Master Thesis

NOx emission mitigation during solid biomass combustion due to additivation.

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Hamburg, 24. August 2018

Statutory declaration

I declare that I wrote this thesis independently without external help. No sources and auxiliary means were used besides those indicated. Indications of sources are given whenever content was taken directly or indirectly from other sources. This thesis was not presented to a board of examiners in this or other form.

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Acknowledgements

Abstract

A greater awareness of the environment has caused that nowadays, the use of energy would be much more sustainable than before. One example is the use of biomass which has solidly established itself in the energy market. Its applications are normally practised in heating systems being the most common system stoves with pellets as fuel.

They are located in residential buildings because their efficient is higher, the combustion is cleaner than the stoves with wood and they are easier to use. However, this does not imply that it does not produce pollutants. The combustion of solid biofuels is generally associated with the formation of NOx, CO and particulate matter among other things.

In particular, NOx emissions have an important impact on the environment and human health. When NO_2 comes into contact with the atmosphere and combine with water vapour, sunlight and oxygen, it converts into acid rain.

Nevertheless, a possible solution to reduce NOx emissions might be the additivation of pellets. Additives such as Fe_2O_3, $MnCO_3$, $(NH_4)_2SO_4$, TiO_2 and Urea have been used in processes of catalysis, selective catalytic reduction (SCR) and selective non catalytic reduction (SNCR).

For this purpose, six types of pellets were produced in the laboratory: one without any additive and five mixes of pellets between ten and twelve kilos with a percentage of additive of 0.5% of the total mass. All these pellets were evaluated, analysed, documented and compared to the European Standard for Solid Biofuel EN 17225-2. The analysis performed was focused on five parameters: diameter and length, bulk density, abrasion resistance, moisture content and ash content. Some of them complied with the minimum standards and others were closer to the European norm.

After the analysis, the combustion was performed. NOx emissions and particulate matter were measured by means of the sensor *Wöhler A 550L* and a probe, respectively. The results show that the additive Fe_2O_3 was capable of reducing the NOx formation. $MnCO_3$ and TiO_2 barely reduced these emissions, while $(NH_4)_2SO_4$ and urea increased the NOx emissions significantly. On the other hand, the only additive which has reduced the particulate matter in comparison to pellets without additive was TiO_2 in contrast to urea which increased them notably.

Finally, the ash obtained from each additive is analysed by x-ray diffraction to obtain the crystalline compounds of each ash. These structures had principally elements such as calcium, potassium, magnesium and sodium being all of them ash forming elements.

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1   Introduction to renewable energy situation in Europe

European countries consume less energy than ten years ago, mainly thanks to the increase in energy efficiency [1]. Good examples of this are Portugal where energy demand has been supplied entirely with renewable energies for four days, and the Nordic countries, especially Denmark, where practically all energy produced is from renewable origin.

Electrical energy from renewable energy is increasing each year. The *Renewables 2018 Global Status* report from *Renewable Energy Policy Network for the 21st Century* (REN21) provides the following graphic about the increase of renewable energy in the world.
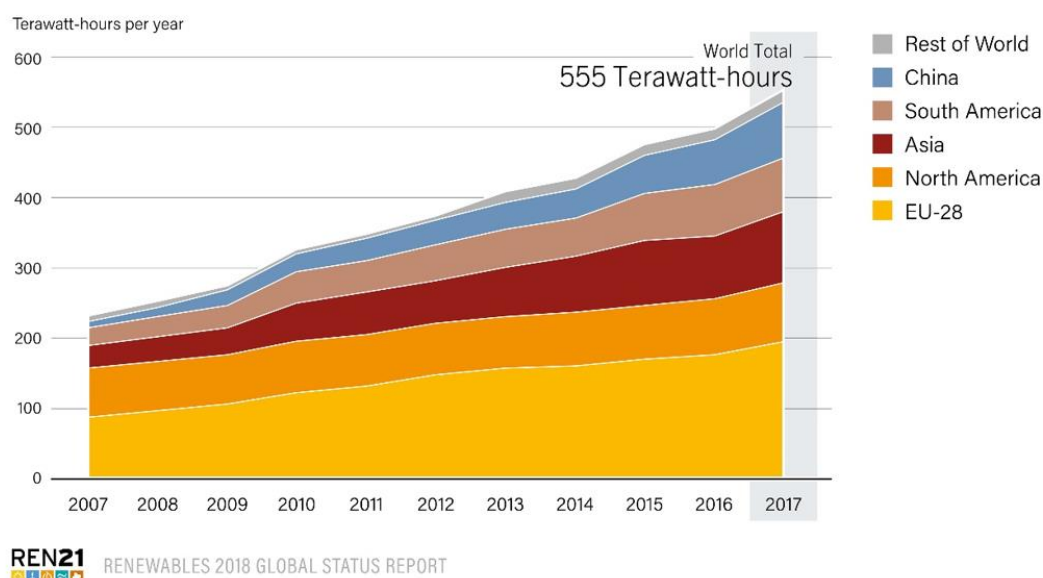
Figure 1. Electricity produced by renewable energies in Europe .

Europe works to fulfil its energy objective for the year 2020 (20% reduction of greenhouse gas, 20% increase of renewable sources in the gross consumption, and 20% in energy efficiency). However, the European Union has also set climate and energy targets for 2030 and 2050.

The proposed objectives for 2030 are as follows [1]:

- 40% reduction of greenhouse gas.
- 27% increase of renewable energy.
- 27-30% increase in energy efficiency.
- 15% of the electricity generated in Europe should be transported to other Member States.

On the other hand, the objective for 2050 is a 80-95% reduction in greenhouse gas emissions compared to 1990 levels.

In order to continue working along this line, the *European Energy Research Alliance* (EERA), the *EUA Energy and Environment Platform* (EUA-EPUE) and *EIT InnoEnergy* encourage the European Institutions to maintain the use of an energy more sustainable as a priority in the next programme for research and innovation (Horizon Europe).

The objective of the *Horizon Europe* is to unify all educational institutions to develop a sustainable energy future. For that, EERA, EUA-EPUE and EIT InnoEnergy call on the European Institutions to include the following principles and recommendations in the design of Horizon Europe [3]:

- Support long-term and short-term priorities and invest in the future knowledge base.
- Build missions with truly transformative potential.
- Align efforts in energy research.
- Accelerate global energy innovation.

Thanks to the different resources that can take advantage of clean energies, they are adopted as a mode of supply in many countries today. However, there are some disadvantages to consider.

In case of solar energy, one disadvantage is the radiation. The level of radiation fluctuates during the year, varying 20% between summer and winter. Due to this, it is necessary to supplement the solar energy with another energy source. The energy produced is approximately one third of the energy that could theoretically be produced [4].

The potential of wind energy is very high. However, the wind is very irregular, both large and small scale. The irregularity of the winds creates control problems in the mode of operation of the machine, fluctuations in energy generated and overexertion in mechanical elements. Moreover, its yield is determined by Betz limit. This means that a wind turbine can convert at most 60% of the kinetic energy of the wind into mechanical energy [5].

As regards hydroelectric energy, the hydroelectric power plants adapt to the required power level, however it is limited by climatology conditions. Electricity generation and energy prices are directly affected by the amount of water stored. Despite that, they play a preferential role in the electricity sector together with thermal plants [6].

Finally, the use of biomass as well as its derivatives has a lower energy density than fossil fuels. This means that more storage space is needed for the same amount of energy. Nevertheless, it does not depend on environmental conditions and it is one of the fastest growing renewable energies in the world. The use of biomass as an energy resource, instead of the commonly used fossil fuels implies a considerable decrease in pollutant emissions [7][8].

1.1 Biomass progress as energy source

At the present time, the European Union Parliament has set itself two objectives in the field of biofuels for 2020: 10% of the fuels used in transport should be renewable (Directive 2009/28/ EC on renewable energies) and fossil fuel suppliers should reduce the intensity of greenhouse gas emissions from their fuels by 6% in 2020 (Directive 2009/30/ EC on the fuel quality directive).

The use of biomass has followed an upward trend every year. The following graphic was extracted from the databased provided by *European statistics* and it shows the progress of biomass respect to the others renewable energy sources until 2016[1].

Figure 2. Source: http://ec.europa.eu/eurostat/web/energy/data/shares.
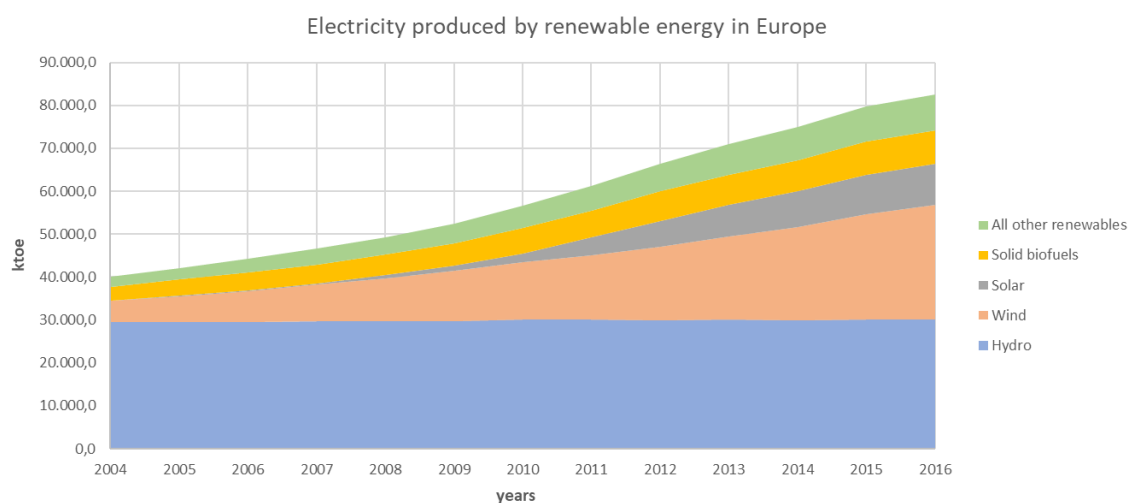
In recent years, biomass has established itself firmly in the energy market. The type of fuel such as pellets or chips have been standardized based on ISO 17225 and olive pits and peels of the fruits with the UNE-164003 and the UNE-164004 regulations respectively.

