nitrogen, sulphur, chlorine, and ashes are neglected due to the low amount of these compounds.

$$CH_{1.44}O_{0.66} + \lambda 1.03\ (O_2 + 3.76\ N_2) \rightarrow CO_2 + 0.72\ H_2O + (\lambda - 1)O_2 + \lambda 3.87\ N_2 \quad (2.1)$$

In the reaction the intermediate compounds are C, CO, H_2, CO_2, C_mH_n, etc.).

The average typical composition of the biomass is $CH_{1.44}O_{0.66}$ [54]. This composition is representative for wood, straw, or similar. As a result of the biomass combustion process the following products can be distinguished:

- Products resulting from the complete combustion such as NO_x (NO and NO_2), CO_2, and H_2O;
- Unburned pollutants such as CO, C_XH_Y, PAH, C, H_2, HCN, NH_3 and N_2O;
- Ash and contaminants such as KCl, SO_2, HCl, Cu, Pb, Zn, Cd, etc.

The combustion process of biomass is characterized by some problems caused from its products. In the case of the combustion of solids fuels, they are divided in solid and gaseous products [48]. The gaseous emissions resulting from the combustion originates some GHG that are released to the atmosphere increasing the average global temperatures to historic maximum records [55]. The treatment of these combustion gases is required when its impact in the environment and human health is harmful. Consequently, national laws limit the levels of some compounds released to the atmosphere during combustion [54].

2.2.1 Gaseous emissions

The gases released during combustion arise mainly from the volatile matter in the biomass composition. The combustion step when this volatile matter is released is characterized by a high reaction velocity. The higher concentration of volatile compounds is present near the particles surface. The release of these volatile compounds can generate some pollutants. In a general way, all combustion applications have the potential to release airborne pollutants such as methane and volatile organic compounds (VOC), nitrogen oxides, sulphur oxides, hydrogen chloride, polyaromatic hydrocarbons (PAH), furans and dioxins, as well as organic and inorganic aerosols [23]. Table 2.4 identifies some of the main pollutants produced by the combustion of biomass revealing its characteristics, sources and effects on human health. Some of these emissions are mainly produced from the incomplete combustion due to low combustion temperatures, short residence times, bad mixing conditions with oxygen (or oxygen shortage) or combinations of these effects [25].

Table 2.4. Main species generated by the gaseous emissions of biomass combustion [56].

Pollutants	Characteristics	Sources	Effect on human health
Carbon monoxide (CO)	Colorless, odorless, strong affinity to blood hemoglobin	Incomplete combustion of carbonaceous compounds	Absorbed by the lungs, impairs the physical and mental abilities; affect fetal development
Hydrocarbons (HC)	Organic gas in the form of particles or components (such as methane, ethylene, acetylene)	Incomplete combustion of carbonaceous compounds	Causes irritation in the eyes, nose, and throat; Prolonged exposure may causes cancer
Nitrogen oxides (NO_x)	Gas mixture ranging from colorless to red-brown	Stationary combustion of solid fuels by oxidation of nitrogen on material composition	Respiratory and cardiovascular diseases
Sulfur dioxide (SO_2)	Colorless gas with pungent odor; tri-oxidation to form oxide sulfate (SO_3) and sulfuric acid in water	Combustion of sulphur contamination by fossil fuels	Classified as slightly irritating to the respiratory system, leading cause of acid rain

Carbon dioxide formation

CO_2 is the main product resulting from the combustion. It is an odorless, colorless and inert gas, which is not harmful to the existence of life. However, if it replaces the oxygen at higher quantities, in concentrations between 3% and 6% can cause headaches, shortness of breath and sweating. Between 6% and 10% can cause headaches, visual disturbances, tremors and unconsciousness. Concentrations above 10% can cause unconsciousness and eventually lead to death acting as an asphyxiant. This compound is a major factor to global warming caused by the greenhouse effect. In the combustion, the analysis of this product can also be a good indicator of the thermal capacity of a device [57].

Carbon monoxide formation

Carbon monoxide (CO) is one of the combustion products more controlled due to its impact in the environment, human health and combustion efficiency. It results from incomplete combustion. The formation of this slightly flammable and very dangerous (due to its high toxicity in high concentrations) gas has been extensively studied. In equilibrium conditions carbon monoxide is given by Equation (2.2):

$$CO_2 \rightarrow CO + 1/2\ O_2 \quad (2.2)$$

In rich fuel zones of the flame, CO levels are necessarily high, since there is not enough oxygen to complete the combustion. In the flame, the concentration of CO is rapidly formed and subsequently oxidized to CO_2 by the reaction expressed in Equation (2.3):

$$CO + OH \rightarrow CO_2 + H \quad (2.3)$$

If the reaction time for the combustion is lower, as in equipments with a reduced combustion chamber, the tendency for incomplete combustion is higher.

Hydrocarbons formation

The unburnt hydrocarbons (HC) are other compounds resulting from incomplete combustion of biomass. They also contribute to ozone formation and some HCs are classified as

carcinogens [25]. HCs are one of the consequences of the thermal degradation of fuels, which do not react with the oxidant. They are usually associated with low reaction rates induced by temperature reduction, in particular by the walls of the boilers. Although these mechanisms are more complex than those associated with the formation of CO, it turns out that the factors influencing CO emissions also affect the way the HC emissions. To reduce their formation is important to control the characteristics of admission of the fuel and the air mixing with the fuel [58].

Nitrogen oxides formation

Nitrogen oxides (NO_x) emissions represent the nitrogen oxides formed during combustion. The main ones are NO, NO_2, N_2O, which are collectively referred as NO_x. The two nitrogen oxides which are mainly studied in air pollution are NO and NO_2. NO_x emissions generated by combustion are obtained through three mechanisms: (1) thermal phase of NO_x, (2) NO_x released and (3) NO_x from nitrogen in the fuel (see Figure 2.5).

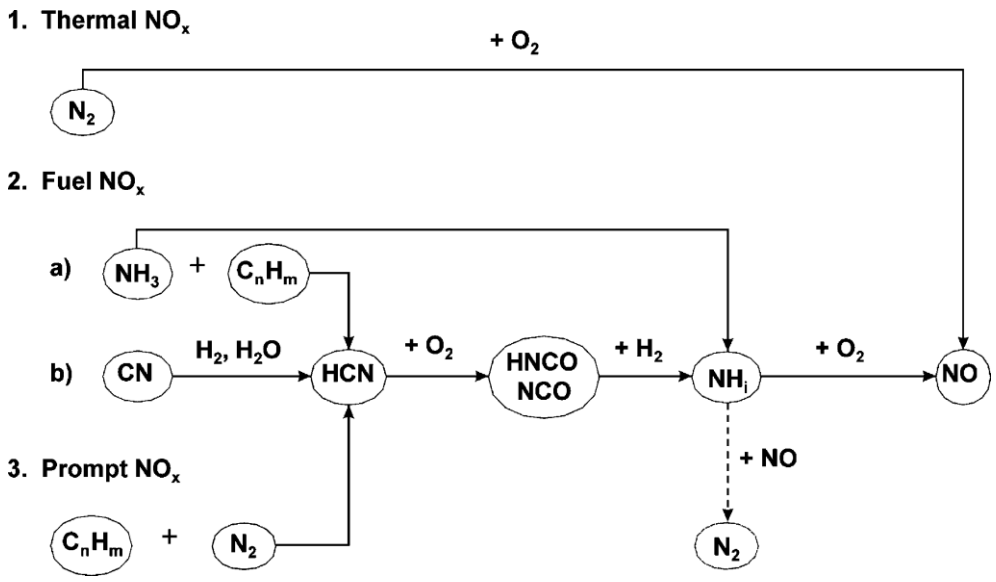


Figure 2.5. Three types of nitrogen oxides release [48].

In solid fuel composition, the majority of the NOx is produced from the fuel-bound nitrogen, which in biomass is present as nitrates. Fuel-nitrogen containing species are released in combustion both during the devolatilization and the char combustion stages [23]. The

combustion control techniques that aim to reduce the thermal NO_x formation by decreasing the flame temperature may not be effective for solid fuels with high nitrogen content. The relative importance of the NO_x formation mechanism depends of the combustion temperatures (Figure 2.6).

The main techniques to NO_x emissions control are based in the combustion modifications and/or treatment of the combustion products. Some techniques promote the reduction of the flame temperature, by reducing the oxygen in the primary zone. The recirculation of the combustion products in a combustion system can reduce the levels of NO_x. This strategy causes the decrease of oxygen concentration in the flame zone and adds an additional amount of inerts gases (N_2 and CO_2), which decreases the rate of heat and reduces the flame temperature.

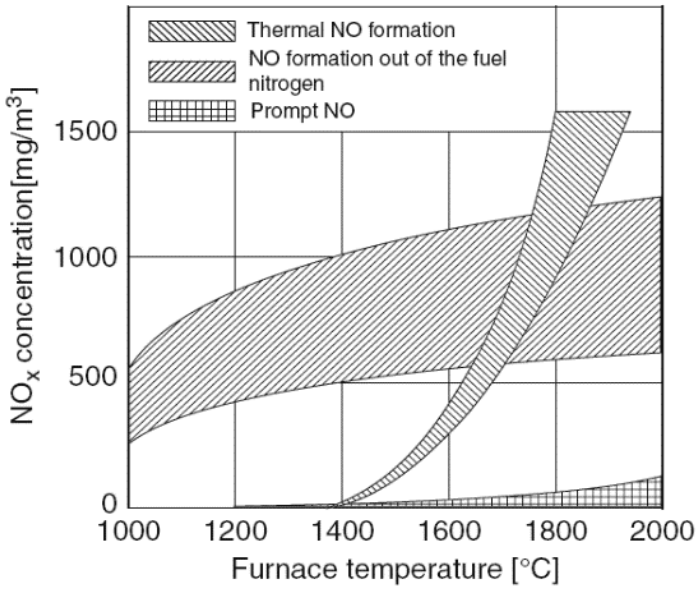


Figure 2.6. Importance of the NO_x formation mechanisms as a function of the temperature [48].

Sulfur oxides formation

Sulphur is a major plant nutrient and is necessary for the metabolism of plants. Normally it is taken up from the soil in the sulphate form although it can be assimilated from sulphur dioxide in the air, and the leaves have the highest content. Sulphur is released as SO_2 during

both volatile and char combustion [23]. Sulfur dioxide **(**SO_2) emissions are the major product of sulphur emissions and the principal contributor to the acid rain. This compound can be very corrosive in the presence of water. The main techniques to eliminate the SO_2 emissions are the removal of sulphur from the fuel and the injection of dry limestone [48]. It can also contribute to the acidification of the atmosphere [25]. Table 2.5 summarizes aspects to be considered in treatments of the principal pollutants from biomass combustion.

Table 2.5. Aspects to be considered in treatments of the principal pollutants from biomass combustion [25].

Parameter	Relevant aspects to be considered
CO_2	Straw, as well as other agricultural residues is considered CO_2 neutral, because released CO_2 re-integrates the vegetal carbon cycle
CO, HC, PAH, tar, soot	Complete combustion: appropriate residence time and oxygen content
Particles	Flue gas cleaning systems
NO_x	Fuel preparation to lower N content (leaching, fuel mixing) Primary measures: air-staging, Fuel staging Secondary measures for N-rich fuels (case of straw): SNCR, SCR
SO_x	Possibilities of reduction (ecologically relevant if fuel S-content > 0.2 wt% d.b.): Efficient fly ash precipitation
HCl	Possibilities of reduction (ecologically relevant if fuel Cl-content > 0.1 wt% d.b.) Efficient fly ash precipitation
PCDD/F	Possibilities of reduction (ecologically relevant if fuel Cl-content > 0.3 wt% d.b.) Complete combustion at low excess air ratio, efficient fly ash precipitation at < 200°C

2.2.2 Ashes

The combustion of biomass has been studied extensively regarding the ash related problems [6, 13, 58–65]. Biomass contains in its composition a number of elements that are problematic to the equipment and to the environment. These elements can be transported in the particulate matter and gaseous emissions, deposited on the internal components of the equipments or ending in the bottom ashes forming slagging or sintering. According to Wang *et al.* [67], the various possible phenomena are release and volatilization of inorganic species, interaction of inorganic elements with formation of salts, interactions between solid phase

particles and release of volatile inorganic species, fusion or partial fusion of low melting point ash components and sintering of unburned char residues and inert solid ash residues due to presence of molten phases. Some studies, e.g., [67, 68] proven also that the composition of these volatiles and residual ashes can differ in terms of some toxic metals such as arsenic, cadmium, chromium, copper, lead and mercury. According to Jenkins *et al.* [15], chlorine has a major impact in the ash chemistry. Chlorine facilitates the mobility of many inorganic compounds, in particular potassium. Potassium chloride is one of the most stable high-temperature compounds, in gas-phase, as alkali-containing species. The chlorine concentration also dictates the amount of alkali vaporized during combustion which is as strongly as the alkali concentration.

Some biomass fuels, such as the wheat straw, presents high levels of potassium and silica from the formed oxides during the combustion (SiO_2 and K_2O) [13]. Others studies, e.g., [21, 69] correlated different alkaline compounds, which have lower fusion temperatures, with acid compounds in ashes to increase the fusion temperature of the ashes. This variation changes the capacity of ash fusibility enhancing the chemistry behavior of the ashes.

Some elements react easily at relatively low temperatures when oxidized with others during the combustion process [11, 13, 15]. Nilsson *et al.* [71] pointed out that agriculture residues have low raw material costs, but can cause serious ash-related problems and should be avoided in small-scale boilers. Some agricultural and forestry residues have been tested with relevant results regarding the particulate matter emissions and ash problems [71–73]. An interesting study presented some alternative residues to produce wood pellets and promote a starting point to the rational exploitation of some non-profitable residues according to the quality standards applicable in the pellets market [75].

According to Saidur *et al.* [29], the ash analysis can be used to predict the biomass ash-related problems that can occur in a boiler. The composition of the biomass ash is strongly dependent on the species and part of the biomass plant. The available nutrients, soil quality, fertilizers and weather conditions have significant impact on the contents of potassium, sodium, chlorine and phosphorus, especially in agro-biomass ashes. Generally, biomass fuels can be divided into three groups on the basis of their ash composition:

- Most biomass fuels have calcium, phosphorus rich and silicon lean. However, the ash of woody biomass is typically rich in calcium and potassium, with high fusion temperatures;
- Biomass fuels with silicon rich and in calcium, potassium lean ashes, are mostly from the group belonging to herbaceous, or agricultural residues, with low fusion temperatures. Some of the biomass fuels, like cereal straws have also relatively high potassium and chlorine contents. Rice husk and bagasse have very high SiO_2 contents in their ashes;
- Biomass fuels calcium, potassium and phosphorus rich ashes, include manures, poultry litters, animal wastes, sunflower stalk and rapeseed expeller from food production with low fusion temperatures.

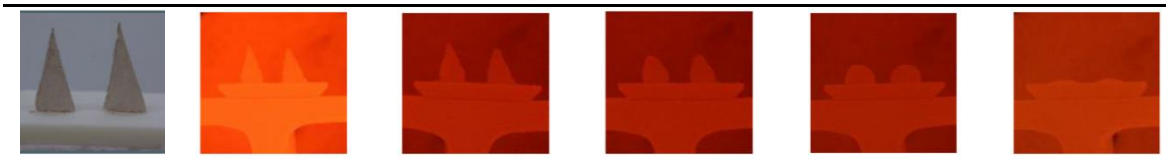
The inherent inorganic material exists as part of the organic structure of the fuel, and is most commonly associated with the oxygen, sulphur and nitrogen-containing functional groups. Inorganic species can also be present in very fine particulate form within the organic structure of some of the fuels, and to behave essentially as an inherent component of the fuel. The extraneous inorganic material, which has been added to the fuel through geological processes, or during harvesting, handling and processing of the fuel. Biomass fuels are commonly contaminated with soil and other materials, which have become mixed with the fuel during collection, handling and storage [76].

Ash characterization techniques

The ash analysis can be used to evaluate levels of some materials that can lead to the formation of deposits and slag. Ash problems can be characterized with the aid of techniques such as:

- Chemistry analysis of elements in ashes, where sulphur and chlorine contents and the major trace elements are identified;
- Ash melting temperatures (Figure 2.7);
- Slagging and fouling indices – ranking methods based on the chemical analysis and ash fusion data (Table 2.6);
- Ternary analysis of elements, slagging and fouling indexes (Table 2.6);

- Chemical fractionation techniques based in water, buffer and acid solutions;
- Scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS) analysis.



Ash (initial geometry)	**Start** Heating	**DT** (Initial deformation temperature)	**ST** (Softening temperature)	**HT** (Hemispherical temperature)	**FT** (Fluid temperature)

Figure 2.7. Evolution of ashes fusion temperature behavior [76].

As referred by Vassilev *et al.* [5], the melting point that occur only for pure substances (mono-component) can be uniform, while biomass ash as a multicomponent system of elements cannot have a specific melting point given its heterogeneity. The biomass ashes present, thus, three or four characteristic and measurable ash melting points over a wide temperature range.

Prediction of ash-related problems

The slagging and fouling phenomena are related to deposition and corrosion in equipments operating with solid fuels. The former is produced at high temperature zones, mainly on combustion chamber walls, whilst the latter is typical at low temperature zones, like heat exchanger surfaces [77]. According to recent studies, e.g., [21, 62, 77], the occurrence of biomass ash-related problems can be predicted with the aid of empirical parameters for slagging and fouling tendencies, as shown in Table 2.6. Most of the ash problems occur at normal combustion temperatures (850 °C a 1400 °C), that are able to melt the ashes and volatilize the fuel [62, 78].

The behavior of the ashes during the biomass combustion has generated high concern to the heating equipment market. The accumulation of ashes is a serious problem on the utilization of some biomass residues generating deposits, agglomeration, clusters and corrosion in the

combustion chamber and internal components of the equipment [66]. Figure 2.8 shows some of the problems related to the biomass ashes. Slagging and fouling in solid combustion pose serious problems in the internal components and in the performance of the equipment. The slag formed in the boiler grate blocks the primary air inlets, impairing the combustion and eventually extinguishing the flame. The fouling in the heat exchanger decreases the useful heat to inadequate levels, increasing the power demand and the maintenance costs.

Table 2.6. Slagging and fouling indexes used in biomass combustion [15, 62, 77, 79].

Index	Formula	Range of values	Slagging and fouling tendency
Alkalis index (AI)	$\mathrm{AI} = \frac{\mathrm{Kg\ (Na_2O + K_2O)}}{\mathrm{GJ(Biomass)}}$	> 0.34 0.34 > AI > 0.17	certain probable
Ratio base/acid ($R_{b/a}$)	$\mathrm{R_{b/a}} = \frac{\mathrm{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}}{\mathrm{SiO_2 + Al_2O_3 + TiO_2}}$	> 1 0.5 < $R_{b/a}$ < 1 < 0.5	high medium low
Total alkalis (TA)	$\mathrm{TA = Na_2O + K_2O}$	> 0.4 0.3 > TA > 0.4 < 0.3	high medium low
% Silica (% Si)	$\%\ \mathrm{Si} = \frac{\mathrm{SiO_2 \times 100}}{\mathrm{SiO_2 + Fe_2O_3 + MgO}}$	<66.1% > 78%	high
Silica/Aluminum and Iron/Calcium index (Si/Al)	$Si/Al = \frac{SiO_2}{Al_2O_3}$ *and* $\mathrm{Fe/Ca} = \frac{\mathrm{Fe_2O_3}}{\mathrm{CaO}}$	0.31 < Si/Al or Fe/Ca < 3	medium to severe
Fouling index (Fu)	$\mathrm{Fu = R_{b/a} \times\ TA}$	> 40 1.6 < Fu < 40 0.6 < Fu < 1.6 < 0.6	Extremely high high medium low
Slagging index (Sr)	$\mathrm{Sr} = \frac{\mathrm{SiO_2 \times 100}}{\mathrm{SiO_2 + Fe_2O_3 + CaO + MgO}}$	< 65 65 < Sr < 72 >72	high medium low

The slag is referred to as slagging when the deposits are in a molten or highly viscous state. Slagging is often found in the radiant (from the flames) section of the furnace. High potassium contents contribute to lower the ash melting point, which can favors slagging. Other elements have been identified as contributing to the hard deposit formation such as silicon, aluminium, and iron. The critical level of silicon was found to between 20 wt.% to 25 wt.% of the fuel ash. However, slagging problems were reported for higher concentrations than this. The deposits can also be caused by the volatile alkali, which also lowers the ash fusion temperature.



Slag	**Deposits**	**Fouling**	**Corrosion**
blocks the primary air to the boiler grate	reduces the heat transfer	reduces the heat transfer and the equipment yield	damages the equipment

Figure 2.8. Problems from the ashes in biomass combustion.

The fouling is formed when deposits build up largely from species that have vaporized and then condensed. They also occur in the cooler furnace regions where heat exchangers are located.

Corrosion is promoted by elements such as potassium and chlorine. It has been shown that even a small concentration of chlorine in the fuel will result in the harmful formation of alkaline chloride compounds on the boiler heat transfer surfaces [25].

The ashes can follow two different ways: fly and bottom ashes. The fly ashes are characterized by easily flow elements or compounds that can go through the flue gas emissions. They can deposit in various internal components of the heating equipments, damage or corrode and reduce the heat exchange, and emit healthy and environmental problematic elements. More specifically, the deposits of ashes in the heat exchangers reduce its capacity, and cause cleaning and mechanical problems in the heating equipment [70]. The

bottom ashes are composed by those that remain in the grate or fall to the boiler ashtray. The most problematic issue is the slagging formation by some ash elements. It can promote the obstruction of the air supply to the fuel combustion and the increase of the fuel bed to dangerous limits [81].

2.2.2.1 Bottom ashes

The bottom ashes are mostly affected by the slagging behavior of some elements. The slag formation is characterized by the formation of reactions in some elements or compounds, normally melting at lower temperatures. According to [5], the biomass ash can melt between 700 ºC and 1500 ºC. The agglomeration or occasionally swelling of the particles begins at 700 ºC, occurs extensively from 900 ºC to 1100 ºC and is complete at 1100-1500 ºC with the fusion of particles or minerals with different melting points. The oxides generally present in ash are (along its melting point): MgO (2800 ºC) > CaO (2613 ºC) > Al_2O_3 (2020 ºC) > SiO_2 (1723 ºC) > Fe_2O_3 (1566 °C) > Na_2O (1132 °C) > K_2O (350 °C) > P_2O_5 (340 °C) [59]. Complex ash transformations and chemical reactions may occur during the combustion of biomass, resulting in the formation of the ash matter [67].

According to Jenkins *et al*. [15, 80], the quantities of CaO, K_2O and SiO_2 have high influence in the ash fusibility. The minimum melting temperature of some compounds with potassium and chlorine are lower in the presence of other compounds in the combustion process. Jensen *et al.* [82] carried out SEM/EDS analysis to verify that the same compounds have different fusion temperatures when mixed in different quantities. At lower temperatures problems with ashes can be also important – some can melt at low temperatures as indicated in Table 2.7.

In order to evaluate these problems biomass mixtures have been tested. For example, the formation of deposits in the co-combustion of pine and olive stones with coal decreased compared with the pure coal firing [65]. Other studies, e.g., [14], [28] verify that biomass fuels with high contents of alkaline compounds cause lower ash fusion temperatures of the ashes compared with coal. Besides the minerals in the raw material, some elements are added in the collection and storage stages [83].

Table 2.7. Minimum fusion temperature for the compounds and mixtures of potassium and chlorine.

Compound	Minimum fusion temperature (°C)
KCl	774
K_2SO_4	1059
KCl + K_2SO_4	694
KCl + $FeCl_2$	355
K_2O + SiO_2	750
$K_2O.4SiO_2$ + $CaO.SiO_2$	740
KCl + K_2SO_4 + Fe_2O_3	577

According to Wang *et al.* [67], the utilization of some additives can prevent the problems associated with the ashes. The main additives referred by these authors are aluminum silicates based additives, which raise the melting temperatures up to 1600 ºC; sulphur based additives in order to convert the KCl to K_2SO_4, which considerable reduces the fouling deposits formed; the calcium based additives which dissolve the potassium silicates and force the release of potassium being through flue gaseous emissions.

The quantity of ash deposits produced is affected by the type of burner and biomass [11]. However, the indexes of sintering are mostly influenced by the chemical composition of the fuel. The primary and secondary air and chamber combustion design have a significant impact in the ash behavior. The regulation of primary air has a more significant impact [84], controlling the rate of carbonous residue burnt and the temperature in the grate [85]. Numerical studies [86] also showed an increase in the temperature of the chamber combustion with the supply of primary air, which has an important role in the combustion efficiency.

2.2.2.2 Fly ashes and particulate matter emissions

Part of this work is focused on the evaluation of the fly ashes and particulate matter from the combustion of alternative biomass fuels in a domestic pellet boiler and large-scale furnace. The combustion of biomass is a source of formation and potential emission of volatile organic compounds (VOC), black mixture of hydrocarbons (tars), polycyclic aromatic hydrocarbon (PAH) and impure carbon particles resulting from the incomplete combustion. The

composition of the gases, tars and chars derived from biomass combustion depend on the heating rate, final temperature, and mineral (especially potassium) content, among others. The distribution of the trace species such as nitrogen, chlorine, phosphorus and the metals between the gases, the tar and the solid material that remains after the volatilization of the light gases (char) is important in relation to their subsequent reaction and formation of pollutants [23]. However, various mitigation technologies were available for the particulate collection which have been shown to be effective in reducing these emissions [87].

Particulate matter formation

According to [88], the particles can be differentiate in two main groups from woody biomass combustion: the particulate matter from complete combustion including inorganic material in the flying ash, and the particulate matter from incomplete combustion including soot, condensable organic particles, and char. The decomposition of the char residue is shown in Figure 2.9. In this representation the particle size can be reduced from 100 μm down to 0.1 μm between 1000 ºC and 1500 ºC. However, the size of a biomass exhaust particle can be between less than 0.01 μm up to greater than 100 μm. However, the majority of biomass combustion aerosols is typically smaller than 1 μm in diameter with the mass distribution centered on 0.2 μm.

The chars formed represent about 10% to 30% of the total biomass. Its combustion, however, form important pathways for the release of many pollutants especially nitrogen and many inorganic species. The fragmentation of the char particles in the combustion occurs after the end of the devolatilization, although in practice a small fraction of char oxidation begins earlier and co-exists with the devolatilisation process. Here, the reaction front passes from the external surface to the center of the particle; the char combustion can be inhibited by the diffusion of escaping volatile products from inside the particle. Biomass char may contain a significant fraction of the original oxygen and catalytic potassium in the biomass, depending upon the temperature it experiences. Consequently, the char combustion behavior can be significantly different at the temperatures found in fixed bed combustion compared to those found in pulverized furnaces combustion [7].

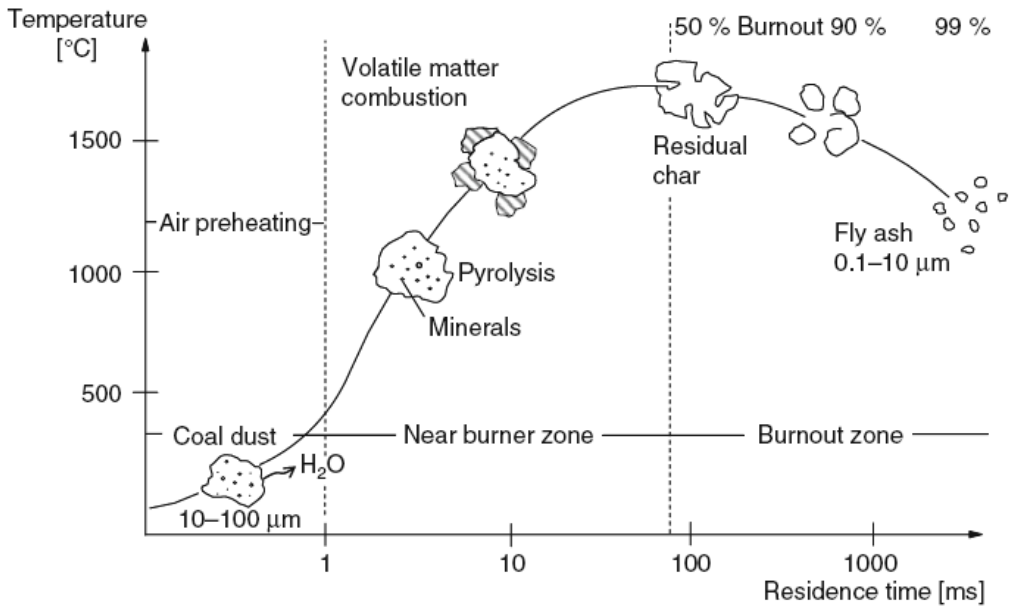


Figure 2.9. Schematic diagram of a char particle fragmentation [48].

The study of the particle size of the dust emissions is an important parameter for the characterization of the particulate matter. According to different size ranges, coarse particles > 10 µm, fine particles (0.1-1 µm or 0.1-2.5 µm) and ultrafine particles < 0.1 µm are distinguished. PM_{10} defines particles as having an aerodynamic diameter < 10 µm. This includes both coarse and fine particles. The size and density of the particles affects the retention period and travel distances in the atmosphere.

Coarse particles tend to land to the ground within hours, while fine particles can remain in the atmosphere for several weeks. The limit values for both particle emissions and ambient PM standards are indicated as mass concentrations. This does not account for the large surface area of fine particles, which can act as a potential carrier for toxic substances. Besides mass concentrations, additional parameters are relevant for the potential impact of particles on environment and human health. In particular, the particle size, the particle shape, the morphology, and the chemical composition are important parameters that need to be considered.

For typical conditions, during the biomass combustion, from various sources (forest, agricultural waste and residential wood combustion), more than one third PM2.5 (particulate

matter with an aerodynamic diameter less than 2.5 µm) are released [17]. Other authors, e.g., [89], referred that the size of particles formed during combustion depends on the time of the particle formation and oxidation stages.

Particulate matter in the ambient air is a mixture of directly emitted primary aerosols and secondary aerosols formed in the atmosphere. PM is partially of natural origin, while anthropogenic emissions lead to additional PM in the ambient air. Coarse particles from primary aerosols originate mainly from mechanical processes (construction activities, road dust, re-suspension, and wind), whereas fine particles are produced through combustion. The main sources of primary particulate matter are biomass combustion. Secondary aerosols are formed in the atmosphere through conversion of gaseous precursors such as sulphur oxides (SO_2, SO_3), nitrogen oxides (NO, NO_2), ammonia (NH_3), and non-methane volatile organic compounds (NMVOC). Beside the secondary aerosols that originate from NO_X and SO_X, secondary organic aerosols (SOA) can also contribute significantly to PM in the ambient air. Among other sources, incomplete combustion of wood is a potential source of SOA.

Investigations on wood combustion show a distinctive increase in PM concentration by dilution with ambient air at low dilution ratios. Cooling with subsequent condensation and adsorption is essential in the first dilution step and leads to a significant increase in particle mass. The further dilution of the flue gas, evaporation, and desorption of volatile and semi-volatile compounds due to a reduction of the partial pressure in the surrounding gas phase becomes relevant. This leads to a reduction of the particle mass. Consequently, the partitioning of semi volatile organics is a crucial factor with respect to the conversion of stack emissions from wood combustion to the ambient air [54].

In terms of particulate mass concentration in the flue gas of wood combustion, two distribution peaks (coarse peak and fine peak) can be distinguished [90]. Normally the coarse particles are formed from residual flying ash particles ejected mechanically from the fuel bed (intractable ash compounds of calcium, magnesium and silica) and are carried by the flue gas upwards. The coarse fly ash particle mode is formed by two mechanisms: the attrition and fragmentation of the quartz sand particles and the coating on their surfaces in the furnaces and the formation of residual ash particles from the ash elements in the fuel [91]. The fine particles formed by sub-micron flying ash particles (< 0.5 µm) are produced from

vaporization of easily volatilized ash components (sulphur, chlorine, sodium, and potassium) and the heavy metal zinc. Under incomplete combustion, also the submicron organic particles (soot < 0.5 µm) can be produced [91]. Elements such as potassium, sodium, sulphur and chlorine present in the biomass are easily released from the fuel during the combustion in the form of fly ashes. It can deposit and cause corrosion in the internal components of the heating equipment [6]. Figure 2.10 represents the development of aerosols, deposits and pollutant formation pathways for potassium, chlorine and sulphur compounds through the combustion of biomass.

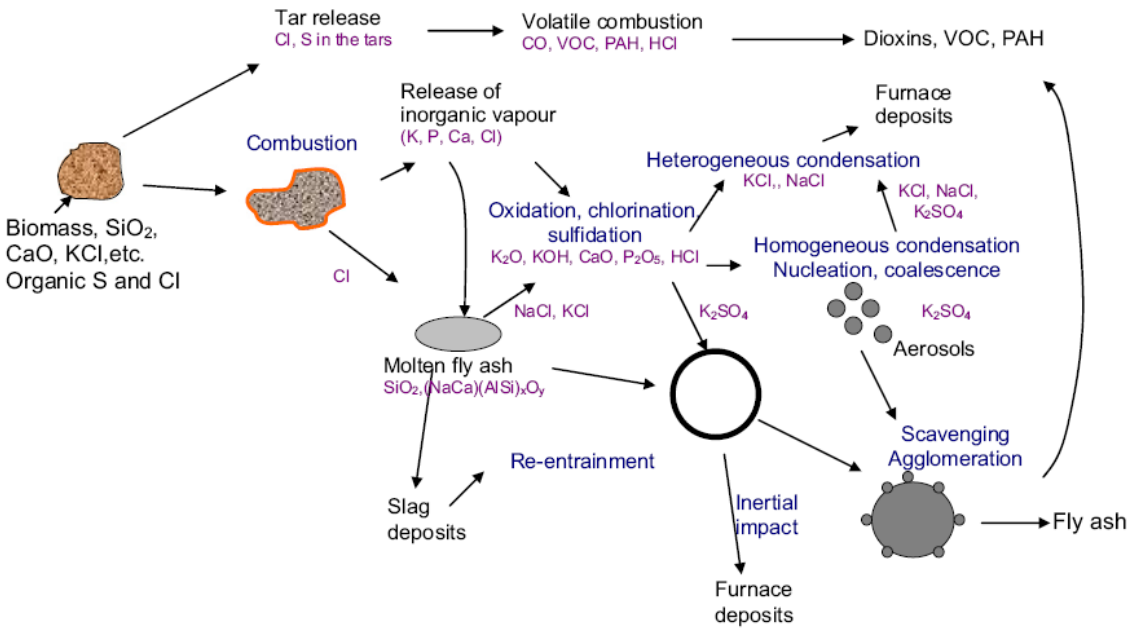


Figure 2.10. Formation of slag, tar, deposits and fly ashes from biomass combustion [23].

Biomass combustion leads to relatively high emissions of particulate matter. The majority of the particulates are smaller than 10 micron (µm) (i.e., PM_{10}) with a high share of submicron particles (PM_1). Submicron and supermicron particles in fluidized-bed combustion are composed of fine particles of potassium, chlorine, sulphur, sodium and calcium and coarse particles of calcium, silicon, potassium, sulphur, sodium, aluminum, phosphorus and iron [46]. In fixed-bed combustion, increasing mass concentrations of particulate emissions are typically related to increasing mean diameter. A dependency of the particle composition on

size can also be found in fixed bed conditions, as potassium, sulphur, chlorine and zinc are mainly found in the submicron fraction, while the content of calcium increases with increase in particle size. If almost complete burnout is achieved by appropriate furnace design, the resulting particulates are almost exclusively formed from ash components in the fuel with salts such as KCl as main components. The main fuel constituents, with respect to aerosol formation, are typically potassium, chlorine, sulphur, calcium, sodium, silicon, phosphorus, iron, and aluminum.

Some authors [54] present an approach for primary particle reduction. It was shown that particles from wood combustion are mainly formed by nucleation, coagulation, and condensation in the boiler as the temperature decreases. Further, these particles are mainly salts and consist mainly of potassium. Potassium is present as a salt in the fuel with a high melting point. If oxygen is available at high temperatures, a high amount of potassium can be oxidized. Potassium oxides have significantly lower devolatilization temperatures than the potassium salts, and they are almost completely vaporized into the gas phase and lead to the formation of particles from the gas phase. If no oxygen is present in the fuel bed, the conversion of potassium to volatiles may be reduced, since the majority of potassium salts can be converted into the grate ash. Since a similar behavior for other ash components in the fuel is assumed, the oxygen content during the solid fuel conversion is regarded as a key parameter for aerosol formation.

According to this hypothesis, an experimental setup was designed based on an understoker furnace that allows wood combustion to occur with extremely low primary air in the fuel bed (or glow bed) on the grate. At such operating conditions, the glow bed height increases significantly, and the furnace design must be adapted. Furthermore, combustion becomes unstable below a certain primary excess air, and an accurate process control is needed. Nevertheless, since fuel composition is the main parameter for aerosol formation, secondary measures are necessary for further reduction in the future. Among those measures, fabric filters are promising due to their high separation efficiency, while electrostatic precipitation is more robust for practical applications [54].

Atmospheric environment and health effects

The emissions of small particles in the atmosphere can be very harmful to the environment and the human health. Depending on the particle size and its concentration, particularly those having aerodynamic diameter bellow 10 μm, they cause a major concern for the human health, and biomass combustion mainly contributes to these emissions [92–96]. Deposition of combustion particles in the human respiratory system depends strongly on particle size. Long exposures to particulate matter can cause serious health problems such as higher morbidity, effects on lungs, and a shorter life expectancy, mainly in individuals with pre-existing heart and lung diseases. Coarse particles are generally filtered in the nose and throat while PM_{10} can settle in the lungs and may reach the alveolar region [54]. Particles larger than 10 μm tend to be deposited in the nasopharyngeal airways, while particles smaller than 1 μm can penetrate into tracheobronchial and alveolar regions and ultrafine particulate matter as small as 0.1 μm can be absorbed by the lung blood barrier and reach other organ systems [89]. According to Ghafghazi *et al.* [90], found that long-term exposure to fine PM from combustion would lead to ~ 6% and ~ 8% increased risk of cardiopulmonary and lung cancer mortality, respectively. Exposure to ultra-fine particulates (0.01–2.5 μm – PM2.5) could increase the risk of severe respiratory disease [90].

The emission of particulate matter by biomass combustion has a high impact in the human health [61] – especially the smallest particles that can be easily spread in the atmosphere and be easily breathed by individuals near the combustion facilities. These fine particles formed, with diameter bellow 10 μm, and the aerosols, with diameter below 1 μm, are the most dangerous, usually composed of potassium, chlorine, sulphur, calcium, sodium, silicon, phosphorus, iron, and aluminum chemical elements [46, 93, 97].

In conclusion, not only the size and concentration of the PM but also the chemical composition of particles influences the severity and type of health effects. These problems need to be in considered when combustion actions are put in to practice.

2.2.3 Combustion technologies

Biomass combustion is mainly used for heat production in small and medium scale units such as wood stoves, log wood boilers, pellet burners, automatic wood chip furnaces and straw-

fired furnaces [54]. The methods available are open fires (up to 3 kW), simple stoves, Patsari cookers and household heating (1-10 kW), fixed bed combustors (up to 5 MW), moving or travelling grate (up to 100 MW), fluidized bed (up to 500 MW) and suspension firing/and co-firing (up to 900 MW) [23]. Co-firing in fossil fired power stations allows the advantages of large size plants (> 100 MW), which are not applicable for dedicated biomass combustion due to limited local biomass availability [54]. Table 2.8 lists some of the main equipments used for biomass combustion and its main characteristics.

Table 2.8. Main equipments used biomass combustion [54].

Equipment	**Typical size range**	**Fuels**	**Ash** (wt.%)	**Moisture content**
Wood stoves	2 kW-10 kW	dry wood logs	< 2%	5%-20%
Log wood boilers	5 kW-50 kW	log wood, sticky wood residues	< 2%	5%-30%
Pellet stoves and boilers	2 kW-25 kW	wood pellets	< 2%	8%-10%
Unterstoker furnaces	20 kW-2.5 MW	wood chips, wood residues	< 2%	5%-50%
Moving grate furnaces	150 kW-15 MW	all wood fuels and most biomass	< 50%	5%-60%
Pre oven with grate	20 kW-1.5 MW	dry wood (residues)	< 5%	5%-35%
Understoker with rotating grate	2 MW-5 MW	wood chips, high water content	< 5%	40%-65%
Stationary fluidized bed	5 MW-15 MW	various biomass, d<10 mm	< 50%	5%-60%
Circulating fluidized bed	15 MW-100 MW	various biomass, d<10 mm	< 50%	5%-60%
Dust combustor, entrained flow	5 MW-10 MW	various biomass, d<5 mm	< 5%	< 20%
Stationary fluidized bed	total 50-150 MW	various biomass, d<10 mm	< 50%	5%-60%
Circulating fluidized bed	total 100-300 MW	various biomass, d<10 mm	< 50%	5%-60%
Dust combustor in coal boilers	total 100 MW-1 GW	various biomass, d<2–5 mm	< 5%	< 20%

2.2.3.1 Fixed grate boiler

The most common technology to burn biomass is the combustion in fixed grate, normally applied to wood stoves or pellet boilers. This technology is normally applicable to small-scale applications. Modern boilers are optimized providing different air supply zones to raise the combustion efficiency.

The existing combustion technologies for wood chips have been adopted for pellet combustion. In the last decades, automatic feed boilers were developed, promoting a higher control of the fuel feeding system, and thereby improving the required of fuel/air ratio control.

Pellet burners are divided according to the feed direction of the pellets into three main types: top feed, underfeed and horizontal feed [75]. Top feed burners were the used in this study and have been specifically developed for pellet combustion in small-scale units.

Obernberger [98] presented a study on the state of the art of the biomass combustion. He concluded that the underfeed equipment, applied to grate combustion, are only suitable for small-scale systems and with low ash content, as wood chips or sawdust. The high ash content of some biomasses such as bark, cereals and straw need efficient ash removal systems. Traditional grate firing systems are suitable for biomass fuels with high water content, varying particles sizes and high ash content. In the grate itself, it is important to maintain a fuel distribution as homogeneous as possible, avoiding accumulation areas that would impair a uniform flow of the primary air through the grate (and through fuel). The absence of these conditions can cause slagging, or higher ash/char amounts residues in some the grate zones. The fuel input in the combustions chamber must to smooth and homogeneous to do not disturb significantly the combustion on the grate bed. Some technologies have been developed to reduce these problems such as moving grates, height control of the bed and primary air fans for different grate zones. Table 2.9 shows some differences from the utilization of the grate furnace systems to other technologies.

Domestic scale applications should be restricted for good quality wood pellets, while other pellets should be reserved for applications in larger plants, which are equipped with flue gas cleaning [54]. However, Roy *et al.* [99] studied a 7-32 kW prototype of a pellet boiler with a burn pot linked to a rotating agitator, which promoted the ash fall by a constant agitator speed

of 2 rpm. The burn pot (grate) was specially designed for continuous agitation of fuel to avoid ash agglomeration. Agricultural residues (from herbaceous crops), with higher ash content than wood pellets were burnt without any ash agglomeration problems. These authors also concluded that the results suggest that grass pellets can successfully be combusted with similar performance and emissions to that of other wood pellets if burned in appropriate combustion installations.

Table 2.9. Advantages and disadvantages of grate furnace systems [98].

Advantages	Disadvantages
Low investment cost for plants < 10 MW	No mixtures of wood fuels and straw/cereals possible
Low operating costs	Efficient NOx reduction requires special technology
Low dust load in the flue gas	Higher excess oxygen decreases the efficiency
Good burnout of fly ash particles	Combustion conditions not as homogeneous as in fluidized bed furnaces
Good operation at partial load possible	
Less sensible to slagging than fluidized bed furnaces	

State of the art in the boiler under study

Fernandes and Costa [100] studied the particle emissions from a domestic pellets-fired boiler. The pine pellet combustion occurred at different thermal inputs from 10 to 21 kW to traditional pine pellets. The analysis were made to quantify and characterize morphologically and chemically the emissions of particulate matter. The results showed that the particle matter emissions varied between 160 $mg/Nm^3@13\%O_2$ and 490 $mg/Nm^3@13\%O_2$, being the emissions mainly dominated by particles with sizes below 2.5 μm and above 10 μm regardless of the thermal input. The SEM/EDS analysis showed ultra-fine particles, formed after the soot formation process, were composed mainly of oxygen, potassium, chlorine, sodium and sulphur. The sub-micrometer (and micrometer) sized particles/ agglomerates, formed from soot, contained mainly carbon, oxygen, calcium, magnesium, potassium and phosphorus. The isolated spherical and irregularly shaped large particles, released from the

fuel bed during combustion, consisted mostly of carbon and oxygen with minor amounts of calcium and magnesium.

Rabaçal *et al.* [101] studied the combustion and emission characteristics of the same domestic boiler [100], but fired with pellets of pine, industrial wood wastes and peach stones. The combustion tests were made at a thermal input of approximately 14 and 18 kW. The results revealed that the type of pellets affects significantly the boiler emissions characteristics. The pine pellets performed significantly better than the pellets of industrial wood wastes and peach stones, which presented higher levels of CO and HC emissions.

Fernandes and Costa [16] studied the formation of fine particulate matter in the domestic pellet-fired boiler referred above. The boiler operated at a thermal power of 16 kW and an O_2 concentration in the flue gas of 16%. A number of selected PM samples were also morphologically and chemically characterized. The results revealed that, inside the flame, the particles present aerodynamic diameters below 1 μm, regardless of the measurement location in the flame. The mass size distributions peaked in the size range of 50−130 nm. In the early zone of the flame, the PM size distributions presented a bimodal size distribution, but this attribute vanishes as the final stages of the combustion process were approached. The soot particles were rapidly formed early in the combustion process, but these carbon-rich particles also oxidized rapidly in the near burner region. The aerodynamic diameter corresponding to the maximum amount of particles increased slightly from the fuel bed until ~ 4/5 of the combustion chamber height. The element mass concentration varied according to the measurement location. In the beginning of the combustion process, the PM is dominated by carbon, with smaller amounts of oxygen and silicon, while in the final stages of the combustion process, the PM composition is dominated by inorganic material. The SEM analyses revealed that large fractions of the alkali metals were present, as chlorides, in the fine PM, and small fractions of the alkalis were present as sulfates.

Fernandes *et al.* [102] described the oxidation behavior of particulate matter sampled from the combustion zone of the domestic pellet-fired boiler described above. The morphology and chemical composition of the collected PM samples were examined in a SEM/EDS. Results obtained from the oxidation tests indicated that the PM samples collected from locations near the visible flame boundary were significantly less reactive towards O_2 than

those sampled from locations along the burner axis. This fact may be due to the higher temperatures occurring near the visible flame boundary, resulting in PM samples with a higher degree of material organization and a lower availability of active sites.

Garcia-Maraver *et al.* [93] investigated the relationship between the fuel quality and gaseous and particulate matter emissions in the domestic pellet-fired boiler also used in this thesis. The boiler operated at a thermal input of 10, 14 and 17 kW for two commercial pellets from pine residues, commercial pellets from cork residues, and in-house made pellets from olive wood and olive pruning residues. The results showed that the gaseous and PM emissions were significantly affected by the fuel type. The high CO emissions of the olive based pellets were attributed to their high particle densities and high length to diameter ratios, while the high NO_x emissions of the olive pruning pellets were attributed to its very high nitrogen content. Among the agro-pellets, the cork pellets originated PM emissions lower than those from the olive wood pellets and much lower than those from the olive pruning pellets. All PM emissions were dominated by particles with sizes below 2.5 μm, which are significantly affected by the fuel ash composition, namely by the amount of volatile inorganic elements potassium and sodium.

2.2.3.2 Pulverized furnaces

Direct firing of pulverized biomass or the co-firing with coal requires particles that are ground to less than 1 mm in size, which presents problems with fibrous biomass, and is difficult and expensive (in terms of energy). The char combustion process is slower than devolatilization and volatile combustion, and therefore it determines the amount of unburned carbon at the end of the combustion chamber, and, because of the interplay between NO_x and carbon-in-ash it also impacts on NO_x emission. Although biomass char accounts for a much smaller fraction of biomass fuels, firing large and wet biomass particles in the existing pulverized coal furnace raises concerns over unburned carbon since variations in furnace temperature, flow profiles as well as inter-particle heat transfer may have a significant impact on the combustion of large biomass particles [23].

State of the art in the large-scale furnace under study

Casaca and Costa [103] evaluated the effect of particle size on the NO_x control through reburning using biomass. The biomass used was rice husk with three different particle sizes. The measurements included the local mean O_2, CO, CO_2, HC and NO_x concentrations, and gas temperatures throughout the combustion chamber of the furnace. The results suggested an optimum particle size range for enhanced NO_x reduction through reburning. The particle burnout also decreased slightly as the NO_x reduction increased, regardless of the rice husk particle size range.

Abreu *et al.* [65] studied the ash deposition of co-firing bituminous coal and biomass (pine sawdust and olive stones). The tests were made with a power input of 150 kW. The variation of thermal percentage of biomass in the blend was varied between 10% and 50% for both sawdust and olive stones. The deposits were collected in a probe during 2 hours of combustion and were subsequently analyzed on a scanning electron microscope equipped with an energy dispersive x-ray detector. The co-combustion results showed that the sawdust has a beneficial effect decreasing the deposition, with high levels silica and aluminum, increasing the high fusion temperatures of ashes. In contrast, the olive stones, raised the deposition rate and produced deposits with high levels of potassium.

Casaca and Costa [104] reported detailed axial and radial flame measurements from the same laboratory furnace, using natural gas, pine sawdust and pulverized coal were used as reburn fuels. The furnace power input varied between 130 up to 200 kW. The results showed a significant reduction on NO_x emissions when using pine sawdust reburning comparing with coal and natural gas reburning. The sawdust reburning also lead to higher particle burnout performance than the coal reburning.

Wang et al. [105] investigated the ash deposit formation during the co-firing of coal with agricultural residues. The agricultural residues used were wheat straw, olive stones and peach stones. The purpose of the work was to evaluate the deposition rate, morphology and composition of the deposits with the type of biomass used in the co-combustion process. The power input was of 140 kW, being 80 kW of biomass and the rest of natural gas. The deposits were collected after 2 hours of exposure and after analyzed on a scanning electron microscope equipped with an energy dispersive x-ray detector. The results showed that co-

combustion of agricultural residues increased the ash deposition rate compared to pure coal combustion. In particular, the use of wheat straw and olive stones present originated deposits with higher degree of adherence to surfaces, due to the alkali metals presented in their ashes, causing low melting points. In the alkali metals were detected high levels of potassium and sulphur that contributed to the sintering degree. Also the high levels of sodium detected can promoted the relatively higher degree of adherence to the surfaces.

3. MATERIALS AND METHODS

This chapter describes the types of raw materials used in this work, the preparation procedures and the physical and chemical analyses performed. The different types of biomass residues used throughout the work were obtained from the wood processing industry and agriculture pruning activities. The residues studied were pine sawdust (SD), furniture residues (FR), cork residues (CR), vine branches (VB), olive branches (OB), kiwi branches (KB) and platanus branches (PB). All residues were collected and then grinded and dried in order to produce either pellets or pulverized biomass. Subsequently, the biomass fuels were physically and chemically analyzed. The residues were treated in specific equipments described in detail in this chapter, namely the system used for the thermogravimetric analyses, the domestic boiler for the combustion of the pellets and the industrial large-scale furnace for combustion of pulverized biomass.

3.1 Biomass selection and collection

The biomass selection took into account the availability of the residues and the lack of their current energetic valorization. The biomass residues were collected mainly from the north region of Portugal, Minho, except the cork, which came from Algarve, the south region of the country. The agricultural biomass fuels (VB, OB, KB and PB) were collected from the fields, after pruning activities. These residues are dependent from the seasonality of its activities. However, SD, FR and CR residues come from processing industries and are produced during the entire year. The majority of residues were collected near Guimarães (FR and KB) and Celorico de Basto (SD, VB, OB, PB), as shown in Figure 3.1. The storage place of the residues is identified in the map as DEM/UM (Mechanical Engineering Department of University of Minho). All combustion tests were performed in the DEM/IST (Mechanical Engineering Department of Instituto Superior Técnico).



Figure 3.1. Areas where the residues were collected.

The biomass fuels from the wood processing industry (SD, FR and CR) were collected with particle sizes below 1 mm. The agriculture biomass fuels were collected as thin branches, with a maximum diameter of 5 cm and a length around 1 to 3 m. The branches were collected with leaves and seeds, simulating a future collection in large-scale. The farmers usually gather the branches on the side of their fields, which facilitates the collection. After the collection, the residues were taken to a warehouse. Figure 3.2 shows the raw biomass residues at the collection time.



Figure 3.2. Raw biomass residues at the collection time.

After stored, the biomass residues were grinded up to a specific particle size distribution. The major grinding process for the agriculture residues was carried out with an opening sieve of 6 mm. Figure 3.3 shows the harmer mill used for the major trituration. The production capacity of this equipment is 150 kg/h and the power 1.5 kW. In the present work, the grinding capacity was around 7, 10, 11 and 15 kg/h for VB, OB, PB and KB, respectively. After this process, the residues were dried to achieve a certain moisture content that prevents organic decomposition (< 15 wt. %).



Figure 3.3. Harmer mill.

3.2 Biomass fuels

3.2.1 Production of pellets

The pellets were produced in a small-scale laboratory pellet production facility consisting of a rotating drum, a hammer mill and a pellet mill. The pellet mill was driven by a 3 phase, 15 kW motor (Figure 3.4). The reference pellets were produced with pine sawdust with particle sizes below 1 mm. The SD and CR (also with particles sizes below 1 mm) come from the industry ready for pellet production. The agriculture biomass fuels (VB, OB, KB and PB)

were produced using the material triturated with the 6 mm opening sieve. It was not possible to produce the pellets of FR in the pellet mill available due to the hardness of the raw material.



Figure 3.4. Pellet mill.

The biomass residues from agriculture had initially a moisture content of approximately 50%. Once dried (down to 15%), the crushed material was used to make pellets. Given the small quantities of residues involved (< 100 kg of each residue), the drying process was carried out by direct contact with air, and occasional stirring to achieve the required moisture. The optimal moisture content of the raw material varies between 12% and 18%. To adjust the water content of the residues to produce the pellets a rotating drum was used to mix the water homogeneously with the biomass. The rotating drum consists of a cylindrical chamber, positioned horizontally, that rotates at 30 rpm, with a maximum power of 1.5 kW. Pellets were produced in an axial 400 kg/h maximum capacity small-scale pelletizer unit with 6 mm diameter holes. The pellet production from the different biomasses requires a distinct mechanical effort and this is reflected in the energy costs. Figure 3.5 shows the pellets of SD, CR VB, OB, KB and PB. As referred earlier, no pellets from FR were made.



Pine sawdust pellets | Cork residues pellets

Vine branches pellets | Olive branches pellets

Kiwi branches pellets | Platanus branches pellets

Figure 3.5. Pellets produced in laboratory scale pellet mill.

3.2.2 Production of pulverized biomass

The production of pulverized biomass was made by a hammer and a knife mill. Firstly the agricultural biomass was grinded on a hammer mill until 6 mm diameter. After the major trituration, the same biomass was grinded in the knife mill, with a sieve 1 mm of diameter.

The capacity of production is between 0.2 to 50 kg/h and the power is 1.5 kW. However, for the production of the different biomasses in pulverized material at 1 mm not exceed the 5 kg/h.



Figure 3.6. Knife mill.

Figure 3.7 represents the final product (pulverized biomass) for the SD, FR, CR, VB, OB, KB and PB. The pulverized biomass is several different in its particle size distribution until, as evaluated in the description of the chapter section 3.4.