In addition, more than 70% of biomass consumed in Europe consists of solid biomass being mostly forestry residues and to a limited extent agricultural by-products such as wood industry by-products, wood from silviculture, waste wood, tall fescue, switchgrass, short rotation coppices miscanthus, hedges or green waste [10].

The applications of the biomass are normally practised in heating systems such as boilers, stoves or chimneys. One of the most frequently used systems is the use of boilers with pellets as fuel. They are more suitable for residential buildings in contrast with wood log stoves because their efficiency is higher, the combustion is cleaner and they are easier to use. They usually have a small fuel storage system from which the pellets are transported by a small worm screw to the combustion chamber. Generally, the heating power is around 10 kW [7][11].

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[1] Hydro is normalised and excluding pumping. Wind is normalised. Solar includes solar photovoltaics and solar thermal generation. All other renewables include electricity generation.

Figure 3 shows a small-scale pellet boiler with a power of 8 kW. This boiler will be used in this project for the experimental investigation with different pellets.

Figure 3. Small-scale boiler 8 kW.

In previous investigations, these types of boilers have presented good results in efficiency as well as control of emissions.

One example comes from the article *Test of a small domestic boiler using different pellets* by J. Dias, M. Costa and J.L.T. Azevedo. It presents an experimental study with a boiler of 13 kW. After working with different types of pellets, the efficiency of the boiler was up to 77%. Moreover, NOx emissions, under boiler steady-state conditions, correlated well with both excess air and pellets nitrogen content [12].

Nowadays, the residential sector is still the main share of wood energy consumption (41%) but is closely followed by the industrial use of wood chips and small scale use of solid biofuels such as woodchips, energy crops or solid agricultural biomass (20%). Pellet consumption in modern appliances is also growing fast, representing 9% of total EU wood energy consumption [10].

1.2 Motivation and aim of the work

Although biomass is considered as renewable source, combustion implies the appearance of polluting products such as particles, carbon dioxide, sulphur compounds or nitrogen oxides.

The objective pursued by this project is to reduce nitrogen oxides through additivation. For that, the first step will be the additivation of the pellets. Subsequently, these pellets will be tested for NOx emissions where will be burned in a small-scale boiler (8 kW).

Finally, using standardized analysis methods, produced gas as well as solid residue (ash) will be examined in relation to their chemical and physical properties.

2 Theoretical background

2.1 Formation and types of nitrogen oxides (NOx)

Biomass combustion systems emit nitrogen oxides (NOx) which should be reduced since they contribute to the formation of acid rain and photochemical smog [13].

The main NOx emissions generated by combustion are compose of nitric oxide (NO), nitric dioxide (NO_2) and nitrous oxide (N_2O).

The generation of NO during the combustion depends mainly on the type of fuel, the nitrogen from the air and the combustion conditions in the burner. These gases are very reactive in the presence of oxygen and high temperatures.

There are differences respect to the generation of NO. The following table identifies the types of NO formation.

Table 1. Types of NO formation

	Thermal mechanism (Zeldovich)	Prompt mechanism (Fenimore)	Fuel-N conversion
CONDITIONS	Formed from the nitrogen present in the atmosphere. It happens around **1400 ºC.**	Formed for combination of nitrogen in the atmosphere and fragments of combustible in the flame zone. It happens around **900ºC.**	Formed from the combustion of nitrogen present in the biomass. Fuel-N conversion is even more dominant due to the temperature conditions in boilers. It happens around **1000ºC.**
MAIN REACTIONS [13]	$O+N_2 \leftrightarrow NO+N$ $N+O_2 \leftrightarrow NO+O$ $N+OH \leftrightarrow NO+H$	$CH+N_2 \rightarrow HCN+N$ $CH_2+N_2 \rightarrow HCN+NH$ $HCN+O \rightarrow NCO+H$ $NH \rightarrow N+H$ $NCO \rightarrow CN+O$ $CN+O \rightarrow CO+N$ $N+O \rightarrow NO$	$Fuel-N \rightarrow HCN$ $HCN+O \rightarrow NCO+H$ $NCO+H \rightarrow CO+NH$ $NH+O \rightarrow NO+H$

In small-scale biomass combustion units, NOx formation through thermal and rapid mechanisms are less dominant than fuel-N conversion, which is the largest contributor to NOx emissions. This is because the range of temperatures of small-scale unites oscillates between 900º C and 1100º C [14].

The formation of NO_2 comes from the reaction of NO with other species which contain oxygen. NO_2 is formed when it reaches the flame temperature. The reactions below show the formation of NO_2 [15].

$$NO+HO_2 \rightarrow NO_2+OH$$

$$NO+O \rightarrow NO_2$$
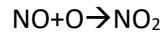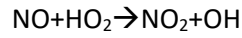
At the same time, NO_2 can be transformed into NO with oxygen and hydrogen as exposed below [15].

$$NO_2+O \rightarrow NO+O_2$$

$$NO_2+H \rightarrow NO+OH$$
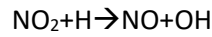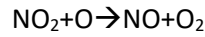
N_2O is formed in the post-combustion zone and it depends on the existing quantity of NH, NH_2, NCO and N_2. The main reactions are shown as follows [15].

$$NH+NO \rightarrow N_2O+H$$

$$NH_2+NO \rightarrow N_2O+H_2$$

$$NCO+NO \rightarrow N_2O+CO$$

$$N_2+O \rightarrow N_2O$$
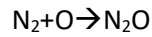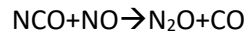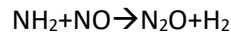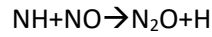
To maintain an overview of this, the following figure represents the conversion of biomass into NOx during the combustion.
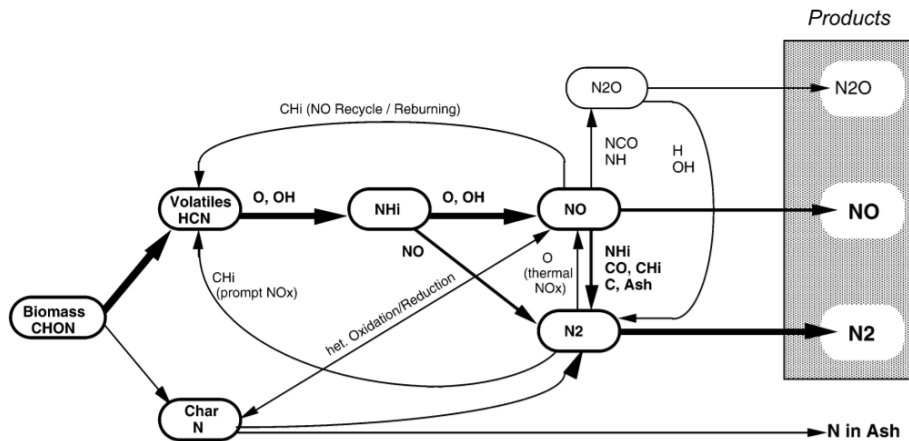
Figure 4. Products of NOx emissions.

2.2 Impact of NOx emissions on the environment and the human organism

Emissions of NOx have an important impact on the environment and the human organism [17]. According to the World Health Organisation (WHO), NO_2 is a toxic gas with potential serious effects on health.

When NO_2 comes into contact with the atmosphere and combine with water vapour, sunlight and oxygen, it might lead to the formation of acid rain. Most of the NO_2 that goes to the atmosphere is emitted in form of NO, which is rapidly oxidized to NO_2 by ozone [18].

On the other hand, it has been proven in epidemiological studies that bronchitis symptoms of asthmatic children increase in association with the annual concentration of NO_2. Moreover, it is responsible of other diseases, such as bronchitis, pneumonia or lung cancer [17].

Another consequence of NOx emissions is the formation of photochemical smog. It is produced from NOx, carbon monoxide (CO), methane (CH_4) and other volatile organic compounds (VOCs), in the presence of solar radiation [18].

It affects the respiratory system producing inflammations that can persist up to 18 hours after exposure to smog. It can cause the development of heart and lung problems and it can increase in asthma symptoms. The worst consequence is the premature mortality [17].

In case of N_2O, it is an important greenhouse gas with an average stay of 100 years in the atmosphere. It makes the ozone layer thinner, reducing it to molecular oxygen (O_2) and releasing two molecules of NO [19]. It is a volatile, colourless and toxic gas, which causes hallucinations and euphoric state in people.

The necessity to reduce the negative effects of NOx emissions, has developed two types of measures to slow down its growth. In the following points will be described the primary and secondary measures to mitigate NOx emissions.

2.3 Mitigation measures of NOx emissions

NOx emissions can be reduced by primary or secondary measures. Primary measures minimize the variables that affect the NOx formation and secondary measures transform the NOx emissions into another substance easier to treat [18][20].

These measures will be described in the following points.

2.3.1 Primary measures

As mentioned above, primary measures prevent the formation of NOx during the combustion stage. They consist in reducing the maximum temperatures of combustion gases or limiting availability of oxygen in some zones of the flame.

However, one problem is that these measures can lead to greater unburned fuel, so this aspect should also be taken into account.

The primary measures are presented below:

- **Air staging**.

Air staging works by introducing air into the boiler in stages, creating a fuel rich zone to reduce the NOx formation in the primary stage and then to burn the unburned fuel in the secondary stage.

Air staging reduces NOx formation mainly by two mechanisms [21]:

- The decrease in the oxygen content in the primary combustion zone contributes to lower fuel and air mixture, which prevents the conversion into NOx.
- Air staging reduces the flame temperature, therefore the generation of NOX decreases.

Some investigations have demonstrated that air staging has an efficiency between 40% and 70% of NOx reduction, depending on fuel-N conversion and other conditions [21].