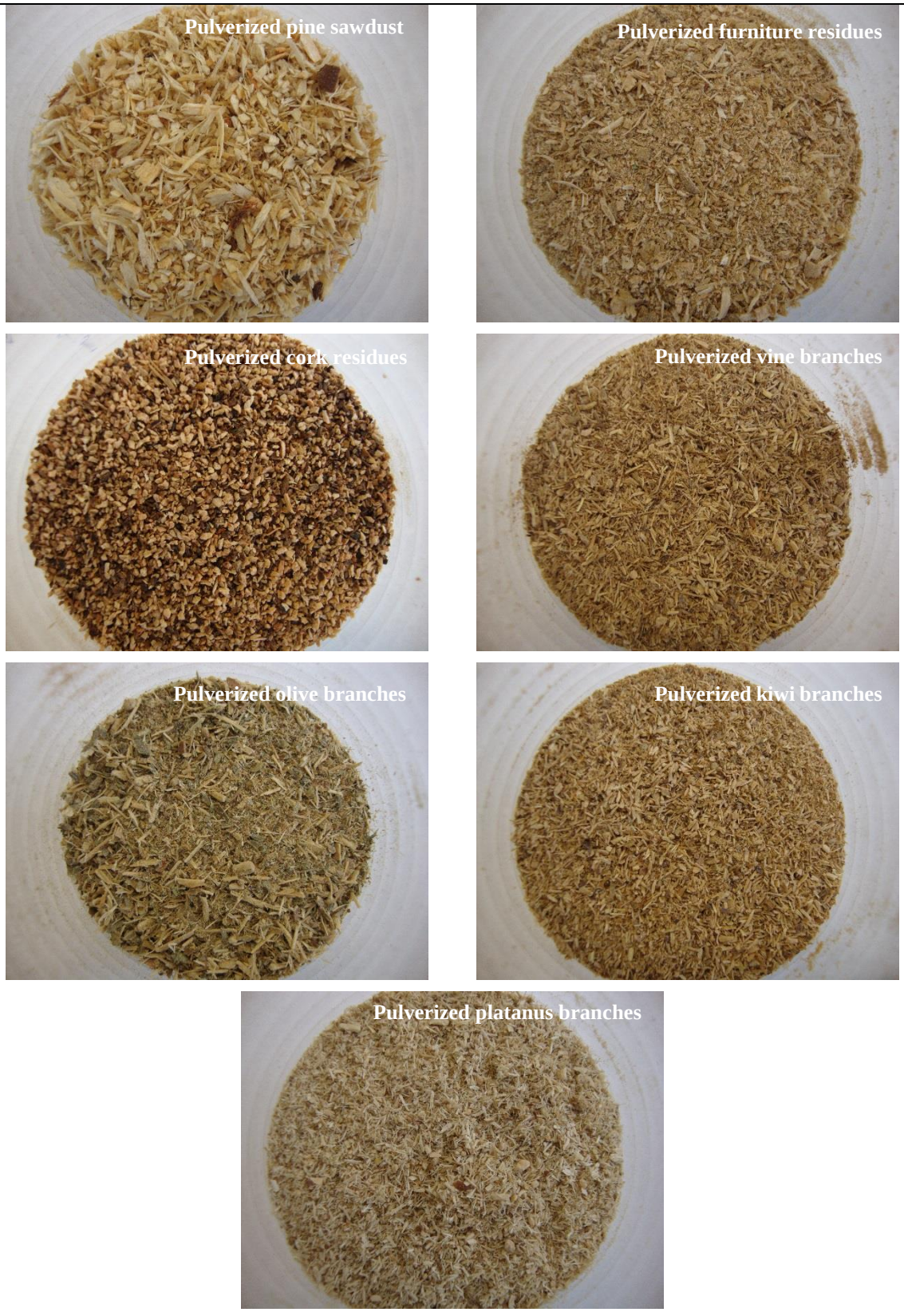


Figure 3.7. Pulverized biomass fuels of SD, FR, CR, VB, OB, KB and PB.

3.3 Physical and chemical analysis of the biomass fuels

Physical and chemical analyses of all biomass fuels were performed in order to assess its characteristics and potential as renewable energy source. These analyses were performed in the waste characterization laboratory of CVR (*Centro para a Valorização de Resíduos*). The proximate, ultimate and ash chemical analysis and other physical properties were accomplished according to the following techniques and standards. The proximate analysis were performed according to standards CEN/TS 15414:2006, CEN/TS 15402:2006, and CEN/TS 15403:2006; the ultimate analysis of carbon, hydrogen and nitrogen was performed according to standard CEN/TS 15104 and the sulphur was measured according to standard CEN/TS 15408; the heat value of each biomass was performed according with the procedures specified in the CEN/TS 14918:2005 standard; and the chemical ash composition was measured by an x-ray fluorescence spectrometry technique.

The physical parameters (bulk density and mechanical durability) of the pellets were also analyzed. The bulk density of each residue was measured following the standard CEN/TS 15401:2006 and the mechanical durability of pellets following the procedures set in the standard CEN/TS 15210-1:2005.

3.4 Particle size distribution

The particle size distribution of the pulverized fuels was obtained with aid of the Malvern particle sizer, model 2600 shown in Figure 3.8. The instrument is based in the Fraunhofer diffraction of a monochromatic parallel beam of light by particles in motion.

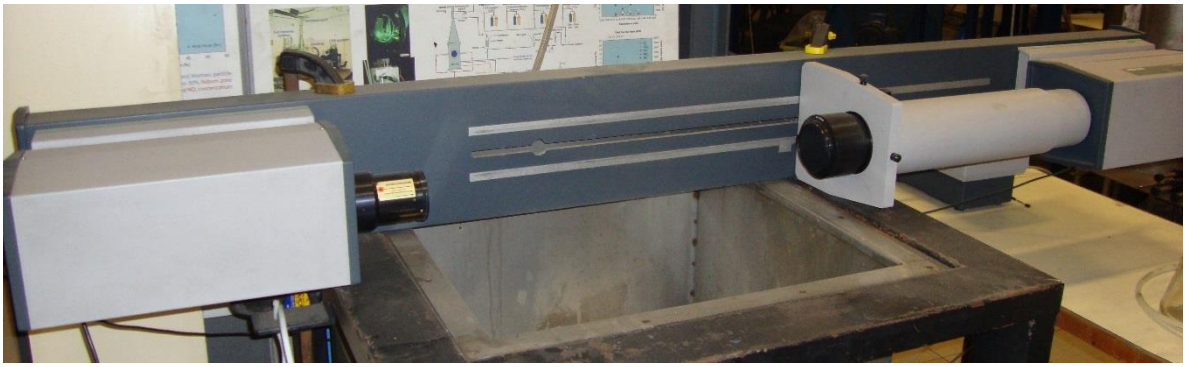


Figure 3.8. Malvern particle sizer.

3.5 Thermal gravimetric and differential scanning calorimetric analysis

The study of biomass combustion can be performed by thermogravimetric and calorimetric analysis (TGA-DSC). This experimental technique analyzes the heat difference by differential scanning calorimetry (DSC) and monitors the mass by thermal gravimetric analysis (TGA). Figure 3.9 shows the equipment used, a TA INSTRUMENTS SDT 2960 simultaneous DSC-TGA, able to measure the temperature, heat flow and weight along the time.



Figure 3.9. Simultaneous DSC-TGA equipment.

The TGA and DTG profiles obtained during the experiments enable the identification of the initial decomposition temperature (T_{in}), peak temperature (T_{max}) and the burnout temperature (T_b) of each sample. These are obtained from DTG curve (1st derivative of the TG curve). T_{in} corresponds to the beginning of the weight loss and is defined as the temperature at which the rate of weight loss reaches 1%/min after the initial moisture loss peak in the DTG profile. T_{max} is the point at which maximum reaction rate occurs. The lowest point on the DTG curve identifies the maximum combustion rate. T_b is identified when the last peak comes to the end, and the temperature at which the sample is completely oxidized. It is taken as the point immediately before reaction ceases, when the rate of weight loss is down to 1%/min [41].

The kinetics analysis of the combustion of biomass by TGA is based on the 1st order Coats-Redfern equation. The 1st order Coats-Redfern equation, based in the Arrhenius equation, was applied to the results in order to achieve the kinetic properties of biomass fuels. This method is considered more appropriate for calculation of the frequency factor, apparent reaction order and activation energy [106]. This equation can be also applied to the 2nd stage (removal and combustion of volatile matter) and 3rd stage (combustion of char) of the

biomass combustion. The parameters obtained from this analysis are the activation energy (*E*) and the frequency (*A*), also known as pre-exponential factor. The equation used in this method is based in the Arrhenius Equation (3.1):

$$K = A\ exp(\frac{-E}{RT}) \tag{3.1}$$

where *T* is the absolute temperature, *K* is the rate of the chemical reaction and *R* is the universal gas constant. The relative mass loss (α) is usually obtained from the typical TGA curve according to Equation (3.2):

$$\alpha = \left(\frac{W_0 - W}{W_0 - W_\infty}\right) = \left(\frac{W}{W_\infty}\right) \tag{3.2}$$

where W_0 is the original weight of the sample, *W* is the current weight of the sample and W_∞ is the final weight of the sample.

The 1st order Coats-Redfern equation is given in Equation (3.3).

$$ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln(\frac{AR}{\beta E}) - (\frac{E}{RT}) \tag{3.3}$$

where β is the heating rate. According to this equation, a plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$ corresponds to a straight line with slope $-E/R$ and an intercept of $\ln(AR/\beta E)$, from which the values of *E* and *A* can be obtained.

3.6 Experimental facilities for the combustion tests

The experimental facilities for the combustion tests include a domestic boiler using pellets as fuel and a large-scale laboratory furnace using pulverized fuel in a down fired burner. Both are located at the Instituto Superior Técnico in Lisboa.

3.6.1 Domestic pellet-fired boiler

The combustion tests were performed in a domestic top feed pellet-fired boiler with a maximum thermal capacity of 22 kW. The boiler used is a model "TERM IDEAL CERAMIC", from the manufacturer Anselmo Cola. The structure and the combustion chamber are made of steel and wrought iron. The boiler has an internal circuit of water

dedicated to central heating and a circuit for the domestic hot water. The boiler has a deposit of 45 dm^3 to store the pellets. The primary air, which passes through the fuel and is the main responsible for the combustion of the carbonous residue and volatile release, is injected from below the grate through the grid holes. The secondary air, necessary to promote the combustion of the volatiles, is injected through a vertical tube, near the grid [107]. The pellets consumption rate is regulated by the boiler load and is measured with the aid of a loss-in-weight technique for which the boiler is mounted on a weighbridge. The pellets are transported from the deposit until the combustion chamber through a screw feeder. Figure 3.10 shows the IST domestic pellet-fired boiler.



Figure 3.10. IST domestic pellet-fired boiler.

The combustion gases exchange heat with the water, in the heat exchanger, at the top of the combustion chamber. Thereafter, the gases flow through a fan and leave the system through an exhaust pipe. The fan is located near the exit of the exhaust gases, inducing depression in the combustion chamber. The boiler operation is fully automatic.

The gaseous emissions were measured with the aid of gas analyzers (Figure 3.11). A probe in the chimney tube, placed at the centerline, collected flue gas samples, according to the standardized measurement methods described in the European technical specification CEN/TS 15883:2009.

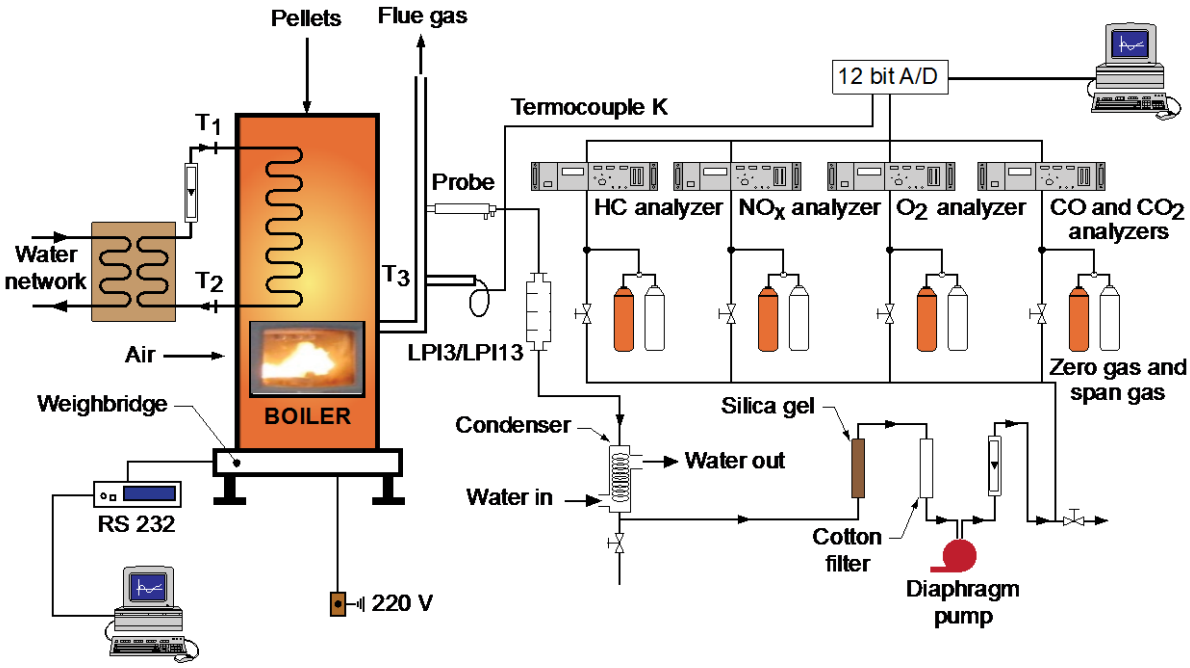


Figure 3.11. Schematic of the IST domestic pellet-fired boiler and auxiliary equipment.

3.6.2 Large-scale laboratory furnace

The IST large-scale laboratory furnace (Figure 3.12) is able to burn several fuels with the aid of a down-fired burner. Figure 3.13 shows schematically the IST furnace and auxiliary equipment. The chamber combustion has a cylindrical form, with its axis vertically to minimize asymmetries by natural convection phenomenon and to prevent the deposition of particles in the walls. The burner is placed at the top of the combustion chamber, thus releasing the fuel particles from the top, which then travel down the combustion chamber. The combustion chamber is composed of eight water-cooled segments, each with an internal diameter of 0.6 m and 0.3 m of height, down-fired along its axis by a swirl burner. Swirl is imparted to the secondary air stream using a moveable-block swirl generator [103]. The furnace roof and the first four segments are coated internally with refractory cement capable of support temperatures up to 1800 °C. Between the refractory and the water jacket is placed a ceramic fiber blanket. The biomass feeding system is placed over a weighbridge (capacity of 300 kg and a sensitivity of 10 g). The pulverized fuel is first fed to a vertical tube with an internal diameter of 130 mm, through which it falls in a tube of 20 mm inner diameter, to be then delivered pneumatically to the burner. The primary air (transport air) is supplied by an

air compressor (10 bar) and its flow rate is measured using a calibrated rotameter. The secondary air is supplied by a fan of variable speed and its flow rate is measured with a calibrated orifice plate installed upstream of the fan [108].



Figure 3.12. IST large-scale laboratory furnace.

Each segment has a pair of circular holes with a diameter of 215 mm, diametrically opposed, for visual observation and introduction of probes. One of the windows of the first segment is used for continuous monitoring of the flame [109].

The first four segments have installed taken static pressure and thermocouple Pt/Pt:13%Rh (type R) devices, diametrically opposed, to monitor and control the pressure within the combustion chamber and the temperature of the inner wall of the furnace, respectively.

The combustion chamber is cooled with water, which is distributed for each segment by two inputs, except the segment located on top that have 4 entries, because of the high temperatures

therein reached there. The cooling water flow, which circulates independently in each of the eight segments, is regulated by a valve and measured using a rotameter. The temperature of the cooling water at the outlet of each segment is measured with the aid of thermocouples Fe/Cu-Ni (type J) [109].

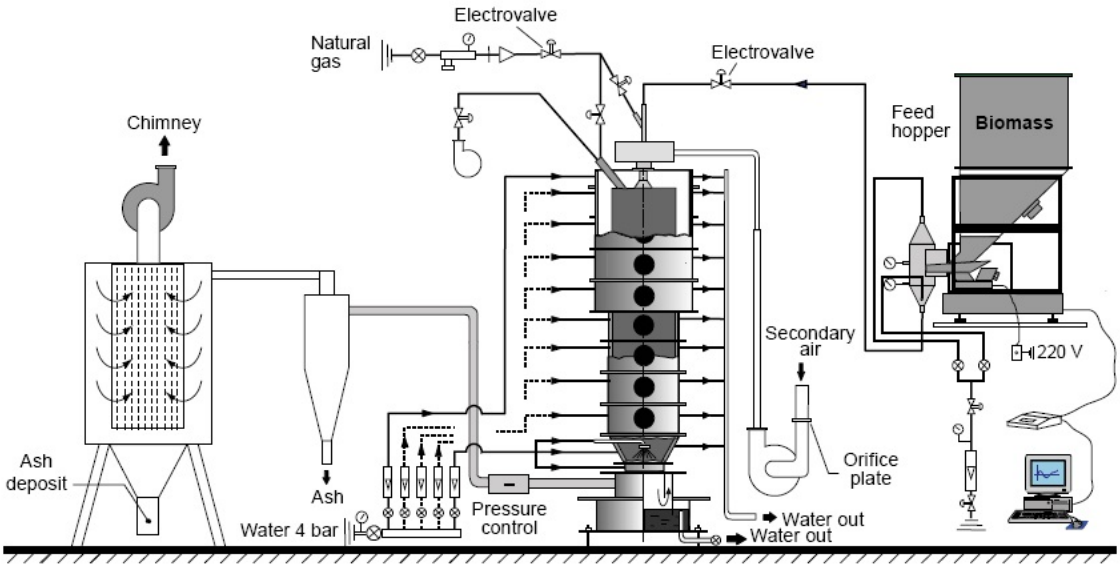


Figure 3.13. Schematic of the IST large-scale laboratory furnace and auxiliary equipment.

Figure 3.14 shows schematically the furnace roof and burner arrangement. The burner consisted of three concentric tubes with the outer tube made of refractory cement with 56 mm inside diameter and ending in a diverging nozzle (quarl) at an angle of 60°. The central tube made of stainless steel, was used for the introduction of the primary (transport) air and the biomass fuels. The intermediate annular tube, also made of stainless steel, was used for the introduction of natural gas during the combustion tests.

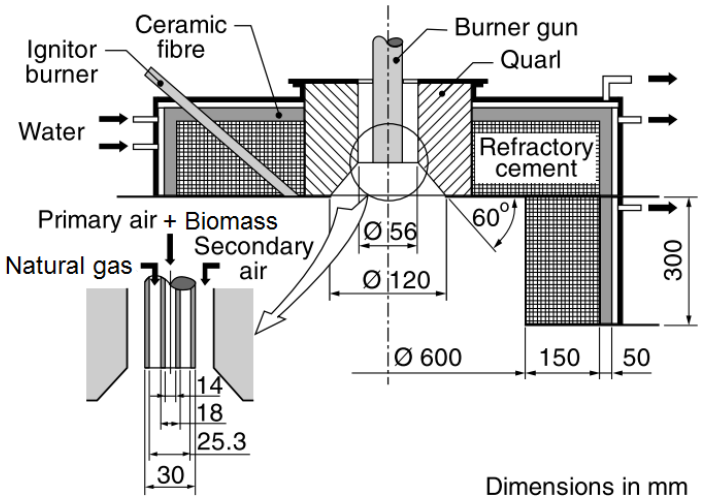


Figure 3.14. Schematic of the IST furnace roof and burner arrangement.

Figure 3.15 shows schematically the furnace exhaust system, which is installed after the last segment of the furnace (see also Figure 3.13). This system helps to reduce the temperature of the flue gases and the amount of particulate matter emitted into the atmosphere. The washing and cooling of the combustion gases is accomplished with the help of a central nozzle which produces a conical shower that is responsible both for the cooling of gases and removal of particles formed during the combustion process. After this central nozzle, two diametrically opposed nozzles, producing flat jets, form a water curtain that enhances the effects described above with respect to the central shower.

The system ends with a cyclone connected to a tank of water that guarantees the sealing of the combustion chamber and the retention of the solid particles removed by the cyclone. The water level is kept constant to prevent any disturbance in the flow within the combustion chamber. The exhaust gases are evacuated tangentially so that, by centrifugal action, the solid particles are pushed towards the walls, which, by the action of water from showers, are then drawn into the water deposit.

The duct that connects the furnace exit to the laboratory exhaust system is equipped with a variable opening for regulating the pressure inside the combustion chamber. In the present work, the tests were conducted at atmospheric pressure inside the combustion chamber so that the measurements were not contaminated with the outside air [109].

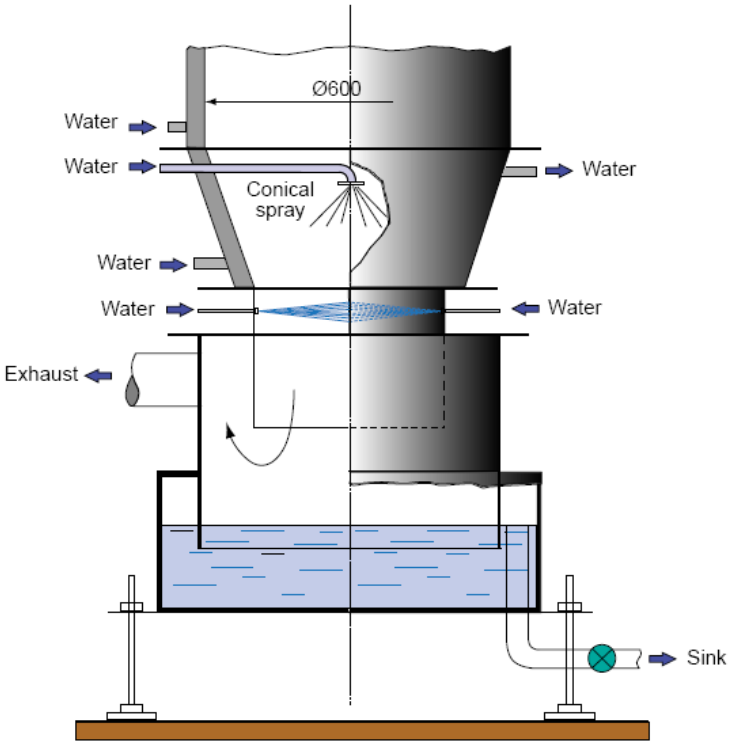


Figure 3.15. Schematic of the scrubber located at the bottom of the IST large-scale laboratory furnace.

3.7 Experimental methods

3.7.1 Gaseous emissions

The gaseous emissions from the domestic boiler and from the large-scale furnace were obtained with a stainless steel water-cooled probes and were analyzed in terms of oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x) and unburnt hydrocarbons (HC) [108], as shown in Figure 3.16. The analytical instrumentation included a magnetic pressure analyzer for O_2 measurements, a non-dispersive infrared gas analyzer for CO and CO_2 measurements, a flame ionization detector for HC measurements and a chemiluminescent analyzer for NO_x measurements. To calibration the analyzers standard mixtures were used before and after each measurement. The analogue outputs of the analyzers were transmitted via A/D board to a computer where the signals were processed and the man values calculated.

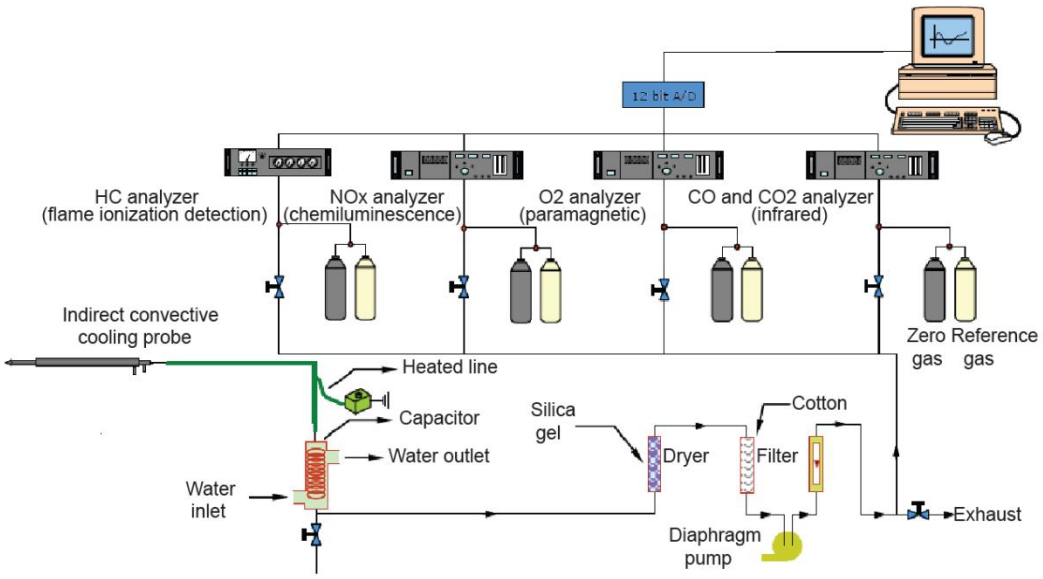


Figure 3.16. Schematic of the gas sampling system.

Figure 3.17 shows schematically the gas sampling probe used in the large-scale furnace [109]. During the tests, this probe was placed of the last segment of the combustion chamber of the furnace.

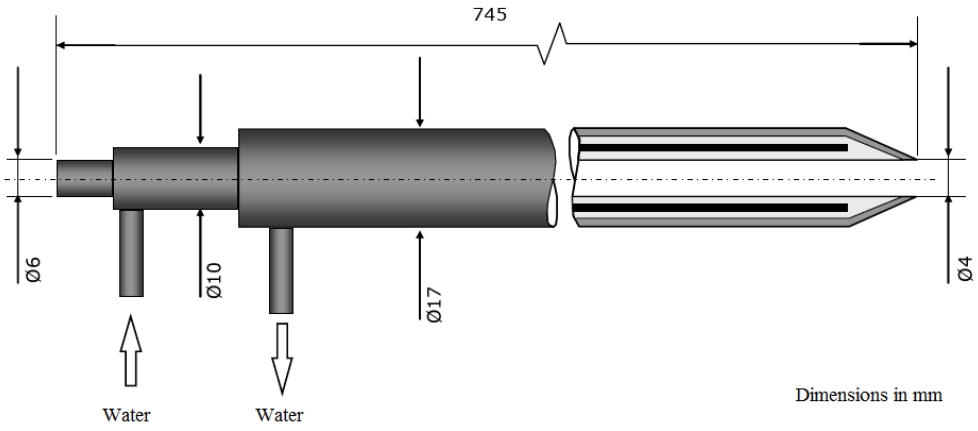


Figure 3.17. Schematic of the gas sampling probe in the large-scale furnace.

3.7.2 Particle burnout

Figure 3.18 shows schematically the system used to collect the carbonaceous residue samples from the large-scale furnace exhaust. The samples were obtained through a water-cooled stainless steel probe. The particles were collected in a glass container, shown in the figure. The compressed air (10 bar) that passes through the ejector causes a depression inside the glass container that is responsible for the suction of the sample from inside the furnace. In the container, the particles were retained in the water, while the gases are expelled through the ejector. Each measurement took about 1 hour, depending on the operating conditions of the furnace.

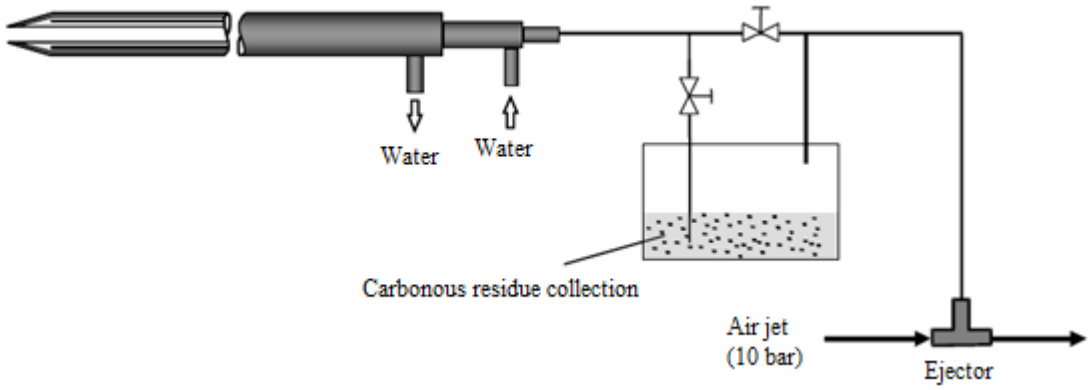


Figure 3.18. Schematic of the carbonous residues sampling system.

After collection, the samples were dried in an oven at 110 °C and subsequently analyzed for the ash content. The particle burnout was obtained using Equation (3.4):

$$\text{Particle burnout (\%)} = \frac{1 - W_k/W_x}{1 - W_k} \times 100 \qquad (3.4)$$

where W_k and W_x are the weight fraction (dry basis) of ash in the collected particles and in the fuel, respectively.

3.7.3 Particulate matter

Two distinct impactors were used to collect and quantify the PM from the domestic boiler and the large-scale furnace.

3.7.3.1 Impactor LPI-3

A three-stage low pressure impactor (LPI-3), from the TCR Tecora, allowed collecting three particulate cut sizes during the same sampling: PM with diameters above 10 μm, PM with diameters between 2.5 μm and 10 μm, and PM with diameters below 2.5 μm. In order to avoid condensation along the impactor inlet and also inside the impactor, a heating jacket (model Winkler WOTX1187) was used during sampling, heating the sample up to 105 °C. The PM was collected on quartz microfiber filters, which were dried in an oven and weighted before each test. The impactor case is supplied with a filter cutter, a device to make a hole in the 1° and 2° stage in order to use flat filter diameter of 47 mm. After each test, the filters were dried again to eliminate any moisture content before being weighted to determine the quantity of PM captured.

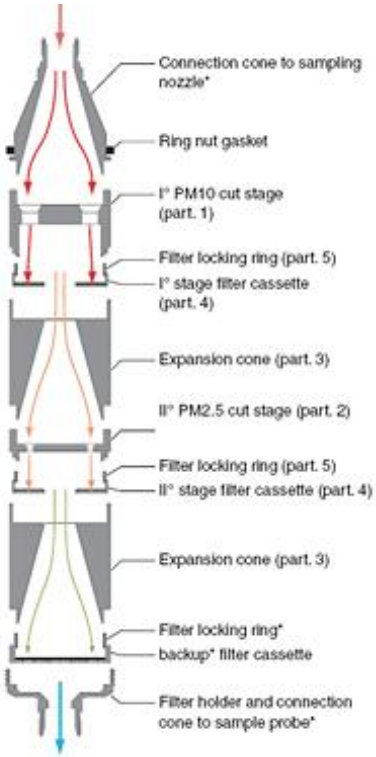


Figure 3.19. Schematic of the working principle of the three-stage low pressure impactor [110].

3.7.3.2 Impactor LPI-13

A 13-stage cascade low pressure impactor (Dekati Low Pressure Impactor, DLPI) illustrated in Figure 3.20, was used to determine the PM mass size distribution. The size classification in DLPI was made from approximately 30 nm up to 10 μm. More specifically, the DLPI has 13 filter stages that collect particles according to their median mass (aerodynamic) diameters; specifically, 0.0282 μm, 0.0559 μm, 0.0927 μm, 0.153 μm, 0.259 μm, 0.379 μm, 0.608 μm, 0.940 μm, 1.59 μm, 2.37 μm, 3.96 μm, 6.63 μm and 9.84 μm, numbered from stage 1 to 13, respectively. The same a heating jacket mentioned to LPI-3 was used here. In each size fraction the particles are collected on 25 mm diameter collection plates that are weighed before and after the measurement to obtain the mass size distribution of the particles. Greased thin aluminum films were used as impactor substrates.

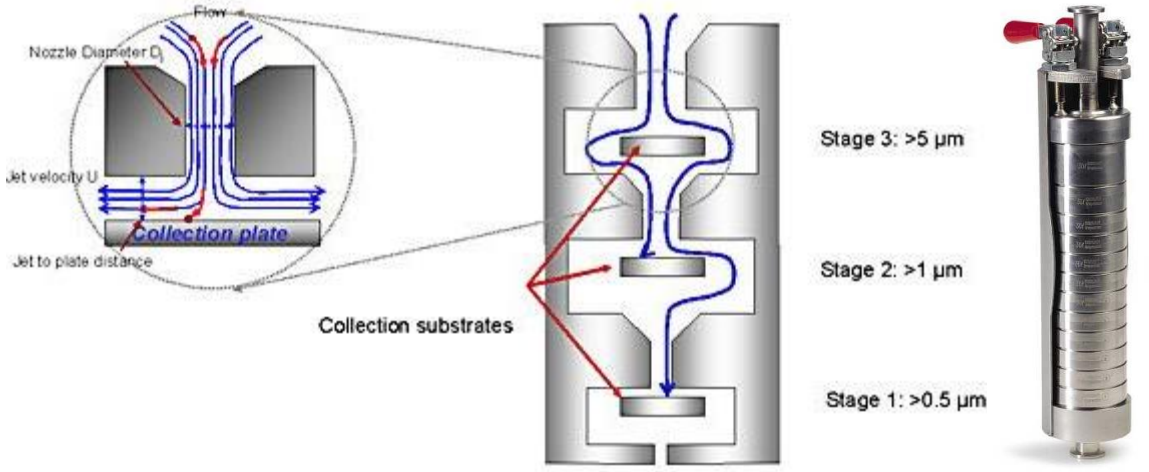


Figure 3.20. 13-stage cascade low pressure impactor [111].

3.7.3.3 Particulate matter probe used in the domestic boiler

In the domestic boiler the particulate matter was collected from the flue gas isokinetically with a probe placed at the centerline of the chimney tube, according to the European standard EN 13284-1:2002 and Annex A of the EN 303-5. PM was sampled isokinetically either for total mass concentration or size fractions. Total mass concentration was achieved with the aid of a total filter holder and size fractions with a flow rate of approximately 8 l/min (measured with a flowmeter). The two low pressure impactors described above were used.

To avoid the condensation along the impactors, a heating jacket (Winkler WOTX1187) was used, heating the flue gas sample up to 105 ºC.

3.7.3.4 Particulate matter probe used in the large-scale furnace

In the case of the large-scale furnace, the PM was collected from the aid of a water-cooled probe placed at the centerline of the sixth segment of the furnace. The samples collected by the probe were diluted with nitrogen using a dilution ratio of approximately 25 times (ratio calculation using the CO_2 concentration measurements at the probe outlet). The total flow mixture, nitrogen and combustion gases (10 L/min), was sent to the low-pressure cascade impactor. As in the case of the domestic boiler, also here the two low pressure impactors were used. In order to avoid condensation along the impactors, a heating jacket (Winkler WOTX1187) was used, heating the flue gas sample up to 150 ºC. Figure 3.21 shows a schematic of the PM sampling probe and associated sampling system used in this study, and Figure 3.22 shows details of the PM sampling probe.

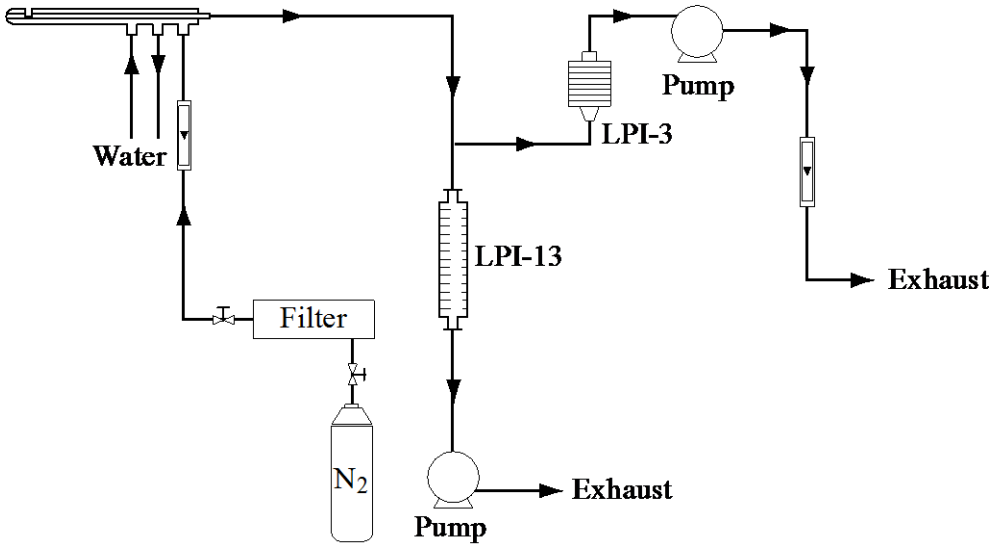


Figure 3.21. Schematic of the PM sampling probe and associated sampling system used in the large-scale furnace.

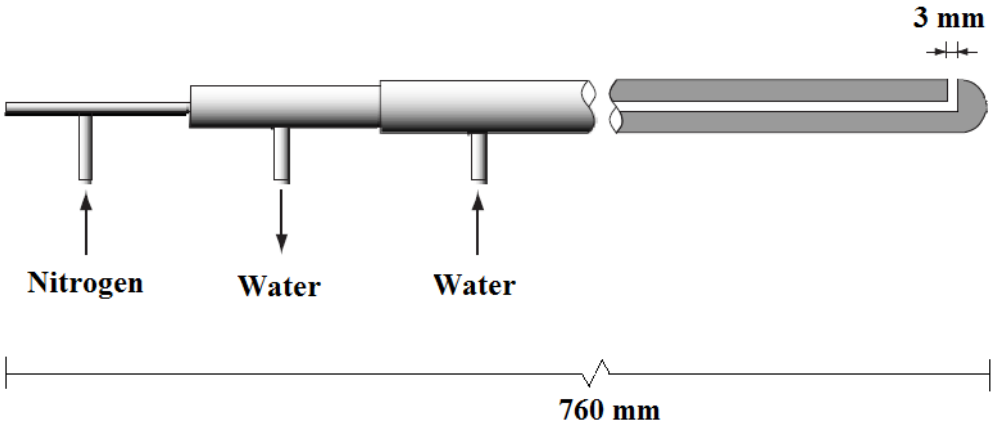


Figure 3.22. Schematic of the PM sampling probe used in the large-scale furnace.

3.7.4 SEM/EDS analysis

The morphology and chemical composition of the PM on selected impactor substrates was observed in a scanning electron microscope (SEM) – JEOL, model JSM-7001F (Figure 3.23). The SEM is equipped with an energy dispersive X-ray spectroscopy (EDS) detector that allows to quantifying the chemical (elemental) composition of a PM sample with a minimum resolution of approximately 1 μm^2. The microscope allows to obtaining three-dimensional images of a selected area of the sample by irradiating the sample by a ray of electrons. For each selected impactor substrate, the PM chemical composition data was obtained from ten different areas of 50 x 50 μm^2.



Figure 3.23. Scanning electronic microscope and auxiliary equipment.

4. THERMOGRAVIMETRIC ANALYSIS AND ASH CHARACTERIZATION OF INDUSTRIAL WOODY AND AGRICULTURAL RESIDUES

This chapter evaluates the seven biomass fuels considered in this thesis (SD, FR, CR, VB, OB, KB and PB) in terms of combustion behavior through thermogravimetric analysis. Moreover, the tendency for slagging and fouling of the present biomass fuels is also examined based on the ashes composition.

4.1 Properties of the biomass fuels

Table 4.1 summarizes the physical and chemical characteristics of biomass residues fuels.

Table 4.1. Characteristics of the biomass fuels.

	Parameter	SD	FR	CR	VB	OB	KB	PB
Proximate analysis (wt.%, as received)	Moisture	6.90	5.70	10.4	10.5	8.70	8.30	9.30
	Volatile matter	77.8	77.2	68.6	70.2	72.6	71.7	73.5
	Ash	0.60	0.80	1.80	2.10	2.50	2.40	1.20
	Fixed Carbon*	14.7	16.3	19.2	17.2	16.2	17.6	16.0
Lower heating value (MJ/kg)	LHV	17.1	16.6	19.2	17.7	18.0	17.9	18.1
Ultimate analysis (wt.%, dry ash free)	C	50.8	57.1	53.8	49.3	47.9	48.2	47.6
	H	5.39	7.32	6.62	6.19	6.20	6.40	5.98
	N	1.55	3.78	0.35	0.67	0.65	0.72	0.54
	S	0.037	0.12	0.034	0.15	0.15	0.16	0.16
	O*	42.22	31.68	39.20	43.69	45.10	44.52	45.72
Ash analysis (wt.%, dry basis)	Al_2O_3	10.4	11.6	1.58	0.5	2.22	1.54	0.765
	CaO	11.3	26.2	70.3	47.59	35.9	44.7	59.92
	Cl	0.01	0.11	2.4	0.042	0.563	0.19	1.03
	Fe_2O_3	10	5.84	0.28	0.699	1.32	0.788	0.592
	K_2O	10.2	6.6	13.55	23.72	28.14	23.24	8.66
	MgO	4.08	4.44	1.67	7.85	4.82	5.8	8.48
	Na_2O	1.57	2.89	2.38	1.0	1.8	1.1	2.69
	P_2O_5	2.51	2.62	1.75	11.9	18.3	15.8	12.9
	SiO_2	47.4	16	3.44	0.824	3.33	1.49	1.29
	SO_3	0.18	3.92	1.62	1.47	1.08	2.49	2.68
	TiO_2	0.65	17.2	0.05	0.043	0.096	0.064	0.0039

*calculated by difference.

4.2 Test conditions used in the TGA experiments

All biomass fuels were initially grinded down to less than 1 mm and placed in an alumina cup with an initial weight of 5 (± 1) mg. In all tests a heating rate of 10 ºC/min, a final temperature of 750 ºC and a flow rate of 100 mL/min of dried air were used. During each TGA the values of the temperature (ºC), heat flow (mW) and weight of the sample (mg) were registered every second.

4.3 Results and discussion

4.3.1 Thermal gravimetric analysis

Figure 4.1 to Figure 4.7 show the weight loss (%), heat flow (W/g) and rate of mass loss (%/min) for the seven biomass fuels examined. The analysis was performed in air, and the mass of the samples was 5 mg. In each figure, the horizontal lines in the left graphs separate the transition phase 'moisture loss' and 'volatile matter loss' (dashed line) and 'volatile matter loss' and 'char residue loss' (continuous line). According to Vanvuka *et al.* [50] the combustion profiles of woody biomass residues may be divided into two distinct stages. The first stage (200-400 ºC) is attributed mainly to volatiles combustion and the second stage (400-600 ºC) to residual volatiles and char combustion. The present results for the woody biomass fuels confirm the occurrence of the stages.

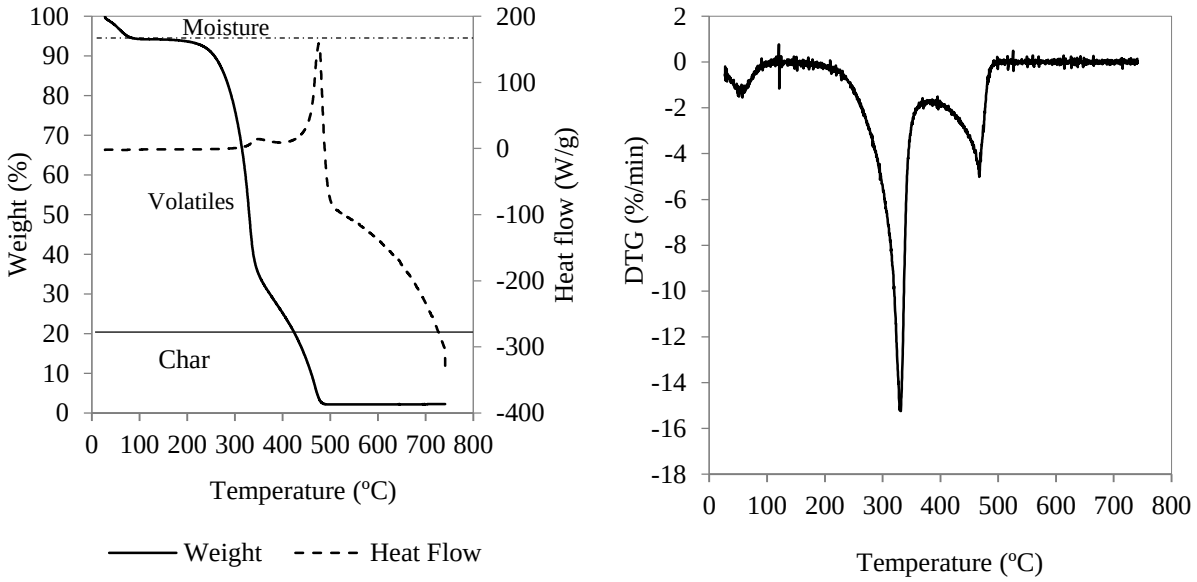


Figure 4.1. Weight loss and heat flow (left graph) and rate of mass loss (right graph) curves for SD.

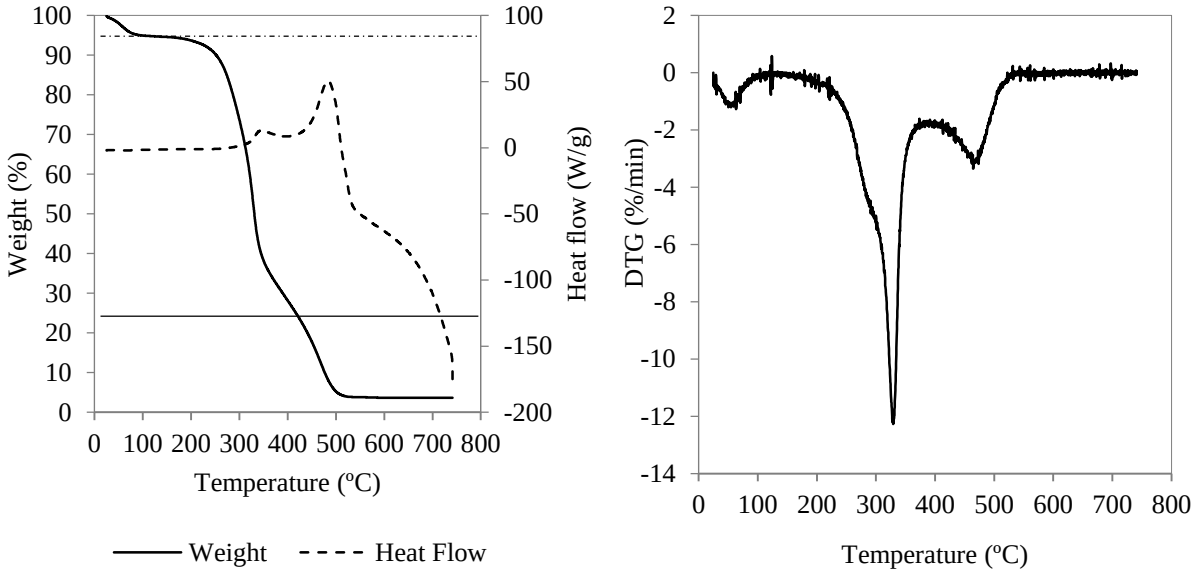


Figure 4.2. Weight loss and heat flow (left graph) and rate of mass loss (right graph) curves for FR.

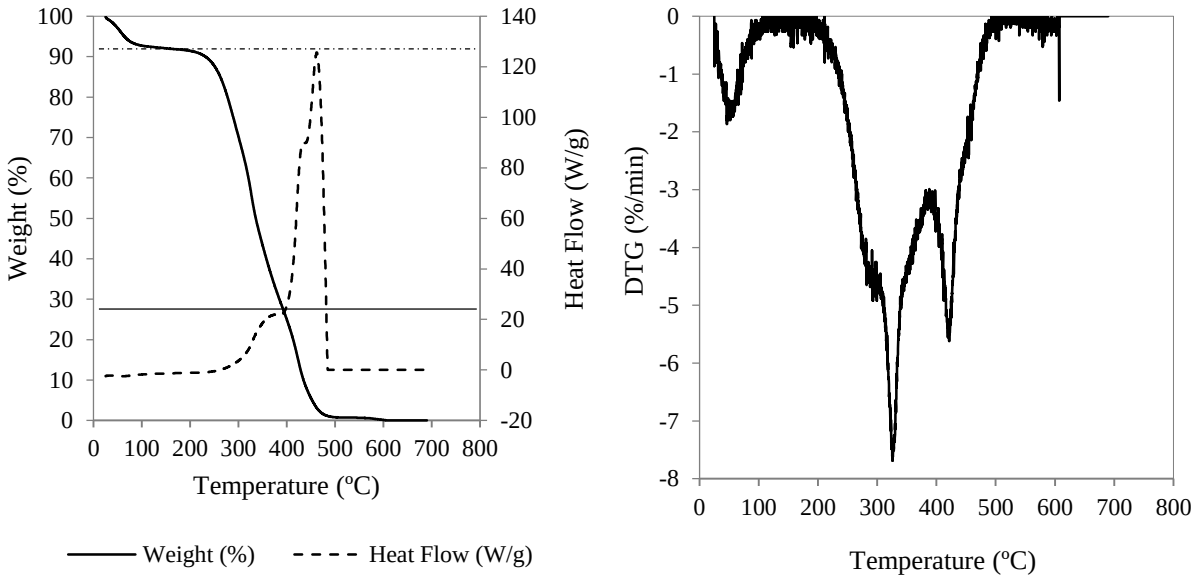


Figure 4.3. Weight loss and heat flow (left graph) and rate of mass loss (right graph) curves for CR.

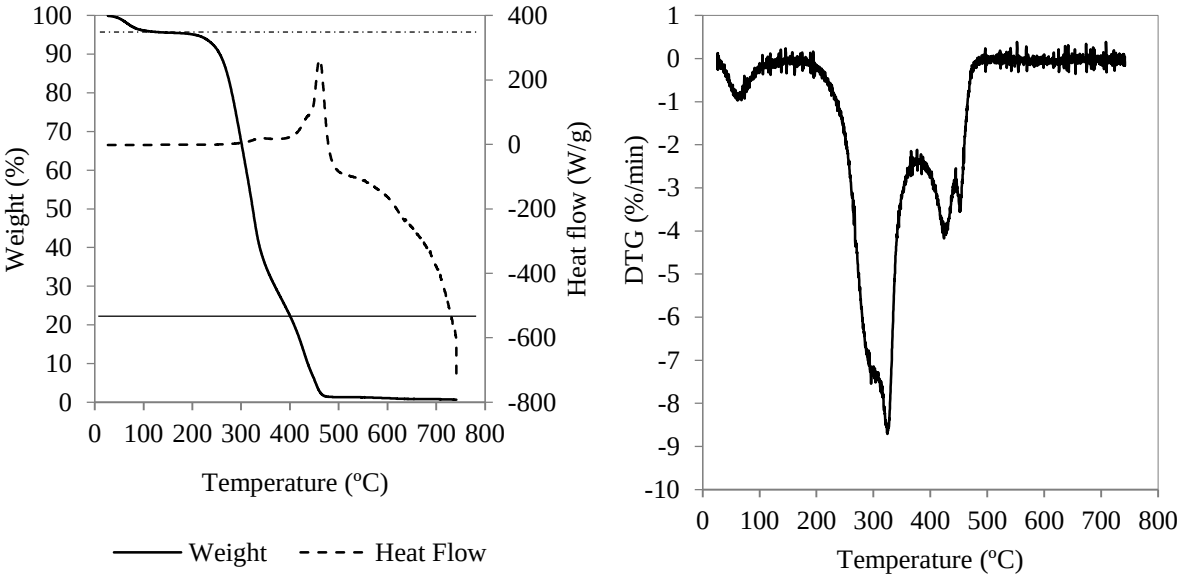


Figure 4.4. Weight loss and heat flow (left graph) and rate of mass loss (right graph) curves for VB.

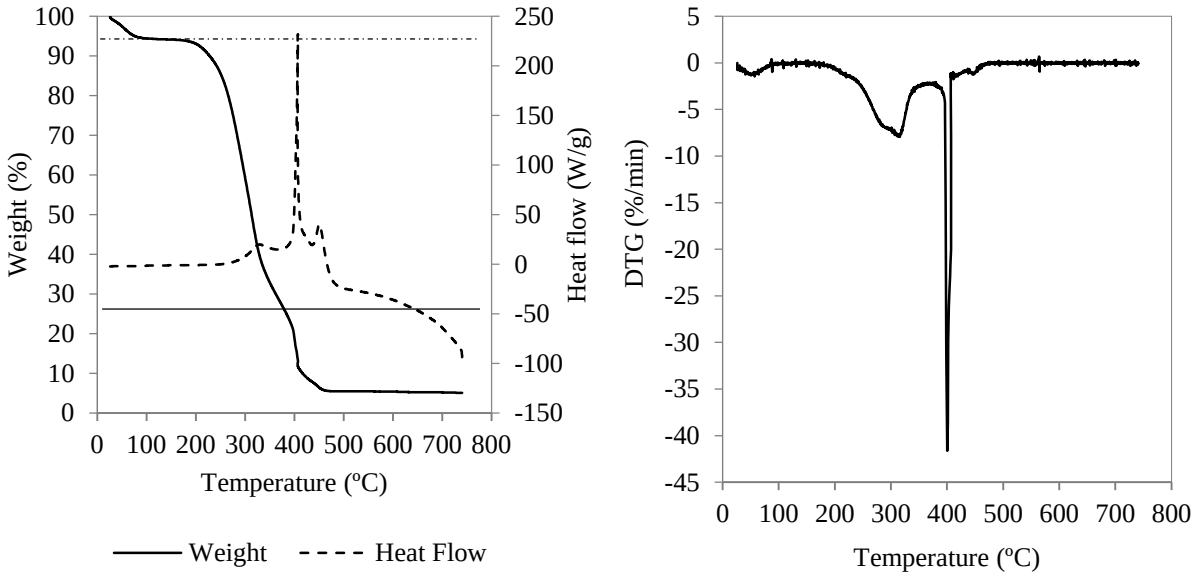


Figure 4.5. Weight loss and heat flow (left graph) and rate of mass loss (right graph) curves for OB.

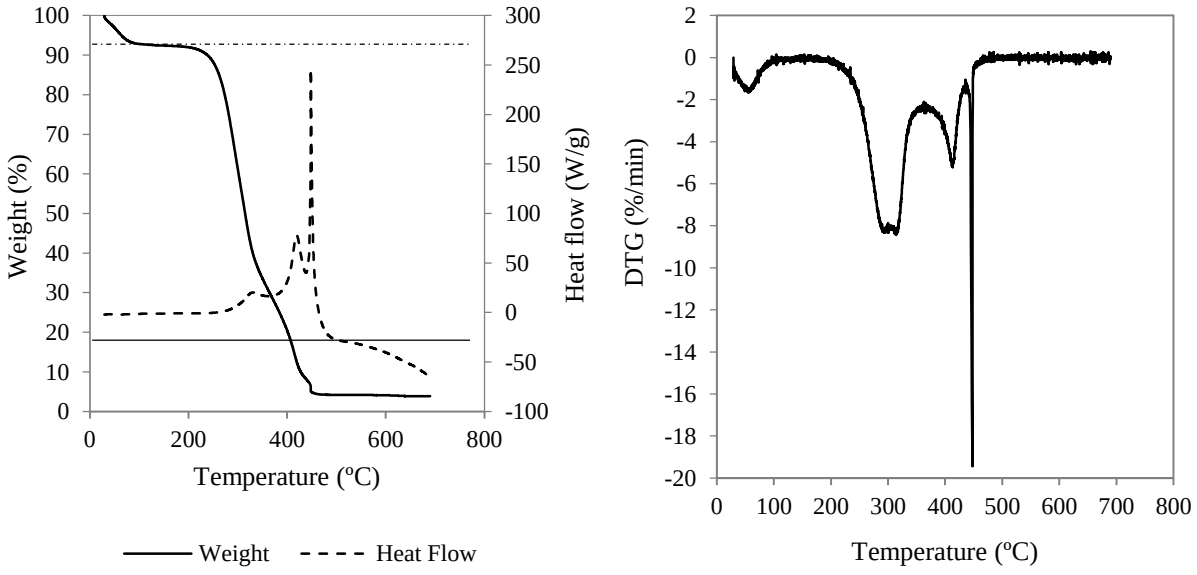


Figure 4.6. Weight loss and heat flow (left graph) and rate of mass loss (right graph) curves for KB.