The figure 5 shows an example of the air staging process.
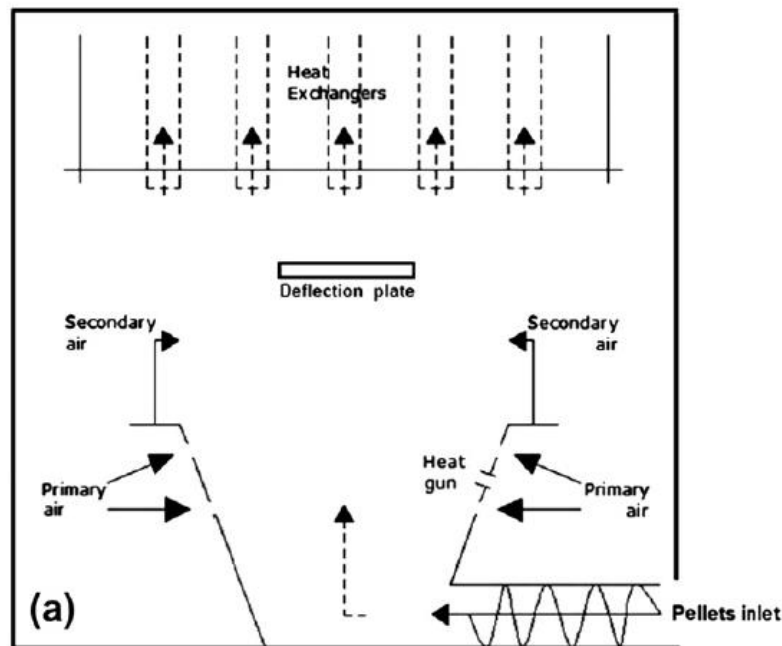
Figure 5. Example of air staging.

- Fuel staging or reburning.

Fuel staging consists in operating in fuel-rich conditions. The first stage works with an excess of air where NOx are developed as a classical combustion. This zone is called "primary combustion". Subsequently, NOx emissions are destroyed in a reducing atmosphere. NOx in presence of hydrocarbons is transformed into nitrogen and other compounds. This is the "reburn zone" [22].

Finally, non-combusted particles as a result of the second zone, are burned in the third stage with an excess of air.

The following figure shows the process of fuel staging in its different stages.
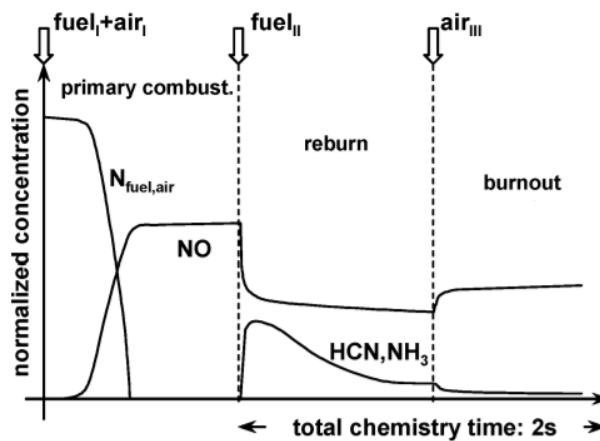
Figure 6. Process of fuel staging.

Figure 7 shows an example of a reburning system.
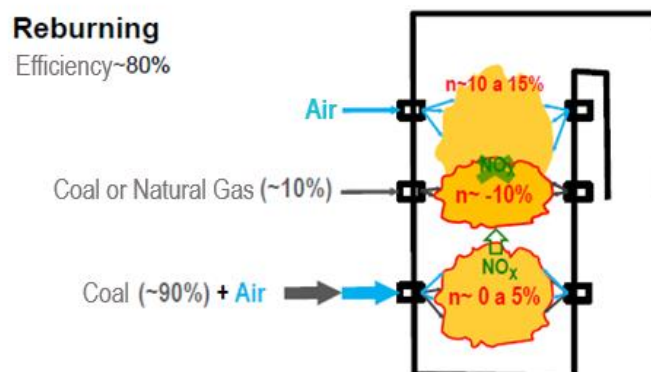
Figure 7. Reburning system.

To have an overview of both systems, the figure 8 below shows a comparison according to the different types of combustion.
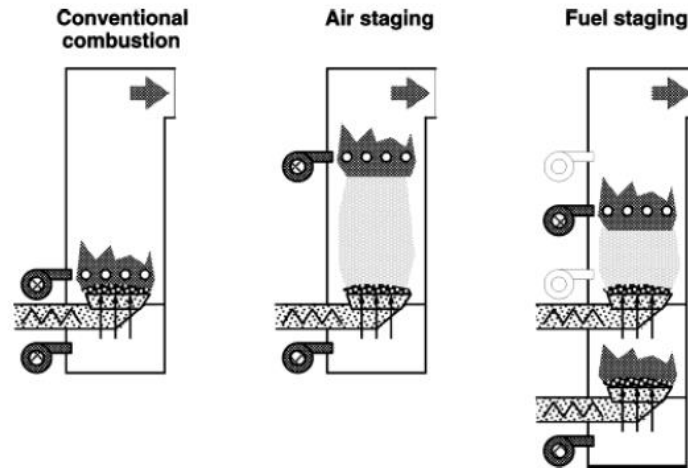
Figure 8. Example of different types of combustion.

- Catalysts.

Catalysis is a process by which the speed of a chemical reaction is increased by using a substance called catalyst. Normally it is used for gasification systems and its aim is cleaning the gas from the gasifier.

There are two types of catalysts for use in biomass conversion. The first group reduce the tar content and work under the same conditions of the gasifier.

The second group operates outside the gasifier and can work with different conditions respect to the gasification unit.

Catalysts materials that are normally used in gasification systems are dolomite catalysts, alkali metal and other metal catalysis and nickel catalysts [25].

- Additives.

Combustion originates emissions of a large variety of organic and inorganic compounds. These include particles, carbon dioxide and monoxide, sulphur compounds, nitrogen oxides and solid and liquid residues.

All these compounds depend on the characteristics of the fuel. In case of biomass, the elemental biomass composition consists mainly of C, H, N, S, Cl, O, K, Na, Mg, Ca, P, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn [26].

This means that there will be particle emissions resulting from the release of inorganic material from the biomass, consisting mainly of K, Cl, S, Na. On the other hand, there will be also nitrogen oxides and sulphur oxide emissions, among others.

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To combat this issue, the use of additives contributes significantly to reduce emissions from the combustion of biomass.

The principal additive groups for particulate matter reduction (consisting mainly of K, Cl, S and Na) are those based on calcium, phosphorus, sulphur and aluminium-silicate additives [27].

2.3.2   Secondary measures

The purpose of secondary measures is to transform NOx emissions in harmless substances that are not harmful to the environment.

They can be implemented independently or together with primary measures. Most of these techniques are based on the injection of ammonia, urea or other compounds, which react with the NOx gases to decompose them into molecular nitrogen and water [20].

There are two methods: selective catalytic (SCR) and non-catalytic reduction (SNCR).

- Selective catalytic (SCR).

Selective catalytic reduction (SCR) is used to reduce NOx emissions with ammonia (NH_3). The catalyst converts the NOx into water and N_2.

Ammonia is vaporized, diluted with air and injected in the gas stream. The active catalyst is vanadium or tungsten. The figure 9 shows an example of SCR in a boiler.
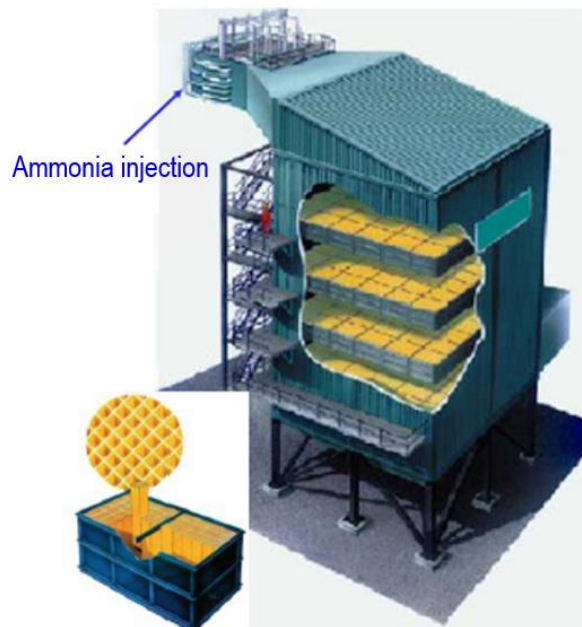
Figure 9. Selective Catalytic Reduction system.

The reactions that take place in the SCR are as follows [28]:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$$
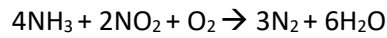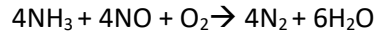
Selective catalytic reduction can be carried out in a temperature range around 250 ºC to 450 ºC [16] and has an efficiency of at least 80%-95% [23].

- Non-catalytic reduction (SNCR).

Non-catalytic reduction does not require the use of a catalyst. Instead, urea and ammonia are added to the flue-gas of boilers. The disadvantage of this system is the control of the temperature.

If the temperature is too low, there are leaks of ammonia gas, otherwise the ammonia is oxidized. The temperature ranges from 870 ºC to 1090 ºC and it has an efficiency around 50%.

The figure 10 shows an example of the use of SNCR in a boiler.
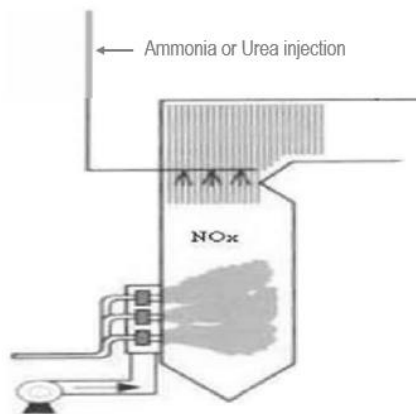
Figure 10. Example of Selective Non-Catalytic Reduction.

3 Experimental approach

3.1 Additive selection

In this project, the main objective is the emission reduction of NOx by means of additives, such as iron oxide (Fe_2O_3), manganese carbonate ($MnCO_3$), ammonium sulphate ((NH_4)$_2SO_4$), titanium dioxide (TiO_2) and urea.