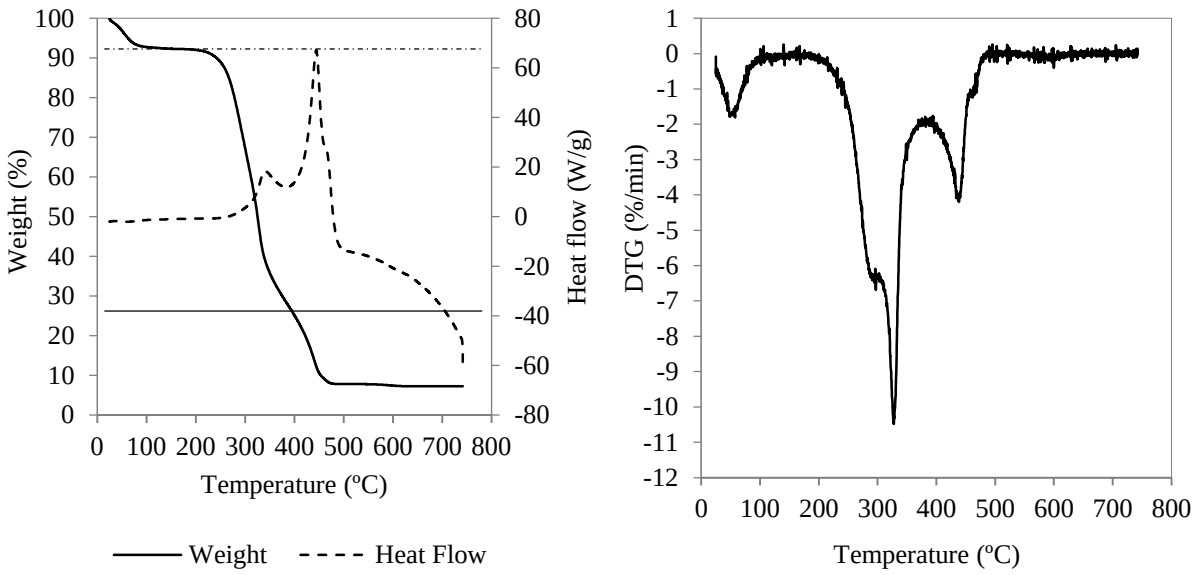


Figure 4.7. Weight loss and heat flow (left graph) and rate of mass loss (right graph) curves for PB.

The figures reveals that in general heat is released between 300 ºC and 500 ºC, reaching the highest value close to 450 °C, for all the biomass fuels studied. SD has the highest heat flow of 158 W/g at 475 ºC, FR 51 W/g at 483 ºC, CR 126 W/g at 462 ºC, VB 262 W/g at 460 ºC, OB 232 W/g at 407 ºC, KB 246 W/g at 448 ºC and PB 67 W/g at 444 ºC. VB, OB and KB are the residues that release more heat (> 200 W/g). Note that mixing residues with distinct peak temperatures can increase this phenomenon [50, 51]. The temperatures at which the maximum heat flow occurs correspond to the end of the greenhouse gases release during the combustion of the residues. At this stage, the volatiles are almost completely oxidized. The peak temperature in the DTG curve is a measure of the reactivity of the corresponding residue. The lower the peak temperature the easier the ignition of the fuel. The burnout temperature is the temperature on the DTG curve where the oxidation is completed [43]. The ignition, peak temperatures and reactivity of the biomass fuels studied are given in Table 4.2.

Table 4.2. Ignition, peak and burnout temperatures and maximum combustion rates.

Parameter	SD	FR	CR	VB	OB	KB	PB
Initial decomposition temperature (ºC)	244	239	236	237	208	234	239
1st peak temperature (ºC)	330	329	326	324	316	314	327
2nd peak temperature (ºC)	467	465	421	424	400	448	438
Burnout temperature (ºC)	481	502	470	465	427	449	466
Burnout time (min)	46	49	45	45	41	43	45
Maximum mass loss rate (%/min) at 1st peak	-15	-12	-8	-9	-8	-8	-10
Maximum mass loss rate (%/min) at 2st peak	-5	-3	-6	-4	-42	-19	-4
Maximum heat release (W/g) at DSC	158	51	126	262	232	246	67
Maximum heat release (ºC) at DSC	475	483	462	460	407	448	444

According to the DTG curves, the initial weight loss takes place due to the moisture release between 25 °C and 200 °C for all biomass fuels. Subsequently, in the first stage, the main weight loss occurs between 180 ºC and 360 °C, corresponding to the devolatilization of the hemicellulose and cellulose components and their respective ignition. In the second stage, the weight loss is associated with the char combustion between 360 ºC and 600 °C. The peak temperatures and corresponding weight losses for the thermal degradation of the hemicellulose, cellulose and lignin for the different biomass fuels are shown in Table 4.3. For SD, the peak temperatures of hemicellulose and cellulose are not distinguishable, with a first peak being observed at 330 ºC with a corresponding weight loss percentage of 50%. For the other biomass fuels, the hemicellulose peak temperatures are between 297 ºC and 312 ºC, with weight loss percentage of 58% to 74%. The cellulose peak temperatures are between 314 ºC and 330 ºC with weight loss percentages of 48% to 56%. The lignin degradation is observed in the range of temperatures between 413 ºC and 467 ºC with weight loss percentages varying between 7% and 17%. The peak temperatures in the DTG curve after the lignin peak for OB (Figure 4.5) and for KB (Figure 4.6) indicate faster ignition for these cases than in the others cases [95].

Table 4.3. Peak temperatures and corresponding weight losses for the thermal degradation of the biomass constituents.

Biomass constituent		SD	FR	CR	VB	OB	KB	PB
Hemicellulose	Peak temperature (ºC)	-	300	297	303	302	301	312
	Weight loss (%)	-	74	71	65	58	60	60
Cellulose	Peak temperature (ºC)	330	329	326	324	316	314	327
	Weight loss (%)	50	52	56	50	48	51	47
Lignin	Peak temperature (ºC)	467	465	421	424	447	413	438
	Weight loss (%)	7	14	17	15	7	15	15

For all biomass fuels studied, the initial decomposition temperature (corresponding to the moisture release), the 1st temperature peak (corresponding to the 2nd stage) and the 2nd temperature peak (corresponding to the 3rd stage) are within the expected ranges. The combustion reactivity regions are proportional to the height of the DTG peak so that OB is clearly the most reactive residue and the CR is the less reactive. In brief, the reactivity of the biomass fuels studied can be ordered as follows: OB > KB > SD > FR > PB > VB > CR. Note that the reactivity of the biomass fuels is due to the combustion of the light volatiles. However, the energy released from biomass fuels is mainly due to the combustion of fixed carbon [8], as can be concluded from the 2nd peak of the heat flow for all biomass fuels analyzed.

Kinetic analysis

Figure 4.8 to Figure 4.14 show the linear regression curves for all biomass fuels studied here. The values between the initial decomposition and burnout temperatures define the total reactivity of combustion. The limit temperatures of the DTG peak areas define the two distinct stages. The second stage data are highlighted by a dashed line, the third stage data in a dashed dot line, and the global combustion data by a continuous line.

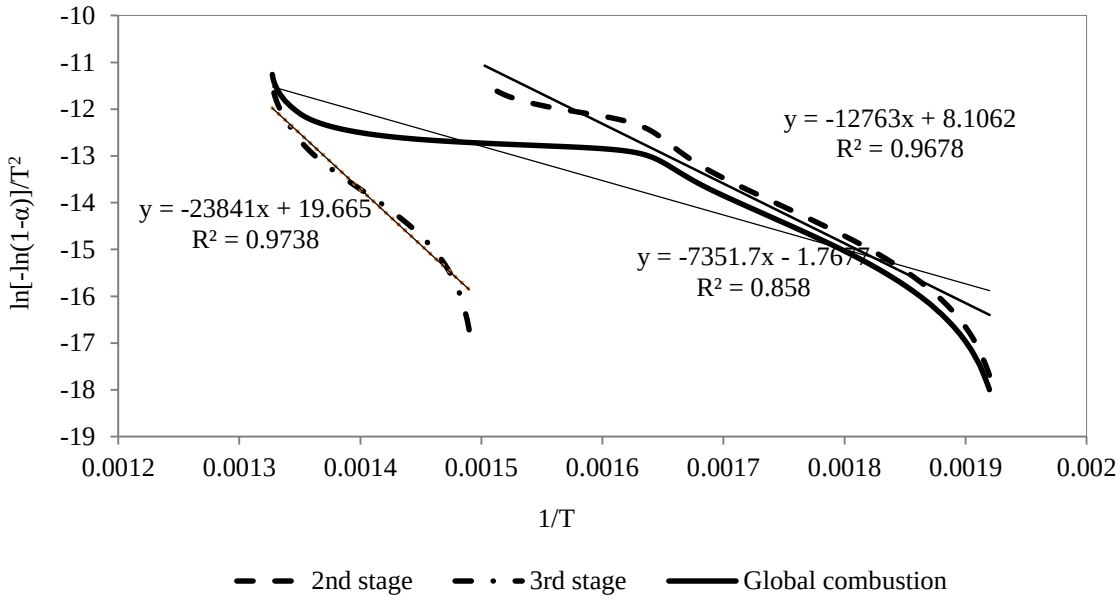


Figure 4.8. Linear regression for the combustion of SD.

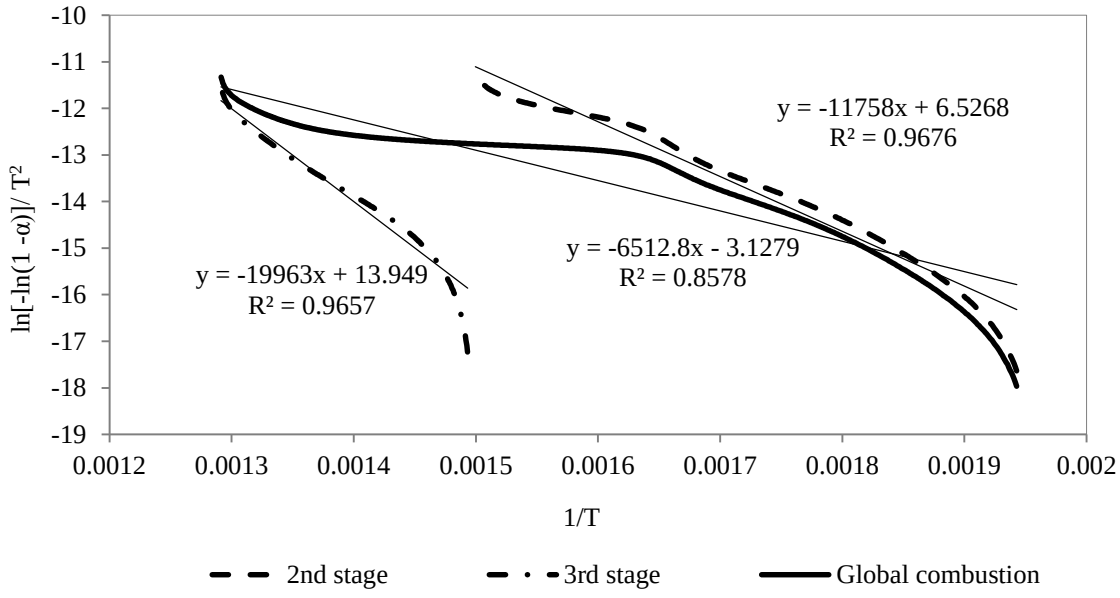


Figure 4.9. Linear regression for the combustion of FR.

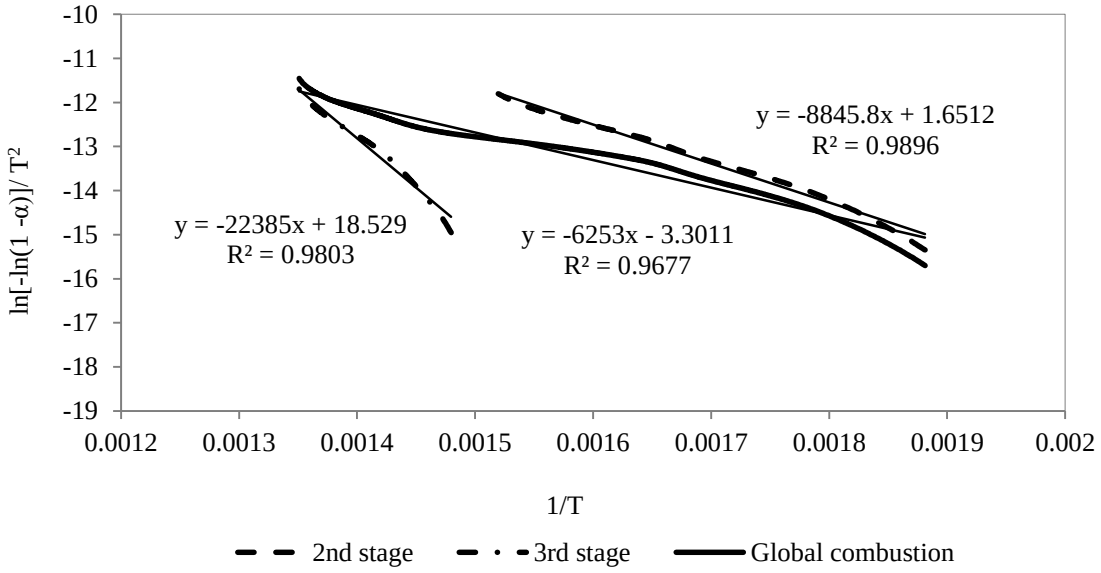


Figure 4.10. Linear regression for the combustion of CR.

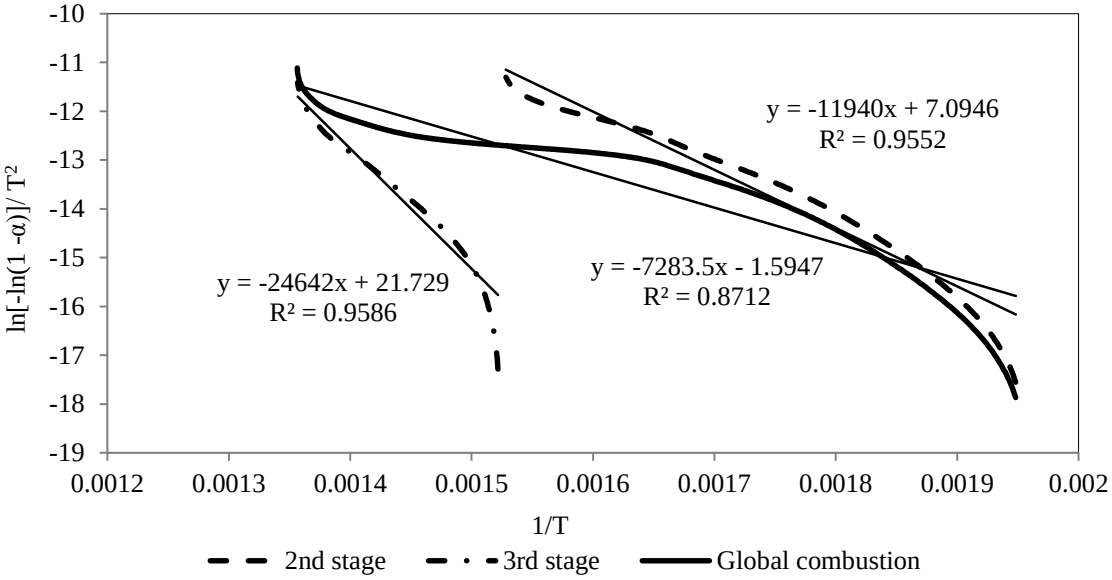


Figure 4.11. Linear regression for the combustion of VB.

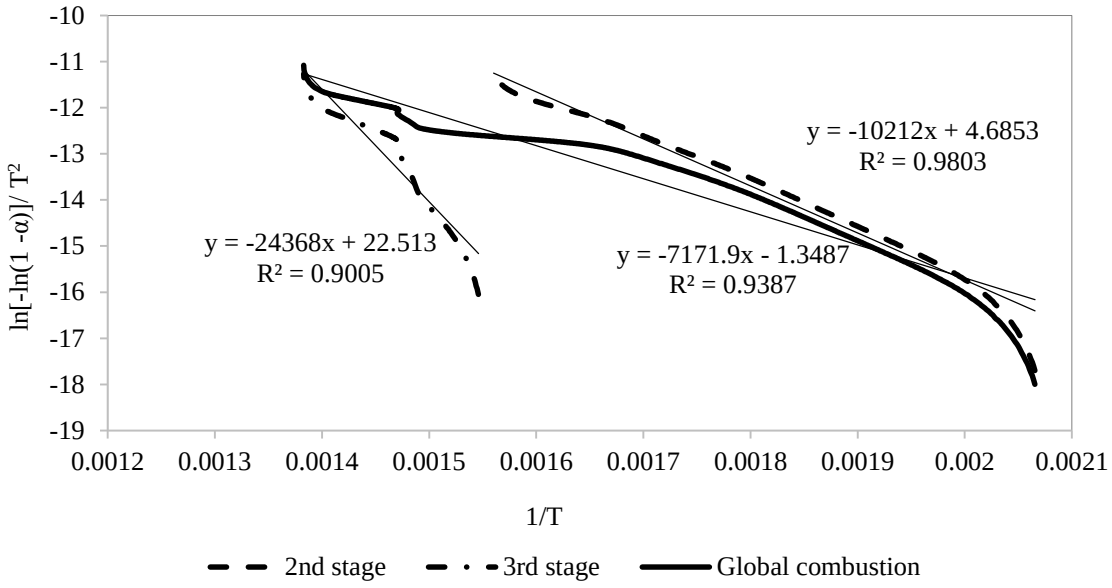


Figure 4.12. Linear regression for the combustion of OB.

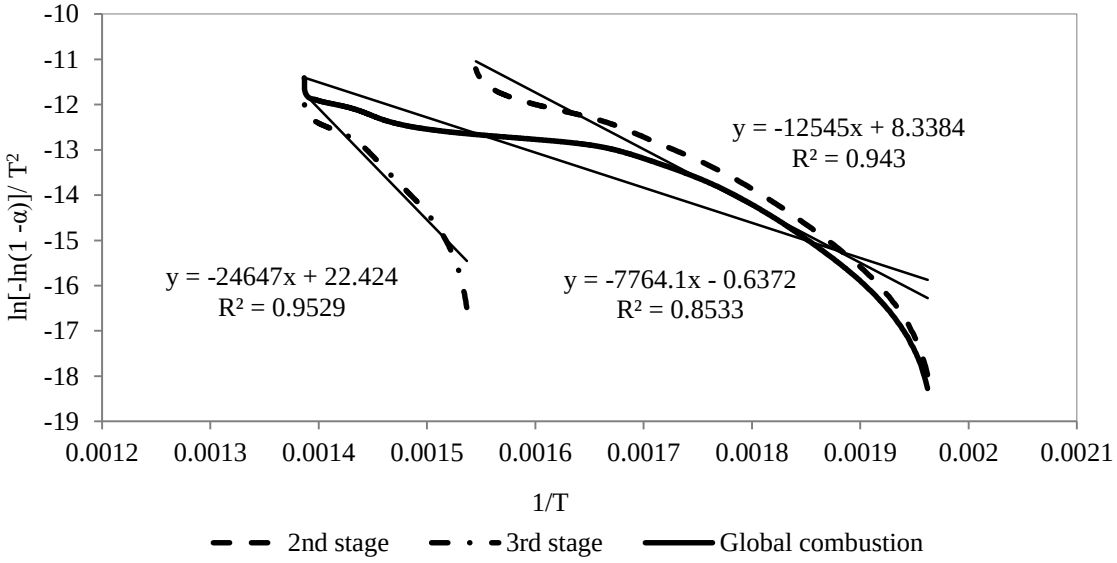


Figure 4.13 Linear regression for the combustion of KB.

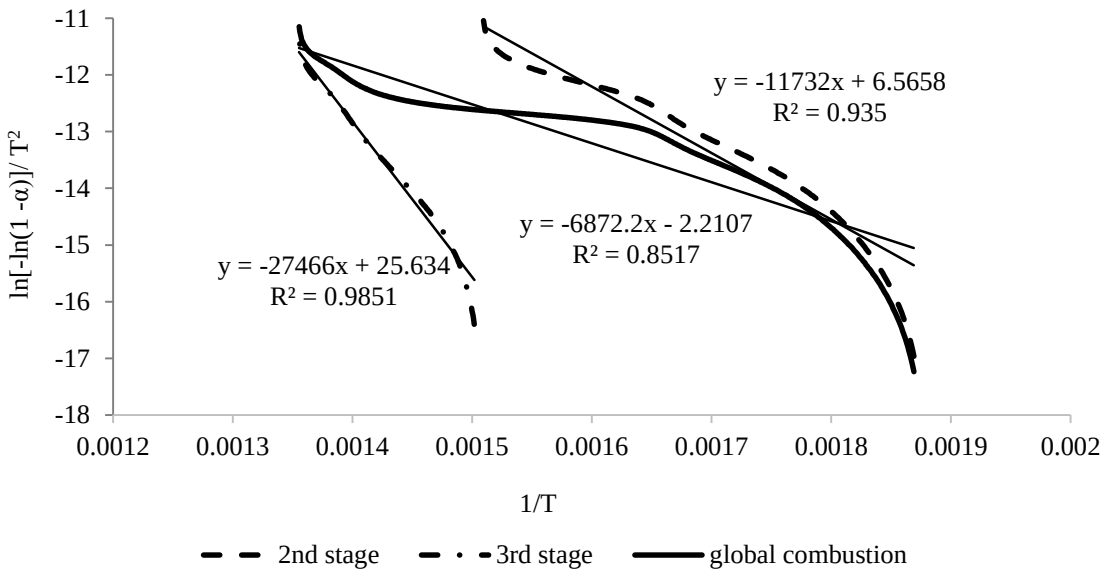


Figure 4.14. Linear regression for the combustion of PB.

The Coats-Redfern method is one of the most widely used methods and is considered as a good approach for the determination of kinetic parameters [106]. In this work, the linear correlation coefficient (R^2) revealed good data fit for most biomass fuels examined ($R^2 >$ 0.90). However, for the global process the correlation coefficient is not as good as desirable ($R^2 > 0.85$). Table 4.4 presents the estimated kinetic parameters for the combustion of all biomass fuels studied.

Table 4.4. Estimated kinetic parameters for the combustion of all biomass fuels studied.

	Parameters	**SD**	**FR**	**CR**	**VB**	**OB**	**KB**	**PB**
	T (ºC)	244-481	239-502	236-470	237-465	208-427	234-449	239-466
Total	E (kJ/mol)	61	54	52	61	60	65	57
	A (s^{-1})	209	48	38	246	310	684	126
	T (ºC)	244-395	239-395	236-393	237-380	208-370	234-375	236-390
2^{nd} stage	E (kJ/mol)	106	98	74	99	85	104	98
	A (s^{-1})	7.05×10^6	1.34×10^6	7.69×10^3	2.40×10^6	1.84×10^5	8.74×10^6	1.39×10^6
	T (ºC)	395-481	395-502	393-470	380-465	370-450	375-449	390-466
3^{rd} stage	E (kJ/mol)	198	166	186	205	203	205	228
	A (s^{-1})	1.38×10^{12}	3.80×10^9	4.16×10^{11}	1.12×10^{13}	2.43×10^{13}	2.25×10^{13}	6.21×10^{14}

According to the global kinetic data, the biomass fuels studied can be ordered in terms of reactivity as follows: KB > SD > VB > PB > OB > FR > CR. The energy activation values vary between 52 kJ/mol and 65 kJ/mol. In regard to the 2nd stage, the biomass fuels reactivity present the following decreasing order: SD > KB > VB > PB > FR > OB > CR, with the energy activation values varying between 74 kJ/mol and 106 kJ/mol. Finally, in the 3rd stage, the biomass fuels reactivity present the following decreasing order: PB > KB > VB > OB > SD > CR > FR. The energy activation values vary between 166 kJ/mol and 228 kJ/mol.

4.3.2 Ternary diagram of ash analysis

Figure 4.15 to Figure 4.17 represent the inorganic elements of the biomass fuels in a ternary diagram. This representation allows observing the fusibility temperatures of the interaction of K_2O-SiO_2-CaO (Figure 4.15), CaO-SiO_2-Al_2O_3 (Figure 4.16) and K_2O-SiO_2-Al_2O_3 (Figure 4.17) mass fractions for each residue studied.

The interaction of some oxides causes the decrease of the fusion temperature as compared to the fusion temperature of the elements. According to García *et al*. [77] a biomass fuel that presents more than 50 wt.% of CaO or SiO_2 combined with more than 15 wt.% of K_2O, has a higher propensity to agglomerate and therefore to deposit.

The values from the ash analysis (Table 4.1) provided the data for the ternary diagrams the (Figure 4.15 to Figure 4.17). In these diagrams the dots represent the biomass fuels. There is no fusibility data available for the agriculture (OV, VB, KB and PB) and cork residues (CR) – as can be seen in the figures these residues are out of the available melting curves in the ternary diagram. The potassium silicates may melt at typical biomass combustion temperatures and cause ash sintering [67]. The SD is located between the formation of $K_2O{\cdot}2CaO{\cdot}6SiO_2$ and $K_2O{\cdot}2CaO{\cdot}9SiO_2$, between 1200 ºC and 1250 ºC, respectively. These temperatures are slightly below the fusibility temperature of the SD (1300 ºC) [112]. The other elements are closer to the CaO maximum percentage (2613 ºC), especially the PB and CR, which indicates very high fusion temperatures for these compounds.

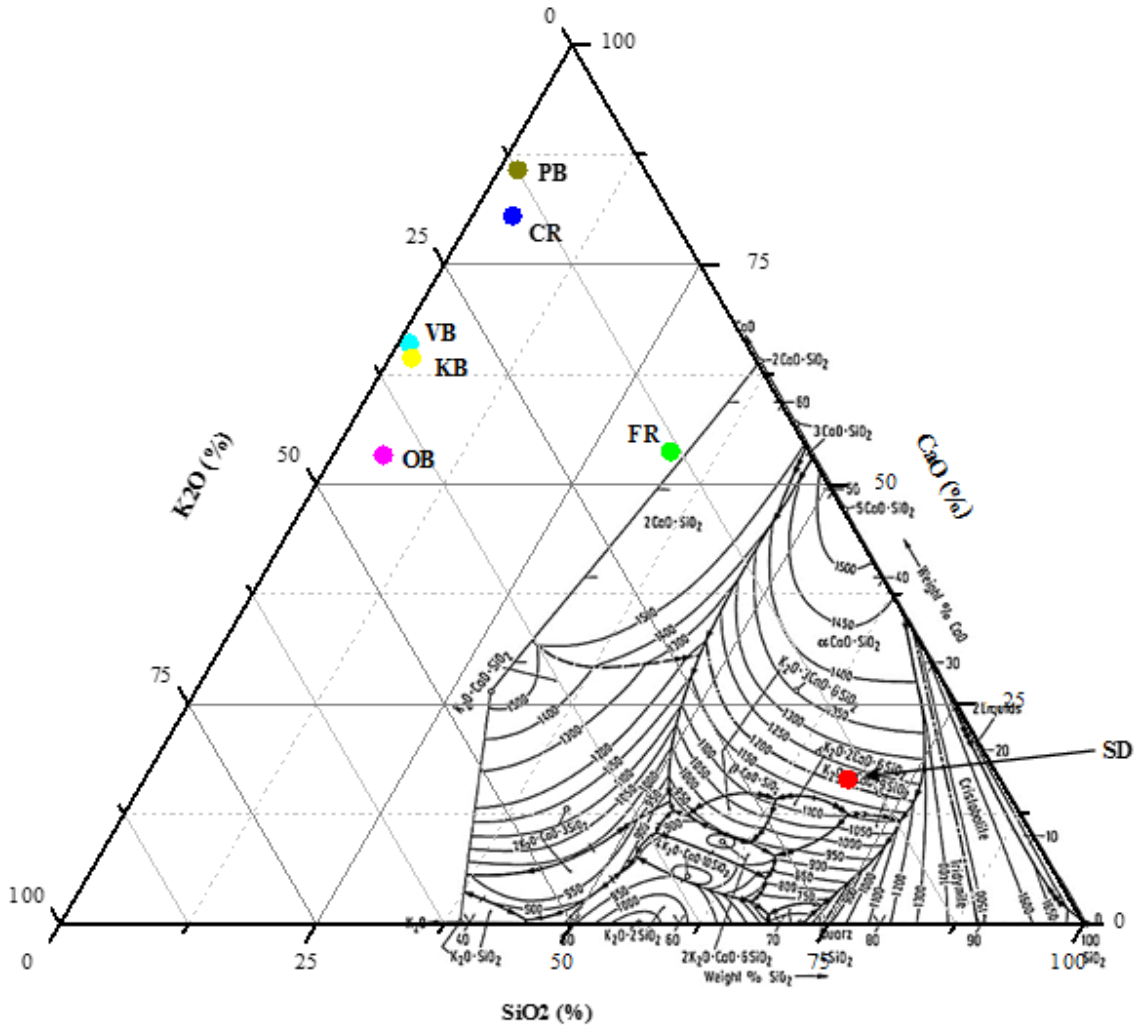


Figure 4.15. Fusibility temperatures of the interaction of K_2O-SiO_2-CaO mass fractions based on [113].