The selection of these additives has been made based on investigations conducted. The use of Fe_2O_3 in combination with calcium takes place in catalysis processes. The combination of Ca-Fe can improve the combustion and inhibit the nitrogen conversion into NOx [30]. Compared with conventional condition, the NOx reduction ratio of sintering process with 8% Ca-Fe oxides additives achieves 27,76% [30].

Another catalyst used in SCR to reduce NOx emissions is manganese (Mn). Its presence decreases the inhibitory effects of H_2O and CO_2 on NOx conversion. In addition, its decomposition into $MnCO_3$ favours the catalytic activity at low temperatures. Manganese catalysts, at moderate temperatures such as 523 K and 623 K, decrease the NOx conversion and it increase the N_2 formation in selective catalytic reduction at low temperature [32].

The next additive is ammonium sulphate ((NH_4)$_2SO_4$). It is well known as fertiliser for certain crops. However, it is used for reducing NOx emissions as well. It has been proved that the use of ammonium sulphate could simultaneously reduce NO and CO during the ignition of biomass in boilers with high CO emissions. On the other hand, the reduction of KCl is possible during combustion and it works better than the sulphation process [25].

The additive TiO_2 is one of the main catalyst in SCR in combination with V_2O_5. It is used in practice as one of the best catalysts for the reduction of NOx by NH_3, because of its high activity at low temperature and of its high resistance to the poisoning by SOx. The use of titanium dioxide for the reduction of NOx by NH_3 increases the production of N_2 at low temperatures [31].

The last additive is Urea whose chemical formula is $CO(NH_2)_2$ [49]. This substance is widely used in SNCR systems. It has the advantage of being an inert, non-corrosive particulate solid and it can be injected with the fuel or it can preferably be dissolved and injected into boiler [49]. A study shows that urea in comparison to ammonia reduces around 8-12% for powdered urea and 24-44% for urea solution [49].

Table 2 shows the classification of the additives used in this project. The additives are divided in two groups according to the mitigation measures of NOx.

Table 2. Classification of the additives.

PRIMARY MEASURE	SECONDARY MEASURES	
Catalyst	**SCR**	**SCNR**
- Iron oxide (Fe_2O_3)	- Ammonium sulphate	- Urea
- Titanium dioxide (TiO_2)	((NH_4)$_2SO_4$)	- Ammonium sulphate ((NH_4)$_2SO_4$)
- Magnesium carbonate ($MnCO_3$)		

3.2 Previous preparation of pellets

Pellets are a natural product catalogued as solid biomass. The material is pressed with cylindrical shape by means of the pelletizing machine. During the process, the quality of the pellets can be affected by several factors such as temperature, humidity, the hardness or the quality of the raw material.

The following figure shows the pellets produced in the laboratory with different additives.
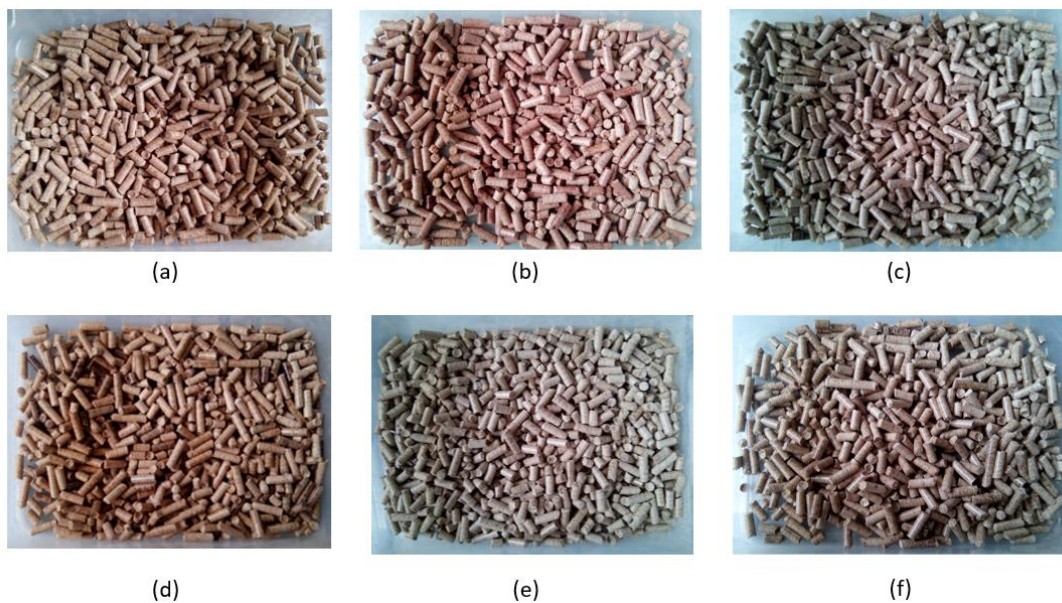
Figure 11. Pellets with different additives. (a) Without Additive (b) Fe_2O_3 (c) $MnCO_3$ (d) (NH_4)$_2SO_4$ (e) TiO_2 (d) Urea.

For this project, the raw material used in the production of pellets are beech wood chips type HB 500/1000; containing approximately 12,6% water.

The quantities of pellets that have been prepared are shown in table 3.

Table 3. Previous preparation of pellets.

Type of pellets	Weight *
100% Beech wood (HB500/1000)	10,5 Kg
Beech wood (HB500/1000) with 0,5% Urea	10,8 Kg Beech wood and 54g Urea.
Beech wood (HB500/1000) with 0,5% Fe_2O_3	12 Kg Beech wood and 60g Fe_2O_3.
Beech wood (HB500/1000) with 0,5% TiO_2	12 Kg Beech wood and 60g TiO_2.
Beech wood (HB500/1000) with 0,5% $MnCO_3$	12 Kg Beech wood and 60g $MnCO_3$.
Beech wood (HB500/1000) with 0,5% $(NH_4)2SO_4$	12 Kg Beech wood and 60g $(NH_4)2SO_4$.

*The reason for different quantities of pellets is due to its behaviour with additives. The following points will describe more precisely the physical properties of each one.

3.3 Pelletizing

The machine used for pelletizing is the model 14-175 Amadeus Kahl GmbH & Co. KG Germany. The power requirements are generally 2-3 kW at 50 Hz and the capacity of producing is around 6 kg per hour. For small quantities, the raw material should be manually fed by way of a feed hopper. For continuous operation a proportioning feed unit is fitted to the press.

Figure 12. Pelleting press model 14-175.

The pelletizing process starts with the storage of the raw material destined for pellets. Subsequently the worm screw transports the material to the feeder. Then, the pressure generated by the roller fills the holes located on the matrix and finally, the matrix provides the form of the pellets.

Figure 13 shows the compression process of the biomass into the holes of the matrix. Each time the gear passes through the holes, it deposits a layer of beech wood creating layered pellets. The holes of the matrix are generally around 6 mm in diameter.
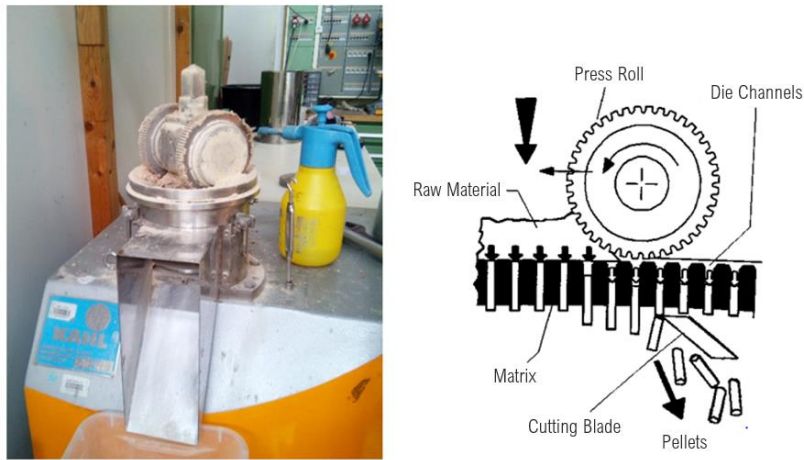
Figure 13. Compression process of biomass in the machine.

In the following figure can be seen the types of matrices used in the production of pellets. The thickness varies with the type of the matrix. This has an influence on the temperatures reached of pellets during its production because the residence time of the biomass is higher in the largest matrix.

(a)   (b)   (c)
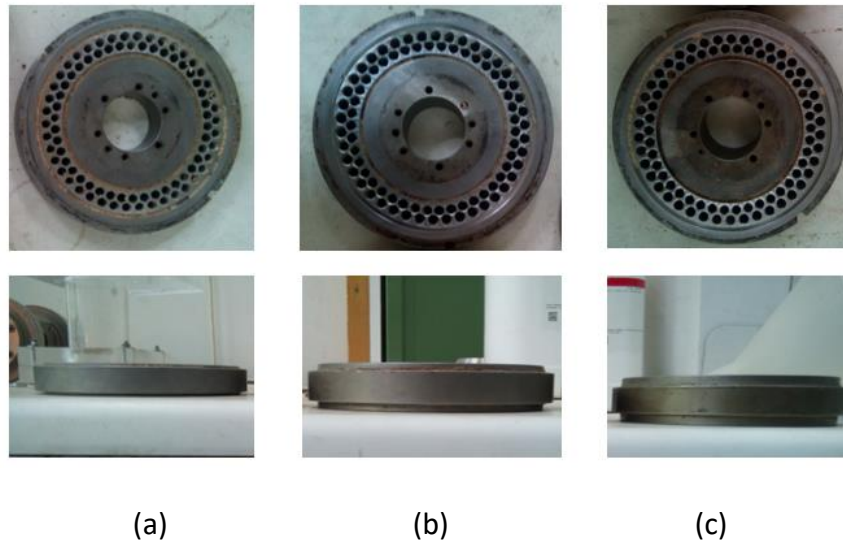
Figure 14. Types of matrices. (a) 1:3 (b) 1:4 (c) 1:5.