SiO_2 and Al_2O_3 can react with KCl at high temperature [67], but for lower levels of aluminum, the reactions occurs at lower temperatures (up to 700 ºC). The potassium is also a key element that originates the in formation of troublesome species via different routes at typical combustion temperatures [67]. The analysis of the ternary K_2O-SiO_2-Al_2O_3 diagram (Figure 4.16) reveals that, in the case of the SD, the most problematical compounds can form $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, which has a fusion temperature close to 1150 ºC. The remaining elements do not have known compounds in this ternary diagram, except the FR, with a compound formed close to 1600 ºC.

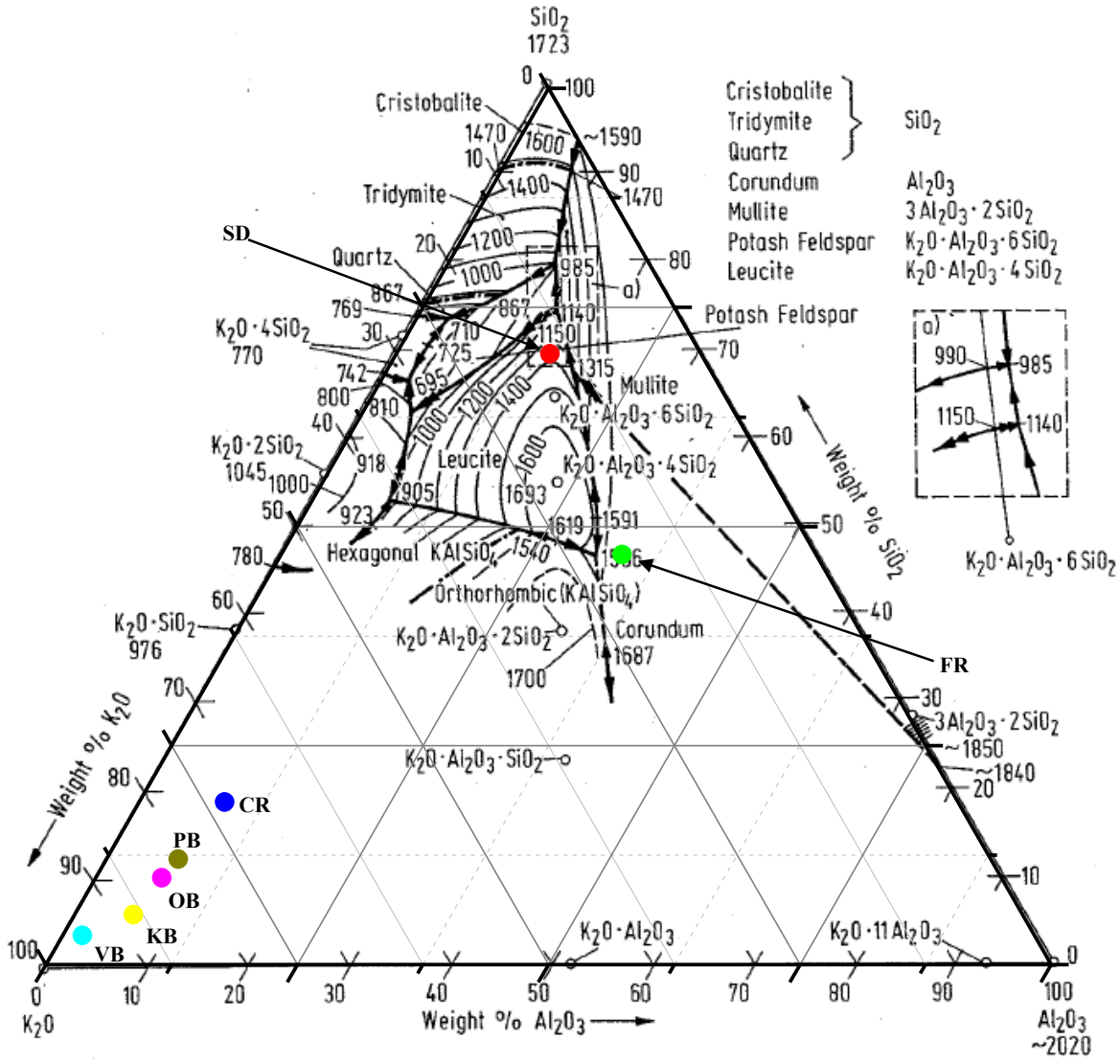


Figure 4.16. Fusibility temperatures of the interaction of K_2O-SiO_2-Al_2O_3 mass fractions based on [113].

There is a clear tendency for interaction between CaO-Al_2O_3-SiO_2, for most biomass fuels (CR, OB, VB, KB and PB) due to their higher content in CaO (> 2300 ºC), as compared to the others. CaO has the highest fusion temperature of the three compounds analyzed. FR residues are prone to the formation of $2CaO$-Al_3O_3-SiO_2 that melts at 1500 ºC. SD is the residue that presents the higher tendency for problems, where formation of tridymite can occur, which melts at temperatures above 1300 ºC. Figure 4.17 also reveals the formation of some problematical compounds. Despite the melting temperatures of the SiO_2, Al_2O_3 and

CaO being 1725 ºC, 2053 ºC and 2612 ºC, the melting temperatures of their mixtures can be lower than 1200 ºC.

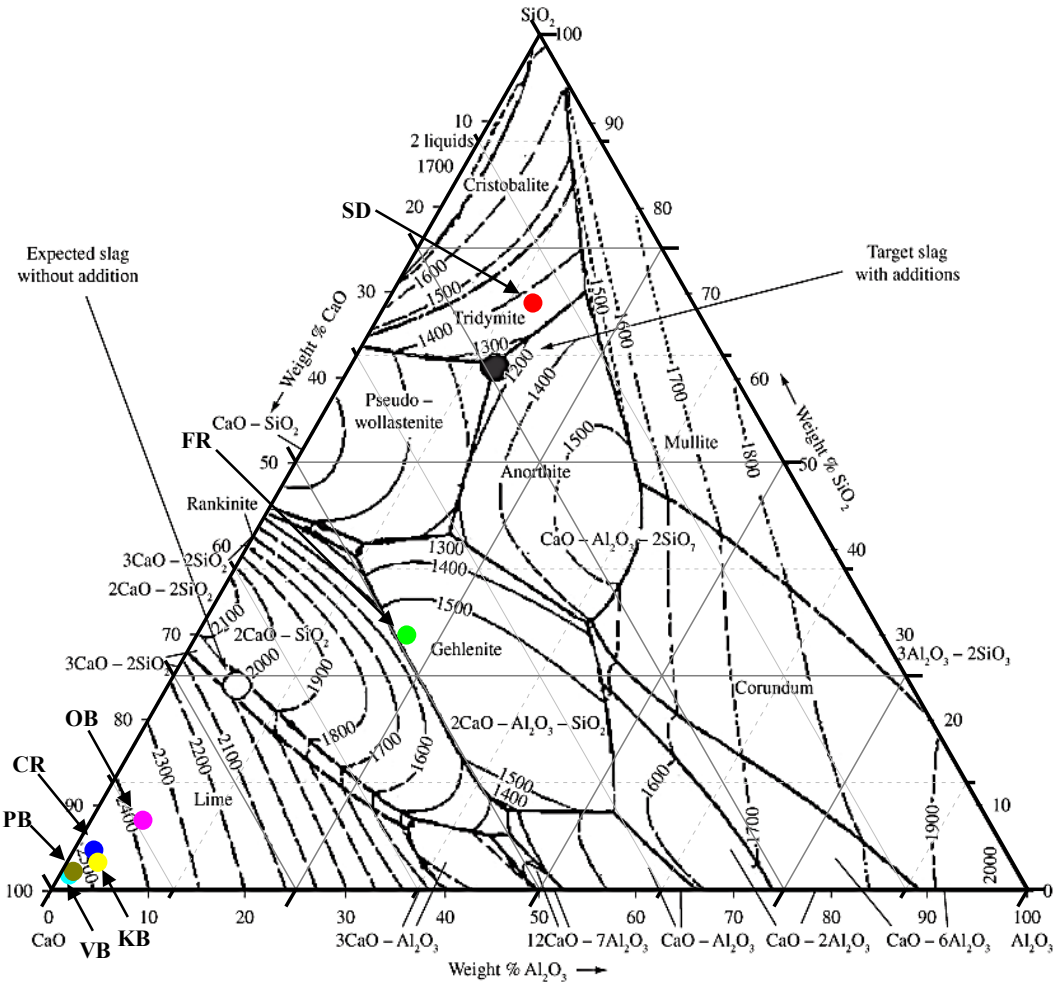


Figure 4.17. Fusibility temperatures of the interaction of CaO-SiO_2-Al_2O_3 mass fractions based on [113].

4.3.3 Slagging and fouling indexes

The slagging and fouling indexes, discussed in Chapter 2, may help to predict problems that can occur in equipments burning biomass combustion Table 4.5 presents these indexes for the present biomass fuels. Note that these indexes do not evaluate the degree of sintering or melting of ashes, just give an indication of the likelihood of these problems to occur.

Table 4.5. Slagging and fouling indexes for all biomass fuels studied.

Index	Indicator	SD	FR	CR	VB	OB	KB	PB
AI	fouling	0.08 l	0.03 l	0.07 l	0.25 m	0.35 h	0.34 m	0.15 l
$R_{b/a}$	fouling	0.64 m	1.03 h	17.39 h	59.15 h	12.75 h	24.44 h	39.02 h
TA	fouling	11.77 h	9.49 h	15.93 h	24.72 h	29.94 h	24.34 h	11.35 h
Si	slagging	77.10 m	60.88 h	63.82 h	8.79 h	35.16 h	18.45 h	12.45 h
Si/Al	deposition	4.56 l	1.38 h	2.18 h	1.65 h	1.50 h	0.97 h	1.69 h
Fe/Ca	deposition	0.88 h	0.22 l	0.004 l	0.01 l	0.04 l	0.02 l	0.01 l
Fu	fouling	7.48 h	9.74 h	277.06 eh	1462.21 eh	381.70 eh	594.95 eh	442.90 eh
Sr	slagging	65.13 m	30.49 h	4.54 h	1.45 h	7.34 h	2.82 h	1.84 h

Slagging/fouling tendency: eh: extremely high, h: high, m: medium, l: low.

The reference residue (SD), comparing with the other biomass fuels, has minor ash fusion problems, with the exception of the levels of Fe/Ca, which are higher. All other residues have, generally, a higher tendency for the appearance of ash deposition and high levels of agglomeration.

The data show a clear tendency to fouling problems (Fu) for all biomass fuels tested, particularly in the case of the agriculture residues (VB, OB, KB and PB), followed by CR.

The slagging index (Sr) shows that only the SD presents a medium tendency to generate slagging, as compared with all the remaining biomass fuels, which present high tendency for slagging. This formula uses the quantity of silica (SiO_2) that is the most important compound to instigate agglomeration in the grate during the combustion process. The Si index and the Si/Al ratio indicate approximately the same problems as the Sr index. One of the reasons is that the silica can easily agglomerate with some elements at the relatively low biomass combustion temperatures (700-1000 ºC). However, some additives can be used to induce the chemical and physical adsorption and reactions, and thereby increase the ash melting temperature. Adding some inert elements/compounds or additives can benefit the biomass ash behavior, opposing some materials with bad properties in order to minimize the slagging and fouling problems [67].

5. PARTICULATE MATTER EMISSIONS AND ASH CHARACTERISTICS IN A DOMESTIC BOILER FIRED WITH ALTERNATIVE BIOMASS PELLETS

The work described in this chapter was performed in collaboration between the Department of Mechanical Engineering of University of Minho and the Department of Mechanical Engineering of Instituto Superior Técnico in Lisboa. The biomass fuels were all prepared (dried and triturated) and the pellets were produced in University of Minho, while the combustion tests were performed in a domestic boiler and the particulate matter examined in a SEM equipped with an EDS in Instituto Superior Técnico.

5.1 Properties of the pellets

Table 5.1 presents the chemical and physical characteristics of the biomass fuels (pellets). The SD is the most commonly used pellets in Portugal and other European countries [10, 101, 114], due to its low ash content, good calorific value and acceptable chemical composition for combustion. The CR residues are from the cork industry and are produced from granulated residues of the bark of the tree (*Quercus suber*), and exhibited higher ash content [115]. The alternative pellets present lower volatile matter and higher fixed carbon than the SD, which implies higher burning times.

SD has lower nitrogen content than the other pellets, which can be explained by the fertilization of crops and can affect the emissions producing more NO_x through the fuel mechanism. SD presents higher sulphur content, which is a source of SO_2 emissions and other corrosive elements [88].

The alternative pellets present high levels of calcium, which is beneficial from the slagging formation point of view due to the increase in the ashes fusion temperature they promote [116]. SD presents more silicon, iron and titanium, but the more problematical elements such as chlorine, sodium and potassium, are predominant in the agriculture and cork residues.

The pellets present bulk densities between 560 kg/m^3 and 635 kg/m^3. The mechanical durability are higher for the alternative pellets, but the values measured are below the European standards [117], except for the OB (> 97.5%).

Table 5.1. Chemical and physical characteristics of the biomass fuels (pellets).

Analysis	Parameter	SD	CR	VB	OB	KB	PB
Proximate analysis (wt.%, dry basis)	Volatile matter	90.2	76.6	78.4	79.5	78.2	81.0
	Ash	0.68	2.01	2.35	2.74	2.62	1.32
	Fixed Carbon	9.12	21.39	19.25	17.76	19.18	17.68
Net calorific value (MJ/kg)	LHV	16.9	19.2	17.7	18.0	17.9	18.1
Ultimate analysis (wt.%, free dry ash)	C	49.9	53.8	49.3	47.9	48.2	47.6
	H	6.08	6.62	6.19	6.2	6.4	5.98
	N	0.06	0.35	0.67	0.65	0.72	0.54
	S	0.2	0.034	0.15	0.15	0.16	0.16
	O*	43.76	39.20	43.69	45.10	44.52	45.72
Ash analysis (wt.%, as dry basis)	Al_2O_3	13.2	1.58	0.5	2.22	1.54	0.765
	CaO	16.20	70.3	47.59	35.9	44.7	59.92
	Cl	0.039	2.4	0.042	0.563	0.19	1.03
	Fe_2O_3	8.45	0.28	0.699	1.32	0.788	0.592
	K_2O	12.5	13.55	23.72	28.14	23.24	8.66
	MgO	9.93	1.67	7.85	4.82	5.8	8.48
	Na_2O	3.03	2.38	1.0	1.8	1.1	2.69
	P_2O_5	2.95	1.75	11.9	18.3	15.8	12.9
	SiO_2	27.6	3.44	0.824	3.33	1.49	1.29
	SO_3	3.37	1.62	1.47	1.08	2.49	2.68
	TiO_2	1.27	0.05	0.043	0.096	0.064	0.0039
Physical characteristics of pellets	Bulk density (kg/m^3)	586	612	578	635	616	560
	Mechanical durability (%)	90.4	96.6	95.1	98.4	93.2	95.1

*calculated by difference.

5.2 Test conditions

Table 5.2 presents the domestic boiler test conditions used in the present trials and the respective flue gas data for each condition.

Table 5.2. Domestic boiler test conditions and flue gas data.

Pellets	Thermal load (kW)	Air inflow (kg/h)	Excess air coefficient (λ)	O_2 (dry volume %)	CO	NO_x	HC
					(mg/Nm^3@13%O_2)		
SD	14.93	98	5.2	16.9	218	91	2
CR	11.31	102	7.1	18.0	3307	311	118
VB	12.67	122	8.0	18.3	5878	327	212
OB	12.80	145	9.9	18.8	5526	281	501
KB	10.89	91	7.2	18.1	6067	487	153
PB	12.13	100	7.0	17.9	2933	469	95

Each test lasted for about 7 hours in continuous operation. Initially the boiler was warmed up during at least one hour, until the combustion was stabilized, with a variation in the flue gas temperature at the chimney entrance below 5 ºC. Afterwards, the collection of PM data started and maintained up to one hour. During these tests, the gas analyzers were measuring permanently the gaseous emissions of O_2, CO, HC, CO_2 and NO_x.

Ashes and PM were collected from the ashtray (bottom ashes), from the grate as agglomerated (sintering/slagging) and with the aid of the LPI filters (fly ashes/PM).

Subsequently, the fly ashes were examined in the SEM equipped with the EDS. In addition, the bottom ashes and slag were analyzed by x-ray fluorescence. Four groups were established for analysis: (1) ash collected from the ashtray, (2) unburnt pellets collected from the ashtray (that present a diameter larger than 3.15 mm), (3) slag collected from the boiler grate, and (4) sintered ashes. The total ash residues were measured to quantify its production in each test and their degree of sintering was examined.

During the combustion tests some problems related with the feeding system and air inlet were identified for some pellets. In particular, during the combustion of the pellets with higher

burnout time, unburned residues accumulated in the boiler grate, which perturbed not only the inlet of new pellets, but also the air inlet. Care was taken in order to minimize these problems during the measurements, namely manually dispersing the residues in the accumulated areas.

5.3 Results and discussion

According to the European standard EN14785:2006, the gaseous emissions and particulate matter were normalized to 13% O_2 in the combustion products.

5.3.1 Gaseous emissions

The data in Table 5.2 reveal that the present boiler operates with high levels of excess air. Despite this, relatively high emissions of CO (~ 6 g/Nm^3@13% O_2) were detected in the combustion of VB, OB and KB. The combustion of these biomass fuels differs significantly from that of the SD (218 mg/Nm^3@13% O_2), which is the boiler standard fuel. The CR and PB presented also relatively high CO emissions (~ 3 g/Nm^3@11% O_2).

In regard to the HC emissions, the combustion of OB originated the highest emission (501 mg/Nm^3@13% O_2) while the combustion of SD originated, as expected, the lowest one (2 mg/Nm^3@13% O_2). The combustion of the remaining pellets originated HC emissions between 95 mg/Nm^3@13% O_2 and 212 mg/Nm^3@13% O_2 in the following order: VB > KB > CR > PB.

Finally, the NO_x emissions were higher for the combustion of KB and PB, close to 500 mg/Nm^3@13% O_2, as a result of the high presence of nitrogen in these biomass fuels [118], followed by those from the combustion of CR, VB and OB (between 281 and 327 mg/Nm^3@13% O_2). Once again, the combustion of SD yielded the lower NO_x emission.

5.3.2 Particulate matter emissions

Figure 5.1 shows the total PM for the biomass fuels studied. PM emissions from the combustion of VB (357 mg/Nm^3@13% O_2) and OB (341 mg/Nm^3@13% O_2) are much

higher than those from the combustion of PB (167 mg/Nm^3@13% O_2) > KB (110 mg/Nm^3@13% O_2) > CR (88 mg/Nm^3@13% O_2) >> SD (22 mg/Nm^3@13% O_2).

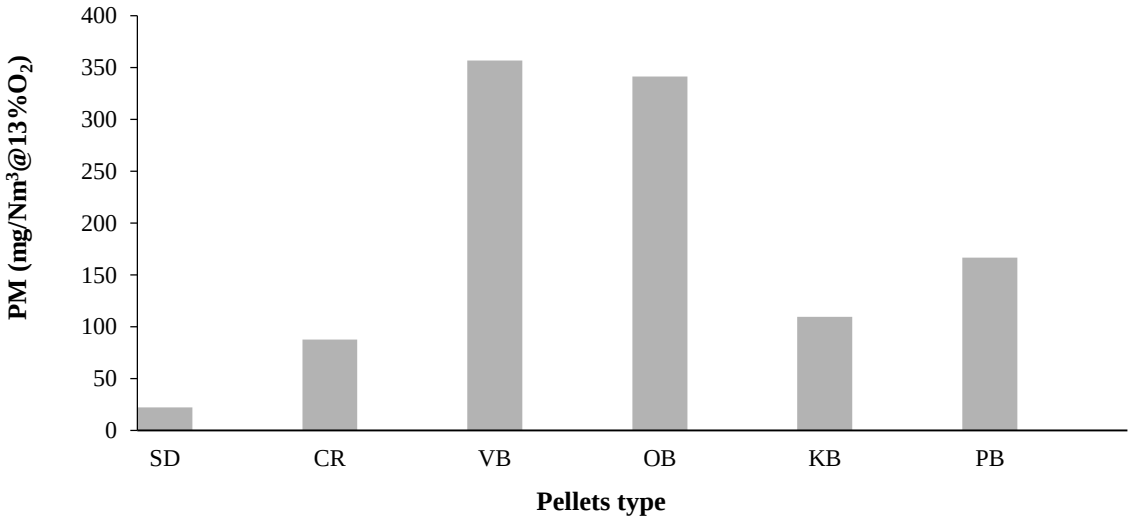


Figure 5.1. Total PM for the biomass fuels studied.

Figure 5.2 shows the PM obtained with the LPI-3 for the biomass fuels studied. Very low PM concentrations were obtained for PM above 10 μm (5 to 13 mg/Nm^3) and for PM between 2.5 μm and 10 μm (5 to 6 mg/Nm^3) regardless of the biomass fuel considered. In contrast, the fraction of PM below 2.5 μm was significantly higher for all biomass fuels; specifically, 436 mg/Nm^3@13% O_2 for VB, 423 mg/Nm^3@13% O_2 for OB, 355 mg/Nm^3@13% O_2 for PB, 308 mg/Nm^3@13% O_2 for KB, 212 mg/Nm^3@13% O_2 for CR and 39 mg/Nm^3@13% O_2 for SD. The PM with diameter less than 2.5 μm are considered for the ambient air quality regulation as a great health concern. PM with diameters between 2.5-10 μm are currently considered as a respirable fraction, as promulgated by the ambient air quality standards, while PM with diameters above 10 μm are considered as non-respirable [119]. According to the results, the greatest mass concentration of particles collected is respirable, which is a concern regarding public human health, especially for the alternative pellets examined in this study.

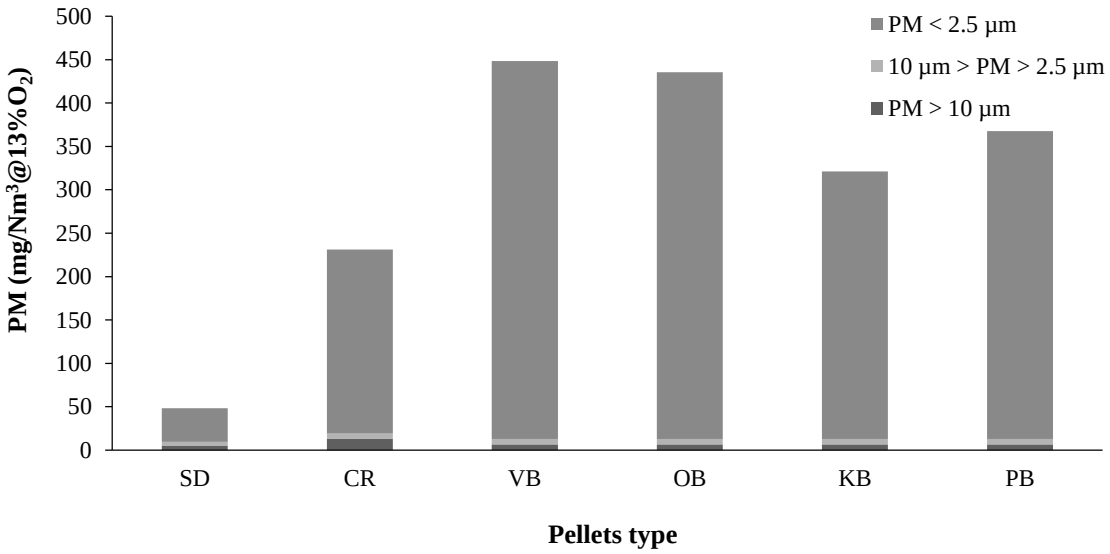


Figure 5.2. PM obtained with the LPI-3 for the biomass fuels studied.

Figure 5.3 shows the size-classified PM emissions obtained with the LPI-13 for the biomass fuels studied. It should be mentioned that the total PM emissions measured with the LPI-13 were systematically lower than those measured with the LPI-3. The differences are due to the small fractions of particles that deposit out of the substrates in the LPI-13 and therefore are not accounted for. In the LPI-3 this effect is marginal. With exception of the cases of the OB and VB, the PM emissions presented a bimodal mass size distribution, as observed by other authors at the exhaust of combustion appliances [97, 99, 120–122].

Figure 5.3 reveals that all pellets present a high concentration of particles between 0.039 to 1.23 µm of diameter. For the unimodal size distribution cases, the PM location concentration maxima depends on the type of pellets; specifically, the OB presents the maximum (148 mg/Nm^3) for a mass median (aerodynamic) diameter (MMD) of 0.32 µm, while the VB presents the maximum (117 mg/Nm^3) for a MMD of 0.59 µm. The remaining pellets present bimodal size distribution with the maxima located at 0.32 µm and 0.765 µm particle diameters. In the case of the PB the maximum concentration values are 59 mg/Nm^3 and 90 mg/Nm^3, in the case of CR the values are 21 mg/Nm^3 and 58 mg/Nm^3, and in the case of the KB the values are 32 mg/Nm^3 and 43 mg/Nm^3. Finally, SD presents lower PM concentration than all other pellets, with a maximum of 6.1 mg/Nm^3 located at 0.32 µm. Exposure to ultra-

fine PM (0.01 µm to 2.5 µm) could increase the risk of severe respiratory disease and the chemical composition of particles influences the severity and type of health effects [90, 92, 123].

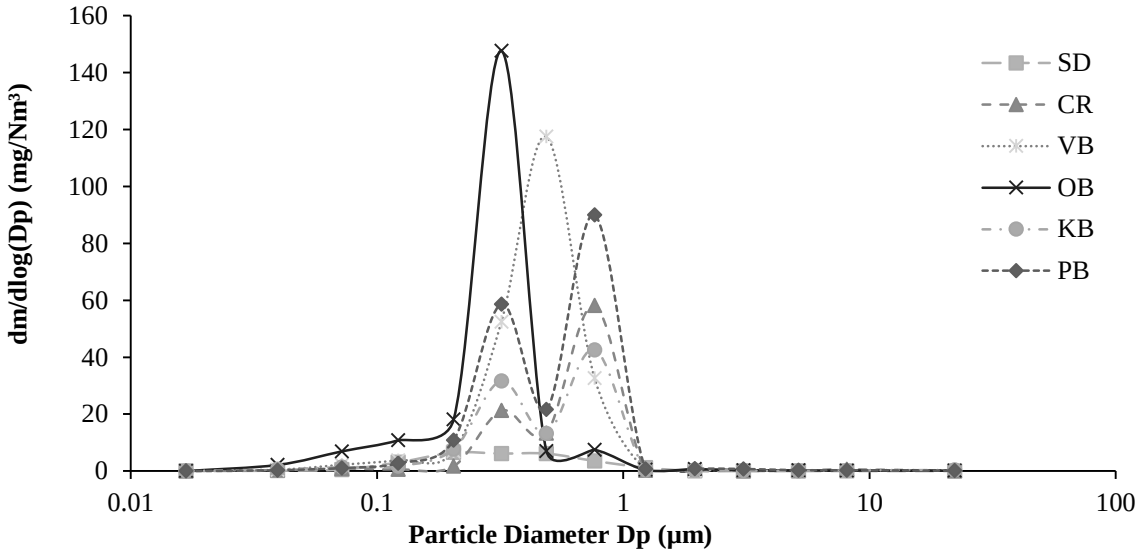


Figure 5.3. Particulate matter of the different types of pellets by LPI-13.

The PM concentration-diameter profiles of the pellets follow the same tendencies in the two LPIs. In other words, the cumulative concentration-diameter profile of PM for the LPI-13, follows the same tendency as those for the LPI-3. VB (42 mg/Nm^3) and OB (36 mg/Nm^3) present the highest cumulative concentrations of emitted particles during combusion, followed by PB (35 mg/Nm^3), KB (19 mg/Nm^3) and CR (18 mg/Nm^3). SD presents the lowest levels of PM emissions (5 mg/Nm^3), which can be explained by the chemical composition of this biomass fuel [90], visible in the characteristics of fly ashes.

5.3.3 Ash characteristics

5.3.3.1 Fly ashes

Figure 5.4 shows typical SEM images of selected PM samples collected with the LPI-13 for the combustion of different pellets. Figure 5.4 (a) show typical submicron PM collected in

various substrates for different types of pellets examined here. In this figure a large number of aggregates can be observed, which were found to be soot aggregates later in the EDS analysis. In Figure 5.4 (b) the presence of aggregates is more pronounced due to a higher amount of inorganics present in the alternative pellets, which contribute to condensation and agglomeration.

Figure 5.5 shows the PM chemical composition in various substrates for the combustion of the PB. Note that in this figure the values represented are the average of the five different areas of 50×50 μm^2 analysed for each PM sample. Figure 5.5 reveals that the composition of the PM under 1 μm (substrates 3, 4, 6 and 7) varies marginally in terms of elements present and its relative concentration. The high volatile potassium is present, together with sulphur and chlorine, which are consistent with previous studies [16, 100].

Figure 5.6 shows the PM chemical composition in substrate 6 for the combustion of various pellets. The PM composition is dominated by carbon. A high carbon content indicates the presence of particulates from incomplete combustion, including soot [91]. Besides this most predominant element, the ones that occur in higher amounts are potassium, followed by sulphur and chlorine. These last two elements vary significantly with the different type of pellets. The sulphur, chlorine and potassium are usually present in sub-micron flying ash particles (< 0.5 μm) resulting from vaporization of these easily volatilized ash components [91]. These compounds are water soluble and can easily dissolve in the condensation that is normally present in the flue gas conducts with weak thermal isolation, which can lead to some corrosion problems due to occurrence of sulfuric and hydrochloric acids [6]. Lastly, some elements such as metals, sodium, phosphorus, cadmium, mercury and arsenic can be found in very small amounts in the PM that results from biomass combustion. These compounds have toxic effects on humans [90].

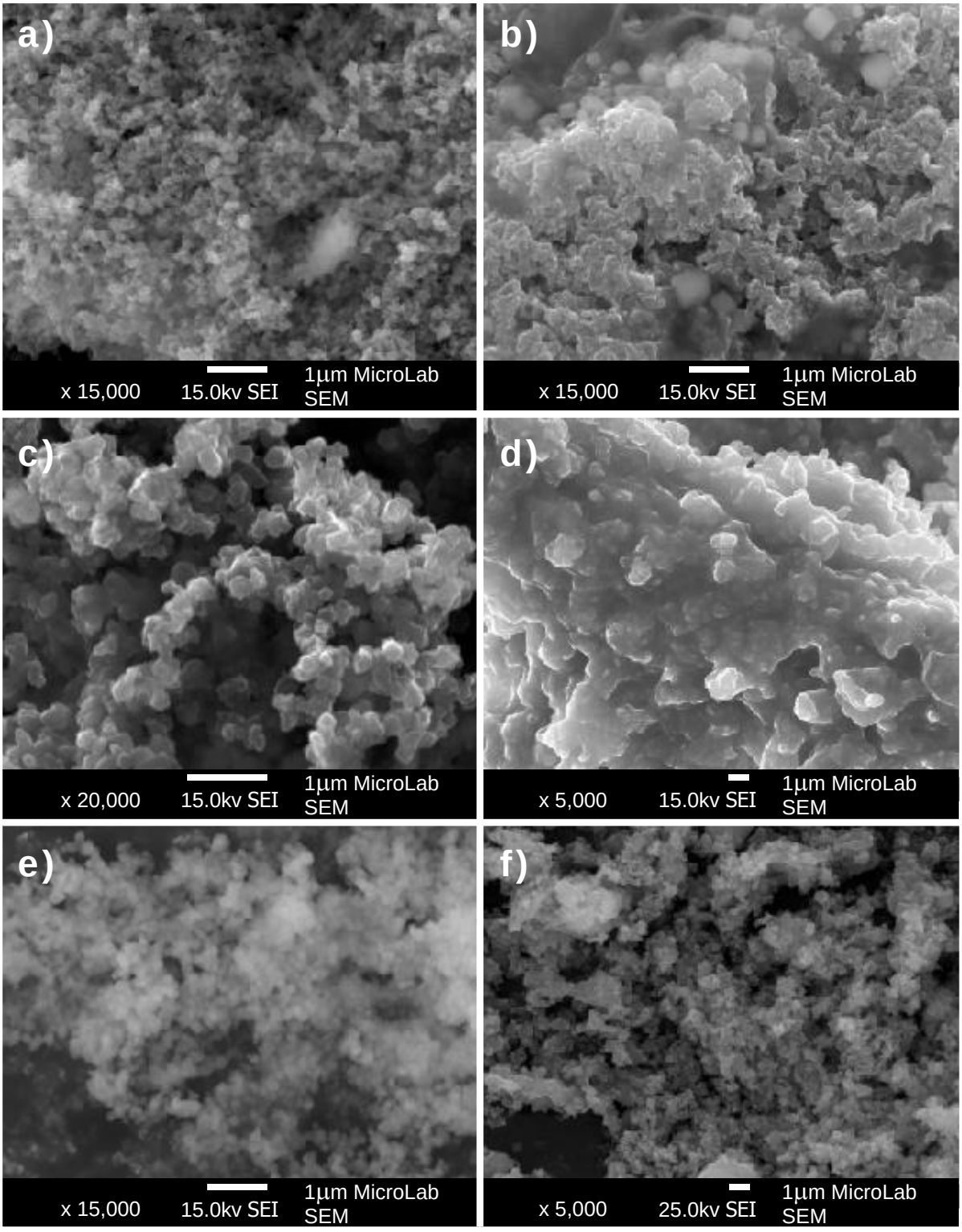


Figure 5.4. Typical SEM images of PM samples collected with the LPI-13 for the combustion of (a) SD from substrate 4, (b) CR from substrate 3, (c) VB from substrate 6, (d) OB from substrate 3, (e) KB from substrate 4, and (f) PB from substrate 6, in a domestic pellet boiler.

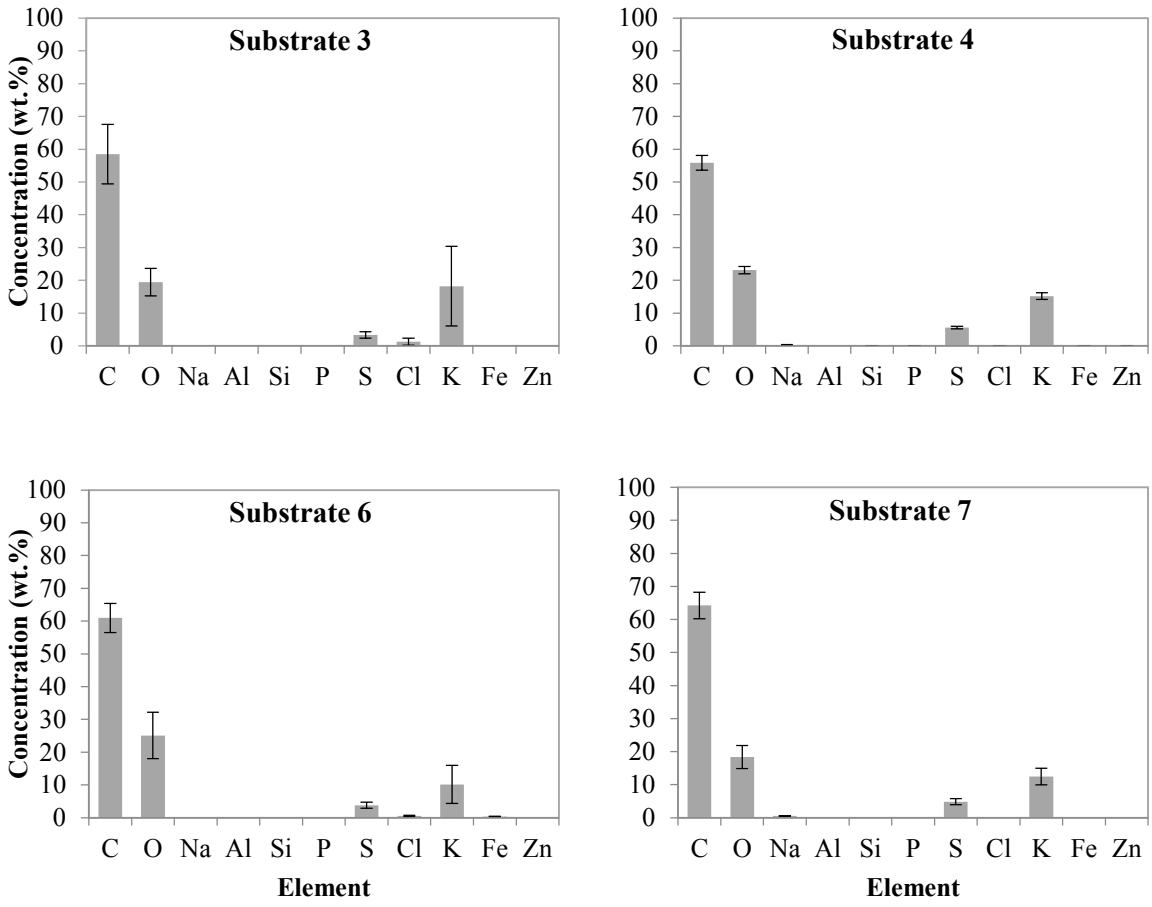


Figure 5.5. PM chemical composition in substrate 3, 4, 6 and 7 for the combustion of PB. Errors bars represent standard deviations derived from 5 independent measurements.

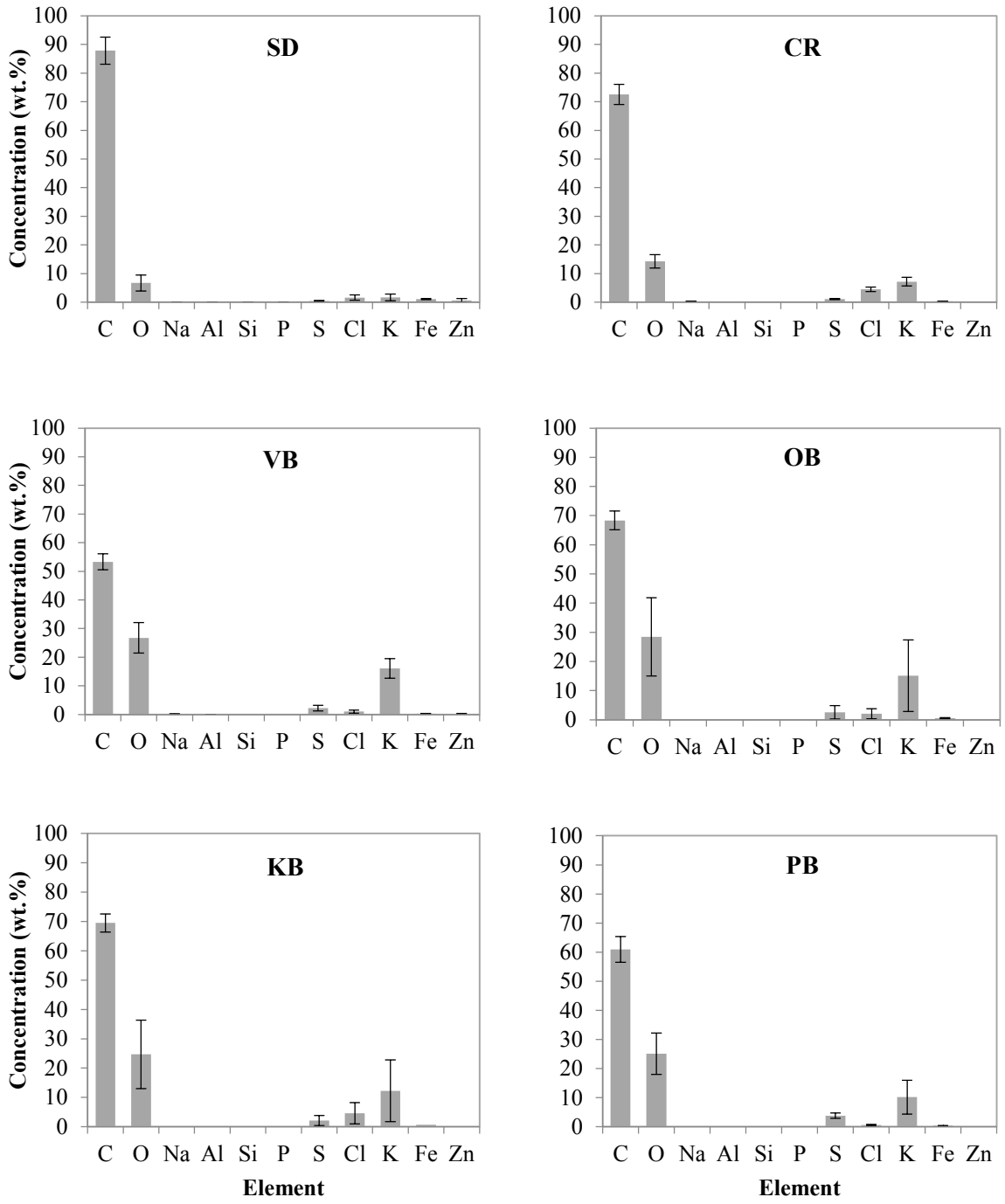


Figure 5.6. PM chemical composition in substrate 6 for the combustion of SD, CR, VB, OB, KB and PB. Errors bars represent standard deviations derived from 5 independent measurements.

5.3.3.2 Bottom ashes

Figure 5.7 shows the ash production from the combustion of the biomass fuels studied. It is observed that the production of ashes and unburnt residues is significant higher during the combustion of the alternative pellets. The amount of unburnt pellets also indicates unfavorable operating conditions of this commercial boiler regarding the use of alternative fuels. Moreover, under favorable combustion conditions, with higher temperatures in the grate, the formation of slag increases, as observed for the combustion of SD. The presence of sintered ashes with low particle diameter and weak sintering intensity observed during the combustion of the alternative pellets is the result of more volatile elements, as the potassium and sodium, in these biomass fuels, which react easily, but forming a porous structure. These elements have also more tendency to deposit, without reacting, or being expelled in the gaseous emissions [11, 124].

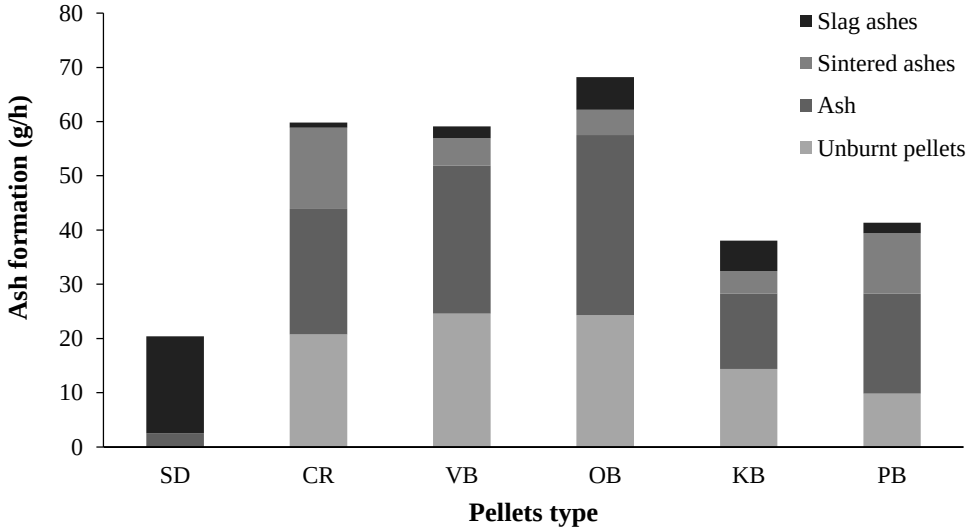


Figure 5.7. Ash production from the combustion of the biomass fuels studied.

The formation of slag in the grate was analyzed, as shown in Figure 5.8. As indicated before, the chemical composition of ashes affects its slag behavior [12, 15]. The quantity of silicon present in the ashes also promotes the blending of some elements at lower temperatures. The presence of higher quantities of slag in the case of the combustion of SD can be explained by

the higher amounts of silicon present in the fuel ashes, which easily reacts with other elements (potassium, calcium and sodium) at relatively low combustion temperatures.

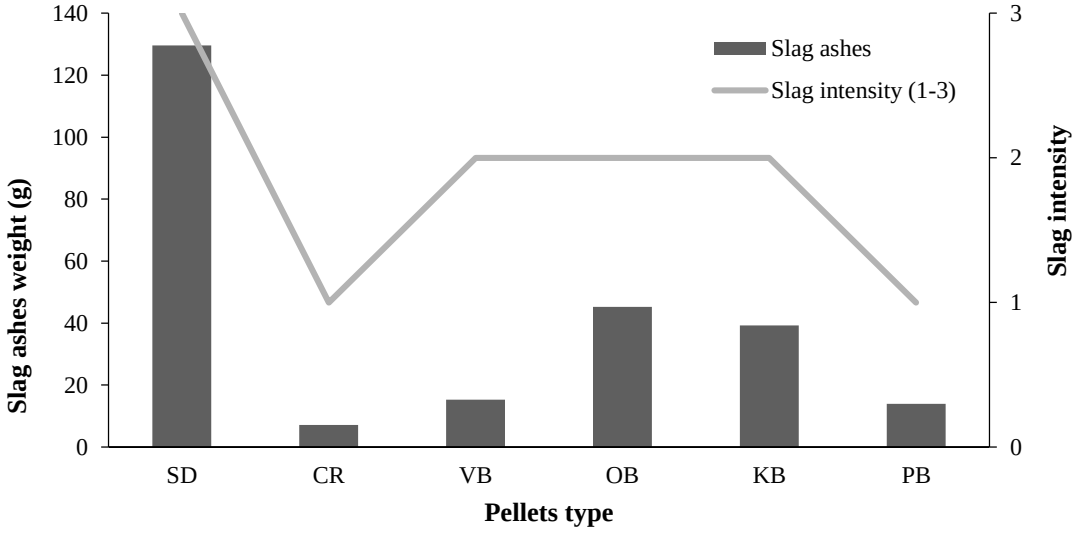


Figure 5.8. Degree of sintering and weigh of slag from combustion of pellets.

Table 5.3 and Table 5.4 show the chemical composition of the bottom ashes and slag for the biomass fuels studied, respectively, obtained by x-ray fluorescence spectrometry. Both tables present in bold the more relevant data. The chemical composition of bottom ashes indicates a general tendency for sintering of some elements. A particular focus on specific elements is needed, according to the different types of biomass. For instance, concerning the high silicon biomass fuels, potassium and calcium are key elements in fouling and slagging generation [125]. The quantity of carbon in the slag ashes is low compared with some other ash elements. However, SD is the residue with the highest carbon content (6.2%), followed by the other residues with values between 1.8% (OB) and 3.6% (VB). Higher quantities of silicon (12%), aluminum (2%) and iron (2%), elements with high fusion temperatures, are observed exclusively for SD. SD have also the problematic behavior of the silicon reacting with other elements at lower temperatures (high tendency to slag) [2]. The calcium, which is very used as an additive in some pellets to minimize the fusion problems of the ashes [67], is more prominent in CR (34%) and PB (32%), less in other pellets, and lower in SD (5.5%). Finally, the magnesium is observed in quantities below 4%, being higher in VB (3.7%), PB (3.6%)

and KB (3.0%). This element plays an important role regarding the melting behavior of the ash material [66]. The potassium is one of the most problematic elements to combustion [88], since it easily vaporizes in fly ashes and reacts with other elements to cause sintering processes on ashes [11]. Its presence is more evident in OB (11.8%), and also high in KB (9.1%) and VB (8.4%). The phosphorus, which forms ash and corrodes heating equipment at high temperature during thermochemical conversion [80], is observed in high quantities in OB (2.1%), PB (1.8%) and VB (1.7%).

Table 5.3. Chemical composition of the bottom ashes for the biomass fuels studied.

Elements (wt.%)	SD	CR	VB	OB	KB	PB
C	**6.221**	**3.569**	**3.644**	**1.822**	**3.536**	**2.055**
N	0.034	0.039	0.055	0.026	0.052	0.014
H	0.268	0.219	0.227	0.220	0.275	0.210
Al	**1.813**	0.394	0.061	0.232	0.179	0.105
Ba	0.045	0.081	0.215	0.043	0.053	0.112
Ca	**5.521**	**33.555**	**23.453**	**16.927**	**21.436**	**32.342**
Cl	0.034	0.357	0.070	0.359	0.670	0.073
Cr	0.033	0.007	n/a	-	-	-
Cu	0.045	0.030	0.052	0.037	0.164	0.061
Fe	**2.015**	0.669	0.213	0.252	0.201	0.354
K	**3.129**	**3.939**	**8.408**	**11.768**	**9.126**	**4.648**
Mg	**2.292**	**1.006**	**3.744**	**1.799**	**2.972**	**3.622**
Mn	0.661	0.512	1.068	0.080	0.121	0.137
Na	0.548	0.320	0.153	0.140	0.111	0.088
Ni	0.003	-	-	-	-	-
P	**0.285**	**0.409**	**1.711**	**2.144**	**-**	**1.841**
Pb	-	-	-	0.029	-	-
Rb	0.027	0.010	0.013	0.016	0.013	0.005
S	**0.309**	**0.302**	**0.654**	**0.600**	**1.087**	**1.026**
Si	**11.853**	**2.544**	**0.203**	**0.701**	**0.178**	**0.351**
Sr	0.065	0.184	0.158	0.141	0.052	0.270
Ti	0.256	0.006	-	0.006	-	-
Zn	0.028	0.017	0.159	0.065	0.087	0.053
Zr	0.021	0.009	0.024	0.021	0.007	0.035
O	64.495	51.820	55.715	62.571	59.680	52.597

The chemical composition of the slag from different pellets leads to similar conclusions as those drawn from the composition of the bottom ashes. The carbon quantity in the slag ashes is lower as compared with that in bottom ashes and ranges from 0.33% (for SD) to 0.77% (in VB). These results confirm that the slag, collected from the boiler grate, reached temperatures high enough, and for a sufficient residence time, so that degradation of most of the carbonous residues in the pellets occurred. However, for each type of pellets, some elements have more tendency to slagging [11]. The content of silicon is higher in pellet ashes compared with the bottom ashes, showing high quantities in the SD. Regarding the pellets that presented higher quantities of potassium in the bottom ashes, the amount of this element is lower in the slag ashes in comparison to bottom ashes, as is the case of OB (12% to 8%), KB (9% to 7%) and the VB (8% to 4%). The ashes of many biomass fuels have low melting points, because of the high content of potassium in the ashes [126]. However, a significant amount of this elements is released as inorganic volatile [124]. Öhman *et al.* [11] also found aluminum, magnesium, phosphorus, manganese, iron and sodium in their slag samples, but with a lower content of potassium. An increase of phosphorus (1.8% to 2.3%) in the PB and an increase of silicon in the CR (2.5% to 7.1%) were also observed. In CR, a decline was observed regarding the calcium content (33.5% to 32.6%). Some authors refer the formation of large quantities of troublesome deposits, consisting mainly of potassium, chlorine and silicates, and to a lesser extent, also of calcium and phosphorus [124].

In brief, this investigation revealed the potential of using CR, KB and PB in small-scale combustion systems without special difficulties. In the case of the pellets of OB and VB, however, the study identified some critical problems that need to be solved before their effective use in small-scale combustion systems. These problems include operational problems during boiler operation, caused by the relatively high ash content of the OB, and high gaseous and PM emissions, which can be overcome through boiler optimization.

Table 5.4. Chemical composition of the slag for the biomass fuels studied.

Elements (wt.%)	SD	CR	VB	OB	KB	PB
C	**0.329**	**0.422**	**0.769**	**0.370**	**0.366**	**0.376**
N	0.003	0.002	0.003	0.002	0.002	0.002
H	0.054	0.119	0.261	0.067	0.082	0.147
Al	2.438	0.882	0.077	0.372	0.284	0.144
Ba	0.057	0.094	0.214	0.101	0.121	0.171
Ca	**6.107**	**32.629**	**25.489**	**22.161**	**25.788**	**36.180**
Cl	-	0.037	-	-	0.099	-
Cr	0.015	0.009	0.006	0.005	0.004	0.005
Cu	0.078	0.034	0.052	0.036	0.208	0.027
Fe	**2.131**	0.816	0.223	0.360	0.255	0.415
K	**3.362**	**2.712**	**3.897**	**8.504**	**6.785**	**2.720**
Mg	**2.662**	**1.336**	**4.207**	**2.703**	**3.952**	**4.691**
Mn	0.754	0.300	1.303	0.116	0.164	0.153
Na	0.830	0.258	-	0.157	0.068	0.039
Ni	0.004	-	-	-	0.006	-
P	**0.303**	**0.537**	**1.949**	**3.306**	**2.877**	**2.272**
Pd	-	-	0.032	-	-	-
Rb	0.025	0.006	0.005	0.006	0.008	0.003
S	-	**0.059**	**0.171**	**0.251**	**0.559**	**0.414**
Si	**15.178**	**7.089**	**0.237**	**1.508**	**0.346**	**0.502**
Sr	0.063	0.166	0.192	0.179	0.058	0.295
Ti	0.265	0.006	-	0.006	-	-
Zn	0.006	-	0.013	0.013	0.015	0.012
Zr	0.021	0.024	0.025	0.026	0.009	-
O	65.317	52.462	60.875	59.753	57.943	51.434

6. PARTICULATE MATTER EMISSIONS AND FLY ASH CHARACTERISTICS IN A PULVERIZED BIOMASS FIRED LABORATORY LARGE-SCALE FURNACE

This chapter focuses on the combustion of pulverized biomass fuels in a large-scale furnace with emphasis on the particulate matter emissions and fly ash characteristics.

6.1 Properties of the pulverized biomass

Table 6.1 presents the main characteristics of the pulverized biomass fuels used. The ash analysis indicates the presence of high levels of calcium in the alternative biomass fuels, especially for CR, which is beneficial from the slagging formation point of view due to the increase of the ashes fusion temperature [116]. However, the most problematic elements (chlorine, sodium and potassium), present higher contents in the agriculture and cork residues. For example, the high content of chlorine in CR and PB can lead to the formation of HCl and increase the corrosion risks and aerosol and deposit formation [72].