3.4 Determination of pellets properties

3.4.1 Dimensions

The dimensions of the pellets were determined by means of a caliper according to DIN EN 17829 norm. Pellets whose length and diameter do not comply with the specifications could cause problems during transport in screw conveyors, in discharge openings of silos and in feeder devices of burners. The standards ISO 17225-1, ISO 17225-2, ISO 17225-6 and ISO 17225-8 norms specify the dimensions of pellets and describe procedures for determining the diameter-related classification according to ISO 17225-2 norm and the length and diameter of pellets [33].

3.4.2 Bulk density

Bulk density is an important parameter for fuel deliveries on a volume basis, which along with the calorific value determines the energy density. It also allows an estimation of space requirements during transport and storage [34].

According to DIN EN 17828 norm, to determine the bulk density an amount of pellets must be measured in a standard volume. The container should have a cylindrical shape and also be resistant to deformation.

In this case, the volume of the container is defined as shown in the figure 15. Its capacity is 0,3725 l.
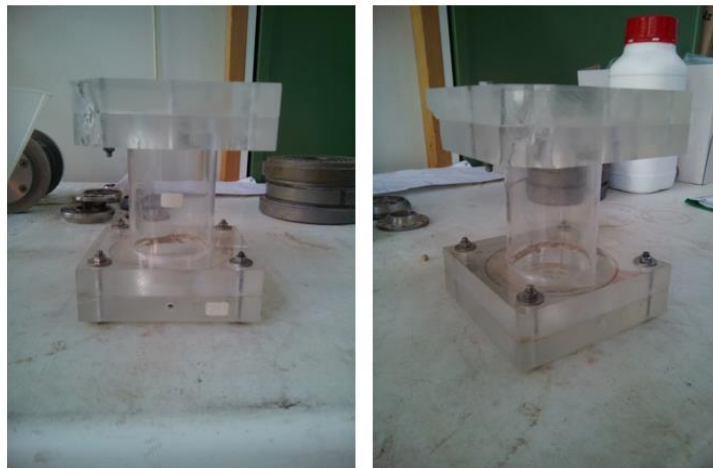
Figure 15. Bulk density.

The cylinder is filled up completely by pellets from a height of 200 mm to 300 mm. Then, the container shall be released from a height of 150 mm on a firm surface. It must be held in a vertical position with respect to the surface. Subsequently, the empty space is filled up to the top of the cylinder. This process must be repeated three times.

Bulk density is calculated as shown in equation (1):

$$Bulk\ density\ \left(\frac{kg}{m^3}\right) = \frac{(m_2 - m_1)}{V_{cylinder}}$$ (1)

Where:

- m_2 is the mass of the filled container.
- m_1 is the mass of the empty container.
- V is the volume of the cylinder in m^3. In this case 0,0003725 m^3.

3.4.3 Abrasion resistance

Abrasion resistance is a measure of the mechanical strength of pressed fuel to impact and/or abrasion due to handling and transport processes.

For the determination of the abrasion resistance, samples are subjected to controlled shocks by colliding the walls of a rotating chamber as shown in the figure 16 [35].
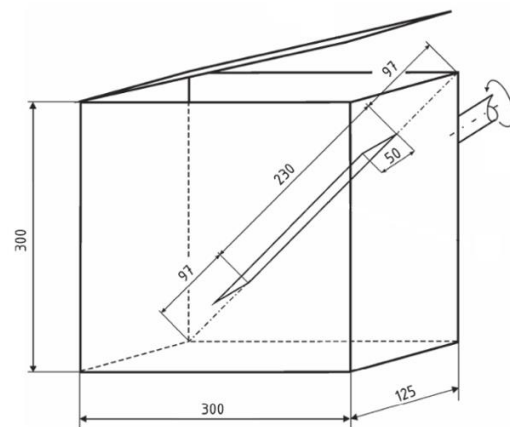
Figure 16. Abrasion resistance chamber.

According to DIN EN 17831-1 norm, samples should contain (500 $\pm$ 10) gr to conduct the analysis. Before introducing them into the chamber, pellets should be screened in a sieve no bigger than 3,15 mm. In this case, the available sieve in the laboratory was 4 mm.

After that, pellets rotate for exactly 10 minutes at a frequency of 50 rpm. Then, pellets are screened again and the new weight should be noted. The mass difference in percent is the abrasion resistance. This experiment must be carried out a total of three times.

The abrasion resistance of pellets shall be calculated according to equation (2):

$$Abrasion\ resistance\ (AR)\ (\%) = \frac{m_A}{m_E}\ x\ 100 \qquad \textbf{(2)}$$

Where:

- m_A is the mass of sieved pellets after treatment in the chamber, in grams
- m_E is the mass of sieved pellets before treatment in the chamber, in grams.

3.4.4 Moisture content

Moisture content measures the amount of water contained in a material. This is an important factor to consider in the combustion as well as the pelletizing process.

If the moisture content is too high, it absorbs part of the heat released in the combustion process when it evaporates and the calorific value and therefore burning efficiency of biomass decreases. In case of the pelletizing process, it is necessary a certain percentage of water for its production because when there is an excess or a lack of water, the material is not adequately compressed and the quality of pellets is not appropriated. The limit established by DIN EN ISO 17225-2 A1 norm is less than 10% in moisture content.

According to DIN EN ISO 18134-2 and 18134-3 norms, samples must be dried at $(105\pm2)°C$ in the oven for at least 24 hours. The mass of the test sample must be at least 1 gram.

After the drying time, samples are transferred to a desiccator at room temperature. It is important to weigh them as soon as possible once they are removed from the desiccator. The determination of the moisture content should be performed at least in duplicate.

The calculation process is shown in equation (3):

$$Moisture\ content\ (\%) = \frac{(m_2 - m_3)}{(m_2 - m_1)} x 100 \qquad \textbf{(3)}$$

Where:
- m_1 is the mass of the empty crucible in grams.
- m_2 is the total mass of the sample with the crucible before drying, in grams.
- m_3 is the total mass of the sample with the crucible after drying, in grams.

3.4.5 Ash content

Ash content is an important parameter in combustion because it is a by-product of the incineration which is deposited in the lower part of the boiler and can be present as volatile part in the combustion gases. In some cases, ash can be used for the manufacture of other products such as the construction industry or agricultural sector [37]. However, the chemical composition of the ash might contribute to slag formation and might increase corrosion in incinerators, so it is important to know the amount of ash contained in a fuel.

The determination of the ash content is based on dry material obtained in moisture content. According to DIN EN ISO 18122 norm, the samples must be heated to (550 ± 10)°C in a furnace during 5 hours.

Samples must be heated in accordance with the following temperature program [37]:

- The furnace temperature is evenly raised to 250°C for a period of 30 minutes to 50 minutes (a heating rate of 4,5°C/min to 7,5°C/min). This temperature remains during 60 minutes to allow the volatiles to escape from the test before burning.
- Then, the furnace temperature increases to (550 ± 10) °C for a period of 30 minutes (a heating rate of 10 ° C/min). This temperature is maintained for at least 120 minutes.

After the above process, samples should be allowed to cool for 5 minutes to 10 minutes. Then, they must be placed in a desiccator at room temperature for 8 hours.

It is important to weigh them as soon as possible once they are removed from the desiccator. The determination of the ash content should be performed at least in duplicate.

The ash content shall be calculated according to equation (4):

$$Ash\ content\ (\%) = \frac{(m_3 - m_1)}{(m_2 - m_1)} * 100 * \frac{100}{100 - Moisture\ content\ (\%)} \qquad \textbf{(4)}$$

Where:

- m_1 is the mass of the empty crucible, in grams.
- m_2 is the total mass of the sample with the crucible after drying, in grams.
- m_3 is the total mass of the sample with ash, in grams.

3.5   Preparation of the combustion process

After the analysis above, the next step is burning the pellets in a stove to determine the NOx emissions and particulate matter generated during the combustion. The stove used is the model HAAS+SOHN 1.17 as shown in figure 17. The power requirements are between 1,8 kW and 8,2 kW [40].

Pellets are fed automatically from the feed tank to the combustion chamber by means of an endless screw which adjusts the amount of fuel.

Figure 17. Stove HAAS+SOHN 1.17.

There are three phases to take into account [40]:

- Ignition phase. The grate is filled with a certain amount of fuel which is burned for approximately five minutes. If during this time an appropriate process temperature is not reached and there is no flame, the safety shutdown is initiated.
- Heating mode. The heat produced depends on the room temperature and the target room temperature. If there is a great difference between these temperatures, the stove will operate at maximum output (8,2 kW). If not, heat production will be reduced (1,8 kW).
- Burner test or cleaning. During two minutes, a ventilation system injects air from the bottom to the top to clean the combustion chamber. The burner test is performed regardless of the heat production delivered by the stove. This test is performed every 30 minutes during the heating mode.

Although the objective of this project is to reduce the NOx emissions by means of additivation, another measurement will be performed: particulate matter formation. This analysis will help to have an overview of the impact of the additives during the combustion.

Particulate matter is formed during combustion of biogenic solid fuels. These particles have an aerodynamic diameter of less than 10 µm, so are harmful to humans and the environment. They are divided into different categories, depending on their size [41]:

- Coarse particles (aerodynamic diameter of at least 10 µm). These particles can penetrate into the nasal cavities and in the pharynx generating respiratory diseases.
- Thoracic airborne particles (aerodynamic diameter between 10 µm and 2,5 µm). In humans these particles attach themselves to the upper respiratory tract, the trachea and the bronchi. Especially in children, elderly persons and injured people can lead to acute health problems.
- Alveolar particulate matter (aerodynamic diameter between 2,5 µm and 0,1 µm). These particles can penetrate the bronchioles and alveoli and can damage lung tissue. They can lead to chronic pulmonary and cardiovascular diseases.
- Ultrafine particulates (aerodynamic diameter less than 0,1 µm). The particles can get into the bloodstream and spread to other parts of the body. They can be a factor in a variety of illness including chronic heart and brain diseases.