The particle size distributions of the biomass fuels studied are substantially different. CR is the most homogeneous fuel with most particles in the size range 784 μm to 1128 μm. On the contrary, FR is the most heterogeneous fuel with a particle size distribution in the size range 20.7 μm to 1128 μm.

Table 6.1. Characteristics of the pulverized biomass fuels studied.

	Parameter	SD	FR	CR	VB	OB	KB	PB
Proximate analysis (wt.%, dry basis)	Volatile matter	90.20	87.79	76.60	78.40	79.50	78.20	81.00
	Ash	0.68	0.68	2.01	2.35	2.74	2.62	1.32
	Fixed Carbon	9.12	11.53	21.39	19.25	17.76	19.18	17.68
Lower heating value (MJ/kg)	LHV	16.9	18.1	19.2	17.7	18	17.9	18.1
Ultimate analysis (wt.%, dry ash free)	C	49.9	43.6	53.8	49.3	47.9	48.2	47.6
	H	6.08	6.3	6.62	6.19	6.2	6.4	5.98
	N	0.06	0.62	0.35	0.67	0.65	0.72	0.54
	S	0.2	0.034	0.034	0.15	0.15	0.16	0.16
	O*	43.76	49.45	39.20	43.69	45.10	44.52	45.72
Ash analysis (wt.%, dry basis)	Al_2O_3	13.2	3.01	1.58	0.5	2.22	1.54	0.765
	CaO	16.20	35.09	70.3	47.59	35.9	44.7	59.92
	Cl	0.039	0.59	2.4	0.042	0.563	0.19	1.03
	Fe_2O_3	8.45	1.95	0.28	0.699	1.32	0.788	0.592
	K_2O	12.5	24.71	13.55	23.72	28.14	23.24	8.66
	MgO	9.93	6.78	1.67	7.85	4.82	5.8	8.48
	Na_2O	3.03	1.69	2.38	1.0	1.8	1.1	2.69
	P_2O_5	2.95	3.34	1.75	11.9	18.3	15.8	12.9
	SiO_2	27.6	4.84	3.44	0.824	3.33	1.49	1.29
	SO_3	3.37	4.31	1.62	1.47	1.08	2.49	2.68
	TiO_2	1.27	3.23	0.05	0.043	0.096	0.064	0.0039
Particle size	% under 20.7 µm	0.2	6.1	0.1	2.1	1.9	2.2	4.0
	% under 32.1 µm	0.4	11.3	0.3	3.8	3.4	3.8	6.9
	% under 46.1 µm	1.0	17.4	0.4	5.5	5.2	5.8	9.9
	% under 71.3 µm	2.6	26.6	0.4	8.2	8.1	8.7	14.1
	% under 103 µm	4.7	33.4	0.5	11.3	11.5	12.3	18.6
	% under 159 µm	9.2	43.6	0.7	16.6	17.9	17.2	25.3
	% under 228 µm	15.1	51.2	1.0	24.9	24.2	25.5	35.4
	% under 353 µm	26.9	61.4	2.8	38	35	36.8	48
	% under 507 µm	43.1	69.4	12.8	56.6	46.9	55.6	67.2
	% under 784 µm	71.7	83.9	50.2	80.4	71.1	80.2	87.1
	% under 1128 µm	100	100	100	100	100	100	100

*calculed by difference.

6.2 Test Conditions

Table 6.2 summarizes the furnace operating conditions and the flue gas data. Note that during all tests NG was used to help the flame stabilization process.

Table 6.2. Furnace operating conditions and flue gas data.

Parameter	SD	FR	CR	VB	OB	KB	PB
Total thermal input (kW)				100			
Biomass thermal input (kW)				60			
Biomass mass flow rate (kg/h)	12.8	11.9	11.3	12.2	12.0	12.1	11.9
Natural gas mass flow rate (kg/h)				3.0			
Overall excess air (%)				15			
Primary air mass flow rate (kg/h)				5.3			
Secondary air mass flow rate (kg/h)	135	116	135	130	126	128	123
O_2 (%, dry volume)	5.48	5.10	5.61	5.61	6.03	4.41	4.19
CO ($mg/Nm^3@6\%O_2$)	7165	6619	4866	17757	14900	8765	5992
NO_x ($mg/Nm^3@6\%O_2$)	30	199	117	157	173	193	119
HC ($mg/Nm^3@6\%O_2$)	161	124	240	1294	1108	634	136
Particle burnout (%)	93.8	95.0	87.5	89.5	88.7	89.5	92.5

6.3 Results and discussion

6.3.1 Gaseous emissions and particle burnout

The CO and HC emissions and particle burnout reflect the combustion efficiency of the different biomass fuels. The CO and HC emissions and particle burnout shown in Table 6.2 indicate that the combustion is more completed for the SD, FR, CR and PB. The NO_x levels are the sum of NO and NO_2 and relates to the nitrogen content of the biomass fuels.

One of the major differences between the various biomass fuels is the particle size distribution. Although all biomass fuels have been milled to sizes below 1 mm, their particle size distributions are considerable different. This factor has a high influence in the combustion of the biomass.

Agriculture biomasses tend to be the fuels with more difficulties to burn due to its chemical properties and higher ash content. The SD and CR are clearly the biomass fuels with lower nitrogen in its composition which is reflected in the low levels of NO_x emissions compared

with the other residues. The particle burnout is higher for the biomass fuels with higher volatile content.

6.3.2 Particulate matter emissions

PM emissions obtained with the LPI-3 revealed that the quantity of PM above 10 μm was marginal (< 5%) so that only the results obtained with the aid of the LPI-13 are shown here. Figure 6.1 shows the size-classified PM emissions obtained with the LPI-13 for the biomass fuels studied.

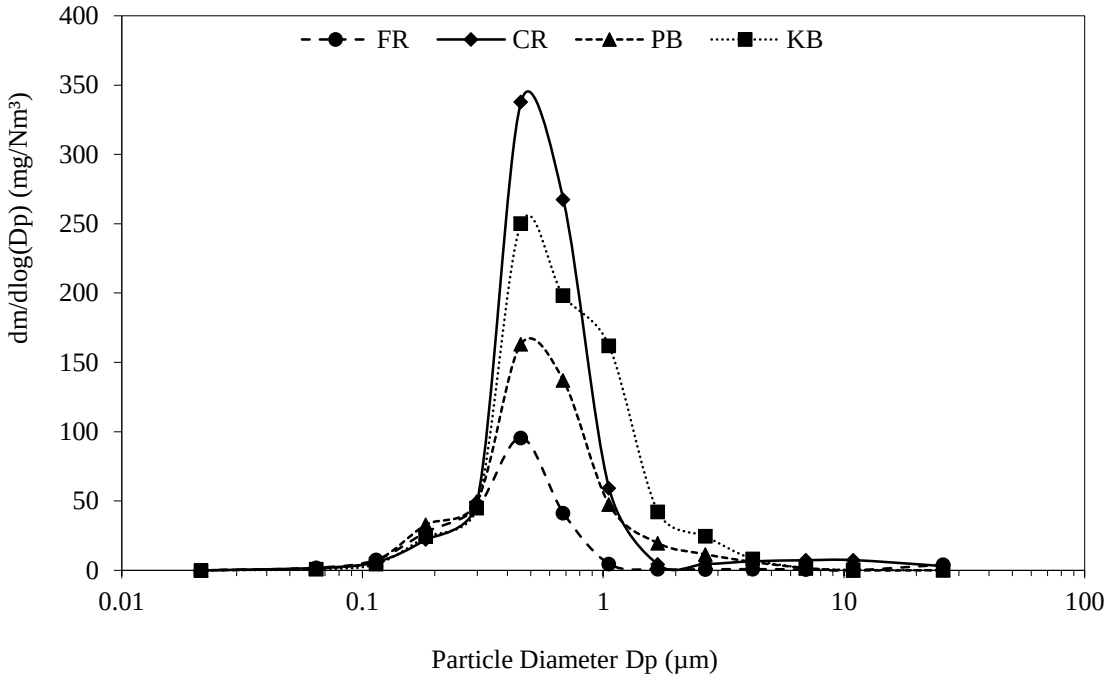


Figure 6.1. Size-classified PM emissions obtained with the LPI-13 for the biomass fuels studied.

The figure reveals that most of the PM formed in the combustion of the present biomass fuels have median mass (aerodynamic) diameters (MMD) around 0.153-2.37 μm. It is also seen that the total PM emissions measured with the LPI-13 present a unimodal mass size distribution for all biomass fuels studied, in contrast with the observations in the previous chapter for the combustion in the domestic boiler.

Figure 6.2 shows the total PM obtained with the LPI-13 for the biomass fuels studied**.** According to the literature survey (chapter 2), FR is the residue most similar to the traditional biomass fuel (pine sawdust). This residue yielded a total PM emissions of 44 mg/Nm^3@6%O_2, which are lower than those of CR (137 mg/Nm^3@6%O_2), KB (126 mg/Nm^3@6%O_2) and PB (79 mg/Nm^3@6%O_2). PB is the second less problematic residue in terms of fine PM emissions due to the low ash content and low quantities of problematic elements in the ash such as potassium. CR and KB are the biomass fuels with higher ash content in its composition, which can affect considerably the PM emissions.

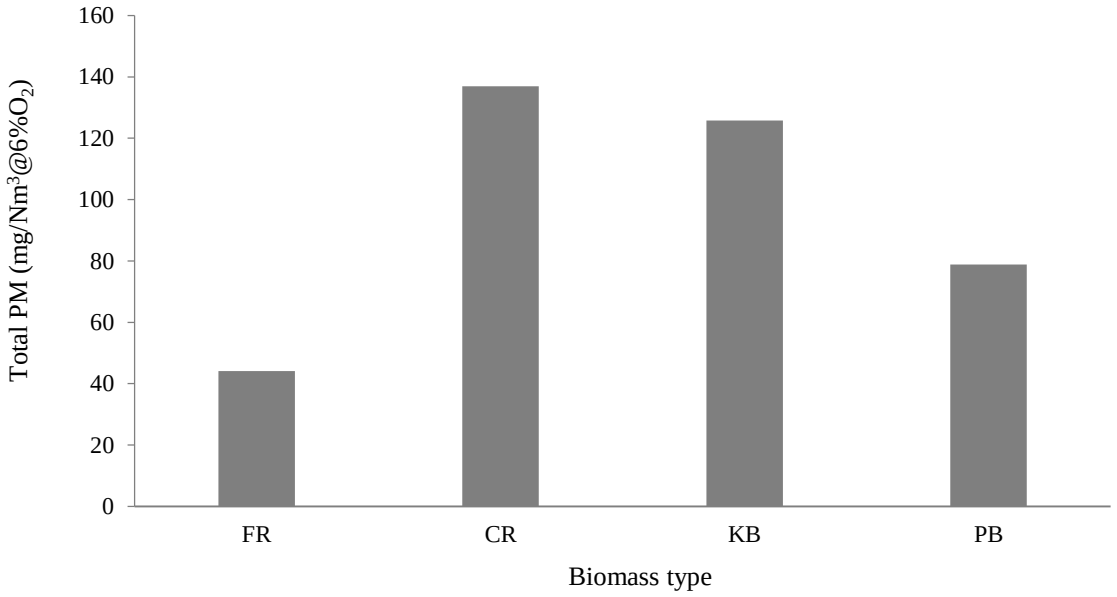


Figure 6.2. Total PM obtained with the LPI-13 for the biomass fuels studied.

6.3.3 Fly ash characteristics

The fly ash characteristics for all biomass fuels were evaluated based on the PM morphology and chemical composition of the samples collected in substrates 3 to 6 of the LPI-13. Figure 6.3 shows the PM chemical composition in substrate 5 for the combustion of FR, CR, KB and PB. The relatively high concentration of carbon in the PM indicates that the majority of the particles derived from incomplete combustion. Products from incomplete combustion typically include carbon particles (soot), condensable organic particles (tar), and the solid material that remains after devolatilization (char). The relatively low burnout level in the

combustion of CR can contribute to the emission of fly ashes with high content of carbonaceous residues – more than 72 wt.% of the PM is carbon, with small amounts of potassium (1.27%), chlorine (0.61%) and sulphur (0.35%). KB yielded PM composed of 64% carbon, FR 61% and PB 53%.

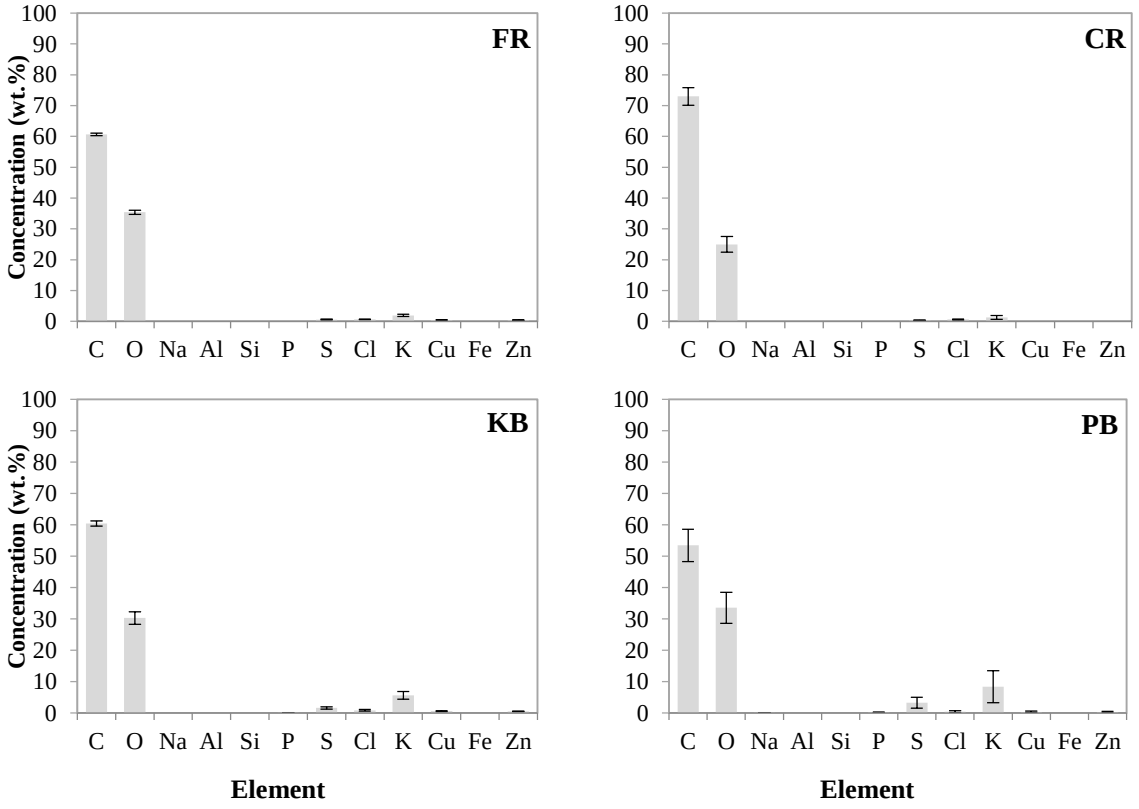


Figure 6.3. PM chemical composition in substrate 5 for the combustion of FR, CR, KB and PB. Errors bars represent standard deviations derived from 10 independent measurements.

Figure 6.4 shows the PM chemical composition in substrates 3, 4, 5 and 6 for the combustion of FR. The results revealed that the PM is dominated by carbon from incomplete combustion with smaller amounts of oxygen and potassium. It is interesting to see that carbon content decreases slightly from the substrate 3 (with particle with MMD of 0.0927 μm) to substrate 6 (with particle with MMD of 0.379 μm). For the remaining biomass fuels the same was observed. This fact suggests that the PM chemical composition varies marginally among substrates, indicating that the existing chemical compounds tend to form different size

aggregates of similar composition. It is observed that potassium reaches the value of 8.41% followed by the sulphur (3.27%), chlorine (0.42%), zinc (0.30%), phosphorus (0.20%) and sodium (0.14%). According to the literature survey (chapter 2), the particle emission from the combustion of biomass is dominated by submicron particles (size lower than 1 μm), both from number and mass perspective [88]. The results show that the main inorganic components of the submicron particles are potassium, sulphur and chlorine. The content of these elements in the fuel has a significant influence on the quantity and composition of the emitted inorganic submicron particles.

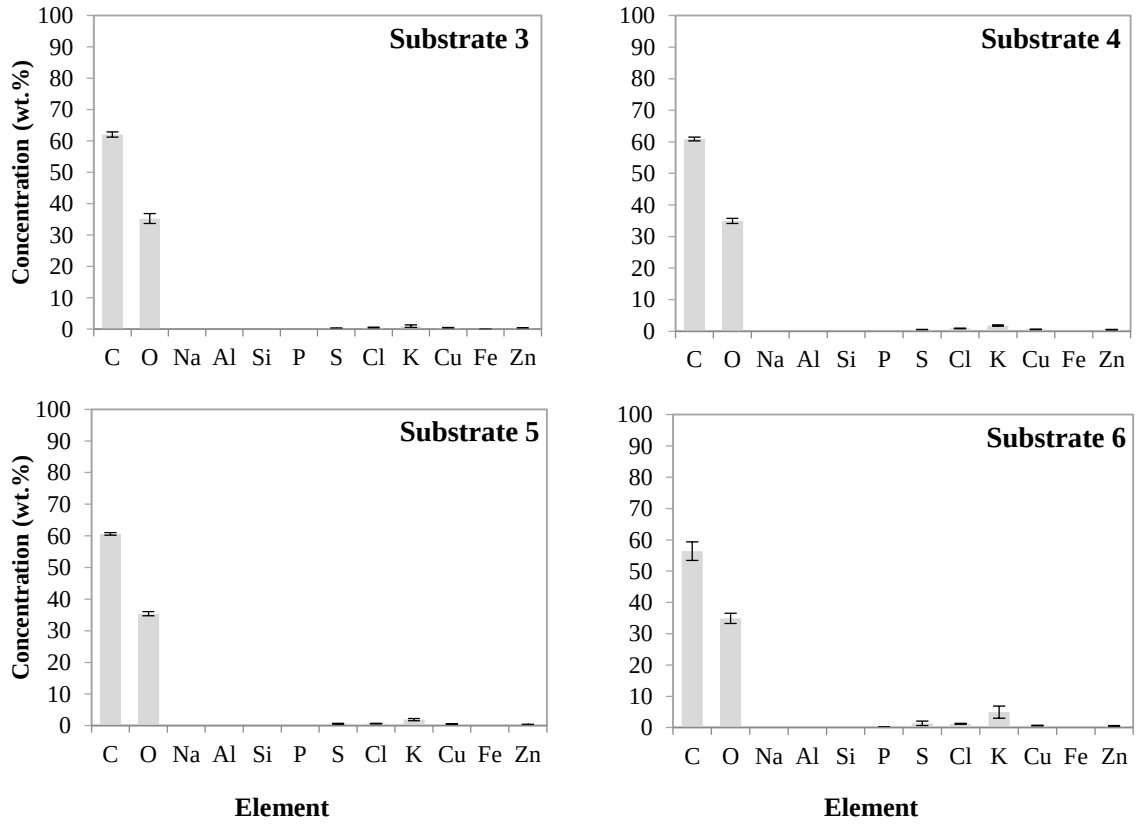


Figure 6.4. PM chemical composition in substrate 3, 4, 5 and 6 for the combustion of FR. Errors bars represent standard deviations derived from 10 independent measurements.

Higher sulphur mass fractions were observed in the upper substrates (corresponding to the larger diameter filters). This element can react with alkali metal chlorides and hydroxides, at lower temperatures, during the combustion process through sulphation reactions. Thus, sulphur content decreases the release of chlorine and the formation of corrosive compounds

during wood combustion, such as $FeCl_2$ or $ZnCl_2$. Potassium sulphate is also generated in small amounts during wood combustion and has been observed as a dominant compound in the aerosol range fly-ash of wood combustion. The chlorine content also plays an important role in forming alkali metal chlorides, releasing the ash forming elements to the gas phase, which leads to fine particulate matter formation. The main ash-forming elements found in the fly-ash of wood combustion (besides chlorine and sulphur) include potassium, sodium, zinc, lead, cadmium, chromium and magnesium [90]. Finally, Figure 6.5 shows a typical SEM image of a PM sample in substrate 4 for the combustion the PB. Aggregates of soot (carbon) with spherical shapes are clearly visible in the image.

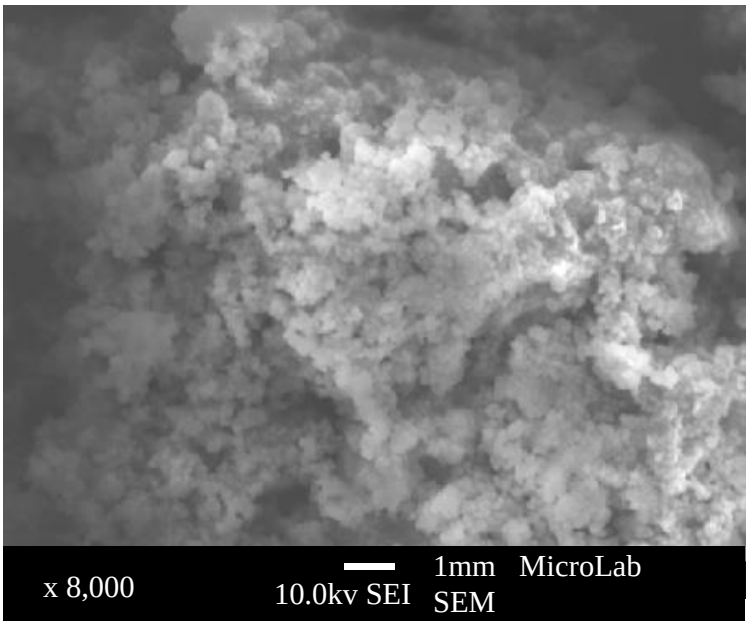


Figure 6.5. SEM image of a PM sample in substrate 4 for the combustion PB.

7. CLOSURE

7.1 Conclusions

Generally, this work proved that a number of alternative biomass fuels may be used for heating applications. The three distinct experimental studies, described in chapters 4, 5 and 6, allowed reaching important conclusions regarding the combustion of biomass in domestic and large-scale boilers. Industrial and agriculture biomass residues are currently an available resource far from being valued, unlike the residues of wood such as pine sawdust, which are currently intensively used. These alternative residues can be a new source of material to produce biomass fuels, taking at the same time some pressure off from other biomass resources, such as pine sawdust. Moreover, the use of agricultural residues, usually burned on the fields, creates an opportunity for rural economic development and energy recovery.

In chapter 4, the biomass physical and chemical characteristics were evaluated as well as its combustion behavior in a TGA. The main conclusions are as follows:

- The physical and chemical characteristics of the agricultural and industrial biomass fuels showed higher calorific values comparable to that of the pine sawdust. The ash characteristics of these alternative residues show high levels of calcium, which may increase their ash melting temperatures.
- Thermogravimetric analysis showed that the combustion of cork residues has the slowest maximum mass loss rate (8 %/min) among the residues studied, while the remaining residues, including pine sawdust, presented values between 9 and 42 %/min. The olive branches presented the maximum combustion rate (42 %/min) and, thus, the lower burnout time.
- Two distinct reaction zones were observed for all biomass fuels. Using the Arrhenius equation, the kinetic parameters (activation energy and pre-exponential factor) were found to be significantly higher in the first reaction zone than in the second reaction zone for pine sawdust, furniture residues, vine, kiwi and platanus branches. For cork residues and olive branches an opposite trend was observed.

- The ternary diagrams of the inorganic elements K_2O-SiO_2-CaO, K_2O-SiO_2-Al_2O_3 and K_2O-SiO_2-Al_2O_3 do not indicate fusion temperatures below 1000 ºC. However, values bellow 1150 ºC are observed for the SD in the K_2O-SiO_2-Al_2O_3 diagram and 1300 ºC in the CaO-K_2O-SiO_2 diagram mainly because of the high quantities of SiO_2 that interact with K_2O, which originates melting temperatures between 1000 ºC and 1300 ºC.
- The chemical analyses indicate high levels of alkaline compounds and low levels of silica in the ashes for most biomass fuels. According to the calculated slagging and fouling indices, there is an increased tendency of deposition of fly ash in the internal boiler components and agglomeration of ash in the boiler grate when using alternative residues, as compared with the pine sawdust.

In chapter 5, the particulate matter emissions and the ash characteristics resulting from the combustion of pellets from pine, agricultural and industrial residues in a domestic boiler were evaluated. The use of alternative biomass fuels as pellets can provide another route for the exploitation of such residues, with the added benefit of energy recovery. In this context, the following conclusions were achieved:

- The pellets from the agricultural residues revealed benefits in terms of energetic value, in comparison to reference wood pellets, despite the higher ash formation and potassium and phosphorus contents. The agricultural residues, however, presented also high quantities of calcium, which may prevent slagging phenomena.
- The combustion of these alternative pellets shows problems concerning the burnout time of the pellets: a deficient fuel/air ratio was observed and these pellets induced the accumulation of unburnt material in the commercial domestic boiler.
- The analysis of the particulate matter revealed higher emission of particles with diameter bellow 2.5 µm, particularly for the vine and olive branches pellets.
- Most pellets present a bimodal mass size distribution related to the particulate matter emissions, with the exception of the vine and olive pellets.
- The particulate matter emissions are dominated by high quantities of carbon (soot) and small quantities of potassium, chlorine and sulphur.

- The bottom ashes presented higher concentrations of calcium and potassium for the alternative pellets and silica for the pine pellets. For both cases, relatively high levels of phosphorus were observed in the ashes.
- The slag composition is different from that of the bottom ashes, with higher presence of silica for all pellets, and phosphorus, potassium and chlorine for the alternative pellets.

In respect to the market value of the pellets studied, a specific target application must be considered. For instance, to obtain best results in terms of energy recovery, the alternative pellets are promising. However, these pellets present problems regarding its combustion products (ashes and emissions). Specially, in the case of the vine and olive pellets, various factors need to be considered to prevent the high levels of fine particulate matter emissions. The grate also needs to be prepared to be easily cleaned from the excess of sintered ashes formed. The domestic boiler needs to be operated in optimized conditions (e.g., air/fuel ratio) to promote a better combustion and reduce the particulate matter emissions.

In chapter 6, the particulate matter emissions and fly ash characteristics from a pulverized biomass fired laboratory large-scale furnace were examined. The main conclusions can be summarized as follows:

- The biomass fuels particle size has a large influence on the combustion efficiency, pollutant emissions and particle burnout. Cork was the residue with lowest particle burnout, although it produced lower emissions of CO given the fuel size homogeneity.
- Particulate matter emissions showed the same tendency for the four biomass fuels, with aerodynamic particle diameter maximum at 0.259 μm. The total particulate matter emissions revealed that cork is the fuel that generated the highest emissions followed by the kiwi, platanus and furniture.
- The SEM/EDS analyses of the particulate matter show that the majority of the particles are composed mainly by carbon (soot). The carbon content tends to be higher in the particulate matter with smaller diameters. In regard to the inorganic elements, higher mass fraction of potassium followed by the sulphur and chlorine were observed.

Finally the main overall conclusions from this work are the following:

- The pine sawdust and furniture residues, which are commercialized products, proved to be the best raw materials for combustion and originated less problematic products
- The alternative biomass fuels studied can represent good alternatives when using equipment that does not require such high quality fuels, such as in industrial applications, but the particulate matter need to be captured to prevent its release into the atmosphere

7.2 Future work

The main suggestions for further work are as follows:

- The high impact (both on equipments and emissions) of the ashes and the particulate matter resulting from alternative biomass combustion can delay the commercial application of these residues. However, the incorporation of small quantities of alternative biomass fuels from industry and agriculture in pine sawdust fuels can minimize the negative effects and produce better results. Hence, it is proposed that future works include the study of mixtures of alternative/conventional biomass fuels.
- This study can be extended to other alternative raw materials available from forestry and agricultural activities.
- A higher power pellet mill should be used in future studies since the high non-uniformity of the mechanical properties of the produced pellets was a problem encountered in this work.
- Combustion tests should be performed with higher thermal inputs, which would require the collection of higher quantities of biomass residues and appropriate logistics.

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