In larger biomass plants, secondary measures are already being installed, such as filtration or catalytic systems. However, these are not economically viable for small combustion plants for private use. In that case, the future is the optimization of fuel. This option is particularly suitable for pellets. Pellets are mainly made from residues from sawmilling, so the manufacturing process allows the raw material to be mixed with another substance such as additives [41].

After the combustion, the ashes produced by pellets will be analyse by means of x-ray diffraction.

3.5.1 NOx emissions

The measurement of NOx emissions is performed using the sensor *Wöhler A 550L.* A cable from the stove is connected to the probe compartment as shown in figure 18. With the aid of the *Wöhler A550* program, it is possible to obtain the emissions of the exhaust gases. The measurement is updated every ten seconds. At the same time, with the program *Tracer DAQ*, the temperature and the pressure from the stove are recorded during the entire experiment.

The sensor provides three parameters of NOx emissions:

- NO_{xv} which is the nitrogen oxide content based on dry exhaust gas as diluted value, in ppm.
- NO_{xn} which is the nitrogen oxide content based on the adjustable reference oxygen value, in ppm.
- NO which is the nitric oxide content based on the adjustable reference oxygen value, in ppm.

The comparison between the different additives will be analysed based on the results obtained from the NO_{xn} values.

Figure 18. Probe compartment sensor Wöhler A 550 L**.**

3.5.2 Particulate matter

For its measurement, the use of filters is necessary to capture these particles. Such filters with its metal support must be previously placed in an oven for one hour at 160 °C for drying. Subsequently, they are stored in a desiccator for eight hours followed by cooling to room temperature. The filters and the metal supports must be weighted after this process. Then, both parts are hermetically sealed in a Petri dish.

To measure the particulate matter, the filter and its metal support are placed inside the sampling probe which is shown in figure 19.

Figure 19. Probe for particulate matter.

The measurement must be performed during the heating mode. The probe is directly inserted into the exhaust gases as shown in figure 20. The regulation of the volumetric flow is performed manually and it must be constantly monitored because the pressure of the probe during the measurement is negative due to a pump as presented in figure 21.
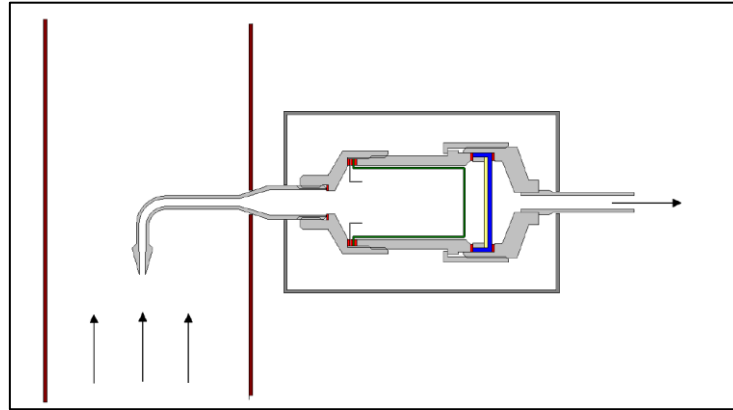
Figure 20. Probe placement.

A total volume of 0,125 m³ from the exhaust gas is extracted through the probe with a flow rate of 1 m³/h. The process is repeated once, consequently, a total of two filters are loaded with particulate matter during 7,5 minutes approximately. After that time, the pump is stopped and the probe is dismantled.

To determine the humidity in the exhaust gases, it is necessary to use a bottle filled with silica-gel. Before and after the measurement of the particulate matter, the bottle should be weighed.

Figure 21. Measurement system of particulate matter.

Particulate matter emissions are given in accordance with VDI 2066-1 based on one cubic meter per hour of dry exhaust gas and 13% of oxygen content in volume [41].

The following equations are used to calculate particulate matter emissions [41]:

$$m_{PM} = \Delta m_{filter} + \frac{1}{2} * m_{probe} \tag{4}$$

$$m_{PM,N}(mg) = \frac{m_{PM}}{V_N} \tag{5}$$

$$V_N(m^3) = V_{GM} \frac{p_{ap} * T_N}{T_{GM} * p_N} \tag{6}$$

$$m_{PM,N,13\%} (mg) = m_{PM,N} * \frac{21\% - O_{2,Ref}}{21\% - C_{O2}} \tag{7}$$

$$m_{PM,N,13\%,dry}(mg) = m_{PM,N,13\%} * \frac{100}{100 - c_{H2O}} \tag{8}$$

$$c_{H2O}(\%) = \left(\frac{\dfrac{\frac{1}{2} * \Delta m_{H2O} * V_{N,mol,H2O}}{M_{H2O}}}{\dfrac{\frac{1}{2} * \Delta m_{H2O} * V_{N,mol,H2O}}{M_{H2O}} + V_N} \right) * 100 \tag{9}$$

Where:

- m_{PM} is the mass of particulate matter, in milligrams.
- m_{filter} is the mass of the particulate filter from the combustion, in milligrams.
- m_{probe} is the mass of particles deposited inside the probe, in milligrams.
- V_{GM} is the volume at the gas meter, in cubic meter.
- T_{GM} is the temperature at the gas meter, in Kelvin.
- V_N is the standard volume, in cubic meter.
- c_{H2O} is the moisture content in the exhaust gases, in percentage.
- c_{O2} is the oxygen concentration in the exhaust gases, in percentage.
- m_{H2O} is the water contained in the bottle with silica gel, in grams.
- P_{ap} is the normal atmospheric pressure, in pascals. The value is 101325 Pa.
- T_N is the normal temperature, in kelvin. The value is 273 K.
- O_2 is the reference oxygen for the calculations, in percentage. The value is 13%.
- M_{H2O} is the molar mass of the water, in g/mol. The value is 18 g/mol.
- $V_{N,molmH2O}$ is the molar volume of the water, in m^3/mol. The value is 0,0224 m^3/mol.

3.5.3   X-ray diffraction analysis

After the combustion, the ash obtained from each additive is analysed by x-ray diffraction to obtain the crystalline compounds of each ash. For that, the samples are pressed on a sample holder as shown in figure 22.
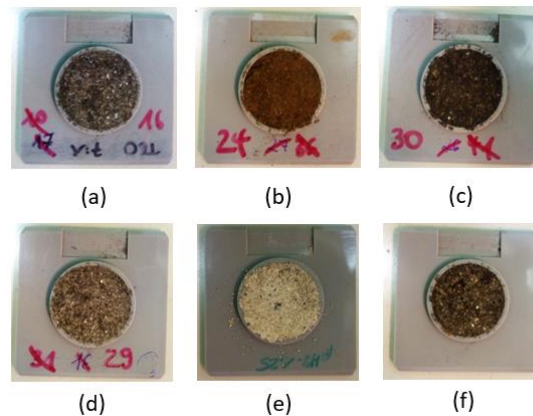
Figure 22. Ash samples. (a) Without Additive (b) Fe2O3 (c) MnCO3 (d) (NH4)2SO4 (e) TiO2 (d) Urea.

The analysis is performed with a Siemens D500 diffractometer using Cu-Kuα radiation at 30 mA and 40 kV with an angle of incidence from 20 to 60 degrees and an average time of ten minutes per sample. The measurements are evaluated using the Bruker EVA [42].

During the analysis, different values are stored in a database, allowing the crystals to be recognized and thus obtain the composition of the ash. Figure 23 shows the position of the x-rays in a visual way respect to the samples.
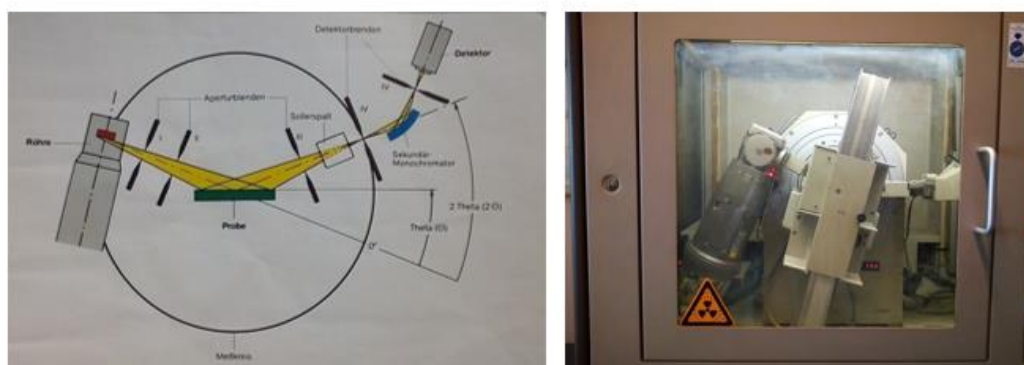
Figure 23. X-ray diffraction.

4 Results and discussion

4.1 Pelletizing results

The table 4 is a summary of the obtained pellets. The type of matrix, quality and production temperature are shown below.

Table 4. Obtainment of the pellets.

Type of pellets	Type of Matrix	Quality	Temperature
100% Beech wood (HB500/1000)	1:5	Good	[95,130]ºC
Beech wood (HB500/1000) with 0,5% Urea	1:5	Good	[80,100]ºC
Beech wood (HB500/1000) with 0,5% Fe_2O_3	1:5	Medium	[75,85]ºC
Beech wood (HB500/1000) with 0,5% Fe_2O_3	1:3	Medium	[75,85]ºC
Beech wood (HB500/1000) with 0,5% TiO_2	1:4	Good	[95,103'3]ºC
Beech wood (HB500/1000) with 0,5% $MnCO_3$	1:5	Good	[98,100]ºC
Beech wood (HB500/1000) with 0,5% $(NH_4)2SO_4$	1:3 and 1:5	Good	[96,101]ºC

The use of different matrices is due to the temperature reached during pellet production. A clear example was the influence of Fe_2O_3 which it favoured the dryness in the pellets.

At the beginning, the matrix 1:5 was used to produced them. However, the pellets were too dry even adding water. It was decided to change to the smallest matrix 1:3 and the pellets were better, although the dryness continued during the production.

In case of $(NH_4)_2SO_4$, the temperature was so high that even reached 130 °C and consequently some pellets were burned. The change to the matrix 1:3 improved the production and the quality of the pellets.

4.2 Analysis of the pellets properties

According to DIN EN 17225-2 norm, a clear classification principle for biogenic solid fuels enables an efficient trade in biogenic fuels and easy understanding between sellers and customers, as well as a tool to communicate with equipment manufacturers [38].

In this project, the analysis of pellets will focus on five parameters: diameter and length, bulk density, abrasion resistance, moisture content and ash content.

Table 5 indicates the requirements of pellets which should comply in accordance to DIN EN 17225-2 norm.

Table 5. Specification of pellets according to DIN EN 17225-2.

Parameter	Unit	A1. Wooden log/Chemically untreated wood residues [37]
Diameter and Length ISO 17829	mm	D06, 6 ± 1; 3,15 < L ≤ 40 D08, 8 ± 1; 3,15 < L ≤ 40
Bulk density ISO 17828	Kg/m^3 as-delivered condition	≥ 600
Abrasion resistance ISO 17831-1	w-% as-delivered condition	≥ 97,5
Moisture Content ISO 18134-1, ISO 18134-2	w-%	≤ 10
Ash content ISO 18122	w-% free from water	≤ 0,7

In the following points are described the previous parameters which will define the characteristics of pellets.

4.2.1 Dimensions

To determine the diameter of the pellets, 10 pellets were selected randomly and measured manually. The values obtained can be seen on Annexes, table 34.

Figure 24 presents an overview of the diameter measurement of pellets. In this analysis the matrix holes were 6 mm. The mean value diameter of the pellets during the experiment was less than 6 mm as shown in table 6. This can be caused by insufficient moisture content in pellets, so they are more compressed by the holes.

As will be seen in section 4.2.4, pellets with Fe_2O_3 have the highest amount of water and in this case possess the diameter nearest to 6 mm. This is probably due to the high content of moisture which can expand the structure of pellets after its production.
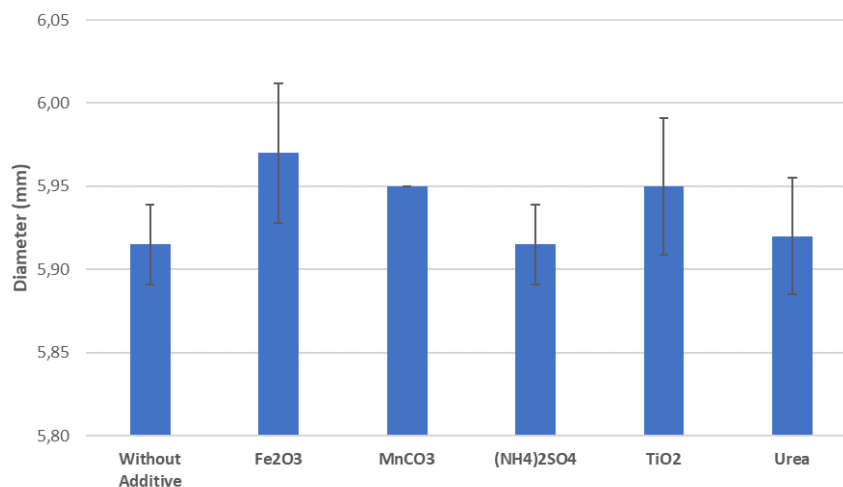
Figure 24. Diameter measurement of pellets.

Table 6. Pellet dimensions results.

	Without Additive	Fe_2O_3	$MnCO_3$	$(NH_4)2SO_4$	TiO_2	Urea
Diameter (mm)	5,91 ± 0,02	5,97 ± 0,04	5,95 ± 0,00	5,91 ± 0,02	5,95 ± 0,04	5,92 ± 0,03
Length (mm)	17,82 ± 1,65	17,62 ± 2,35	16,86 ± 1,59	18,38 ± 3,98	17,87 ± 2,69	18,59 ± 1,55

For the determination of the length, 30-40 g of the pellets must be separated. From this amount, 40 pellets were measured with a caliper. The values obtained can be seen on Annexes, table 35.

Figure 25 shows the length measurement of pellets. Despite the use of different types of matrices, the length lies within a range of 16,86 mm to 18,59 mm. According to DIN EN 17829 norm, all the samples should have an average size between 3,15 mm and 40 mm, so the results comply the European Standard norm.
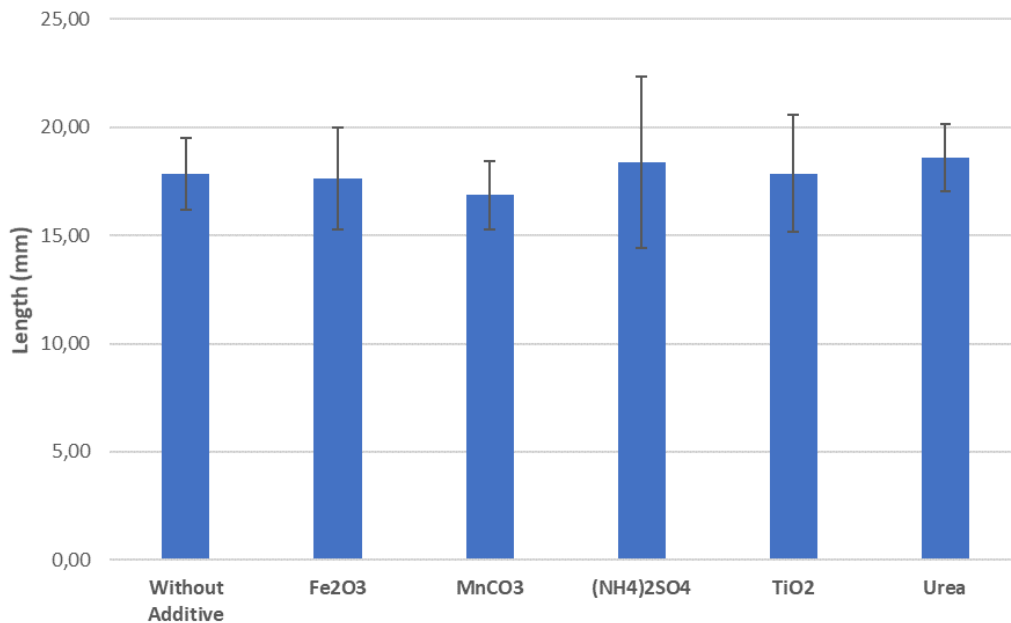
Figure 25. Length measurement of pellets.

4.2.2 Bulk density

The results obtained are presented in table 7.

Table 7. Bulk density results.

	Measure 1 (kg)	ρ (kg/m3)	Measure 2 (kg)	ρ (kg/m3)	Measure 3 (kg)	ρ (kg/m3)	Mean value ρ (kg/m3)	Deviation
1	1,73	778,52	1,73	783,89	1,74	810,74	790,93	17,26
2	1,72	751,68	1,73	773,15	1,72	757,05	760,57	11,18
3	1,73	783,89	1,74	789,26	1,74	800,00	791,02	8,20
4	1,74	805,37	1,74	789,26	1,74	789,26	794,59	9,30
5	1,74	810,74	1,74	800,00	1,74	789,26	799,95	10,74
6	1,74	789,26	1,74	800,00	1,74	789,26	792,83	6,20

Sample identification is shown as follows:

1. Without Additive
2. Fe_2O_3
3. $MnCO_3$

4. $(NH_4)_2SO_4$
5. TiO_2
6. Urea

Figure 26 shows an overview of the results obtained of the analysis. The mean values are between 790,93 kg/m$_3$ and 799,95 kg/m$_3$. According to DIN EN 17828 norm, bulk density should be more than 600 kg/m^3, so the results are within the recommended range.

In order to establish a relationship between dimensions and bulk density, Fe_2O_3 has the highest diameter with the minor value of bulk density. However, the other additives do not have the same inverse relationship. One example is $(NH_4)_2SO_4$ which has the lowest diameter and it does not have the maximal value in bulk density. The experience in this analysis was that it was more difficult to refill the cylinder after the impact with the rest of the pellets than Fe_2O_3. A possible explanation for this could be its structure, they were more compacted and starker than $Fe_2O_3.$ Moreover, the addition of Fe_2O_3 made pellets more porous and easy to undo. This affects the weight because they become lighter.
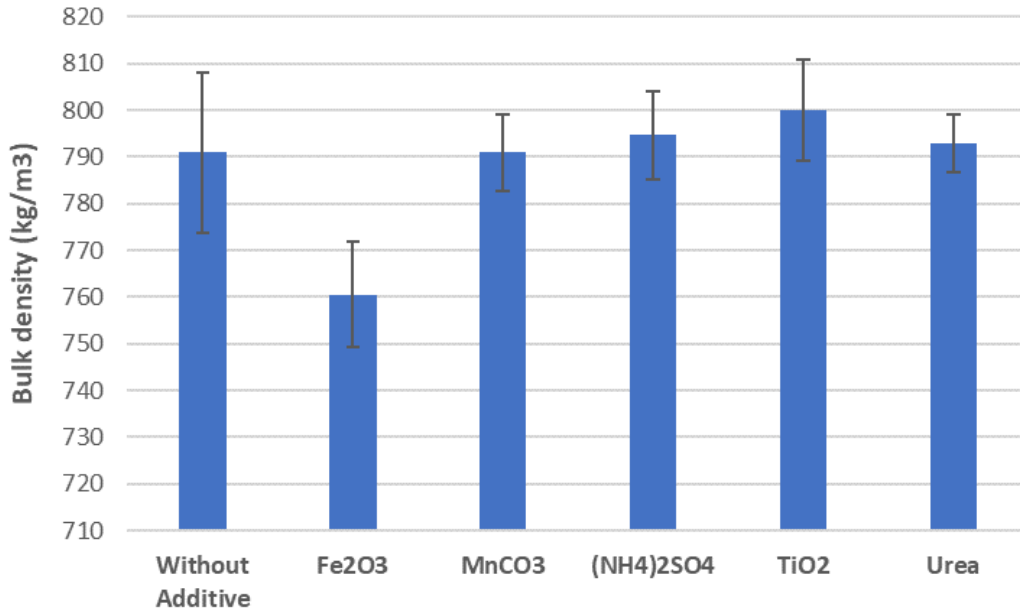
Figure 26. Bulk density content.

4.2.3 Abrasion resistance

Results obtained during the analysis are shown in table 8.

Table 8. Abrasion resistance results.

	Weight 1 (gr)	AR %	Weight 2 (gr)	AR %	Weight 3 (gr)	AR %	Mean value (%)	Deviation
1	476	95,20	476	95,20	478	95,60	95,33	0,23
2	442	88,40	452	90,40	436	87,20	88,66	1,62
3	478	95,60	486	97,20	489	97,80	96,86	1,14
4	450	90,00	450	90,00	468	93,60	91,18	2,08
5	454	90,80	464	92,80	470	94,00	92,52	1,62
6	480	96,00	488	97,60	489	97,80	97,13	0,99

Sample identification is shown as follows:

1. Without Additive
2. Fe_2O_3
3. $MnCO_3$

4. $(NH_4)_2SO_4$
5. TiO_2
6. Urea

Figure 27 presents the results of the analysis conducted. According to the European Standard norm (EN ISO 17831-1), the abrasion resistance should be higher than 97,5 %. The results show a mean value between 88,66 % and 97,13 % which are below the acceptable standard value.

The lowest value belongs to Fe_2O_3 with 88,66 % ± 1,62. As stated in the former section, the addition of Fe_2O_3 weakened the pellets making them more porous. In its production, the content of fines was higher than the rest of the pellets. When the pellets came out of the machine, they came accompanied of a considerable amount of fines.

The same happened to $MnCO_3$. When pellets reached 100°C, they came accompanied of fines as well. However, it has one of the highest mean value with 96,86 % ± 1,14. A possible explanation is the use of the matrix 1:5, inasmuch as the residence time of the biomass is higher in the largest matrix.

As regards the use of TiO_2 and $(NH_4)_2SO_4$, there is not a specific reason for these results. Its production was practically without fines. In case of $(NH_4)_2SO_4$, the matrix was changed for 1:3 because the temperature reached 130 °C and some of the pellets were burned. A possible reason for them can be a decompensation in the feeding system, because sometimes the addition of biomass was manually and there was no control of the quantity.

Pellets without additive and urea present good abrasion resistance. Nonetheless, its results are not above the established value. The explanation might lie in the pressing of pellets during its production.
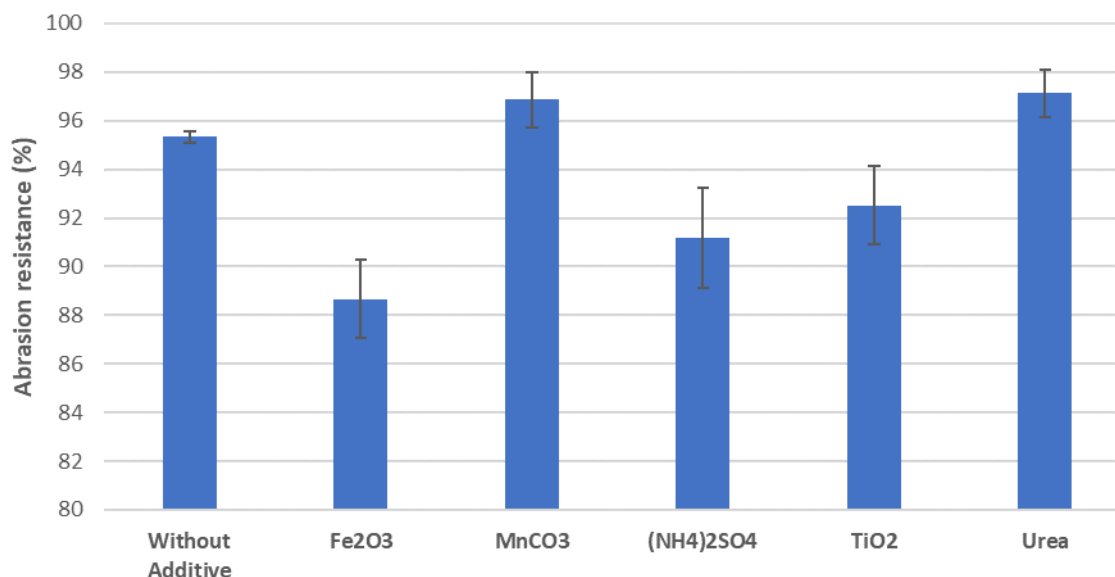
Figure 27. Abrasion resistance content.

4.2.4 Moisture content

The analysis was performed using different amounts of pellets. The first analysis was carried out with 6 g in each sample due to the laboratory material available. The figure 28 shows the prepared samples before drying.

(a)   (b)

Figure 28. (a) Identification of the samples with 6 g. (b) Prepared samples before drying, 6g

The moisture content of the pellets produced can be seen in table 9.

Table 9. Water content samples with 6 g

Samples	Weight of crucible (g)	Total weight before oven (g)	Total weight after oven (g)	Moisture content (%)
1. Without Additive	35,14	42,53	42,25	4,02
2. Urea	23,85	29,65	29,44	3,81
3. $MnCO_3$	19,21	24,90	24,69	3,87
4. $(NH_4)2SO_4$	19,65	26,96	26,71	3,60
5. TiO_2	9,91	15,34	15,18	3,01
6. Fe_2O_3	13,30	22,52	22,02	5,78

The second analysis was performed with 50 g in each sample to guarantee a good measurement of moisture content.

(a)   (b)

Figure 29.(a) Identification of the samples with 50 g. (b) Prepared samples before drying, 50 g

The results of this second test are shown in table 10. The moisture content in the samples 4,5 and 6 are quite similar in both analyses. Samples 1,2 and 3 lie within an interval between 3% and 4%.

Table 10. Water content of samples with 50 g

Samples	Weight of crucible (g)	Total weight before oven (g)	Total weight after oven (g)	Moisture content (%)
1. Without Additive	72,77	123,25	121,19	4,26
2. Urea	85,97	136,04	134,06	4,12
3. $MnCO_3$	89,47	137,52	135,64	4,06
4. $(NH_4)2SO_4$	76,66	126,37	124,66	3,56
5. TiO_2	72,85	121,98	120,53	3,04
6. Fe_2O_3	81,58	131,74	128,96	5,87

Figure 30 shows an overview of the moisture content in both analyses. Here it is possible to compare the influence of the additives on the beech wood, being TiO_2, $(NH_4)_2SO_4$ those with less water absorption.
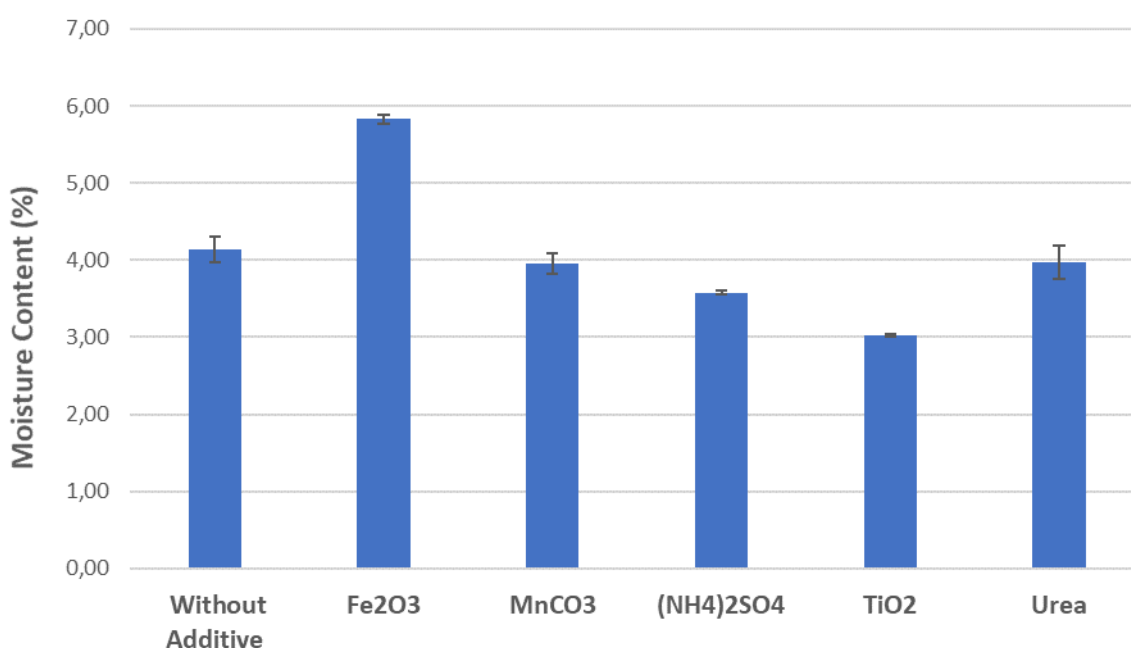
Figure 30. Percentage of moisture content.

The values lie within between 3,01 % and 5,87 % with a standard deviation of 0,02% and 0,06% respectively. Consequently, all the percentages agree with the limit of 10 % of water content established by DIN EN ISO 17225-2 A1 norm.

The greatest concentration of water resides in the use Fe_2O_3, which increases the porosity of the pellets and absorbs more water vapour of the environment. On the contrary, the additives TiO_2 and $(NH_4)_2SO_4$ contributes to higher evaporation and do not retain as much water in the final

product as Fe_2O_3. The mean value for moisture content on all of the samples is 4%. Here are located the rest of the additives and 100% beach wood.

4.2.5   Ash content

Both analyses were performed with the dry pellets from the first and second analysis of moisture content respectively as can be seen from figure 31 and 32. The numbering is the same as moisture content:

1. Without Additive
2. Urea
3. $MnCO_3$

4. $(NH_4)2SO_4$
5. TiO_2
6. Fe_2O_3
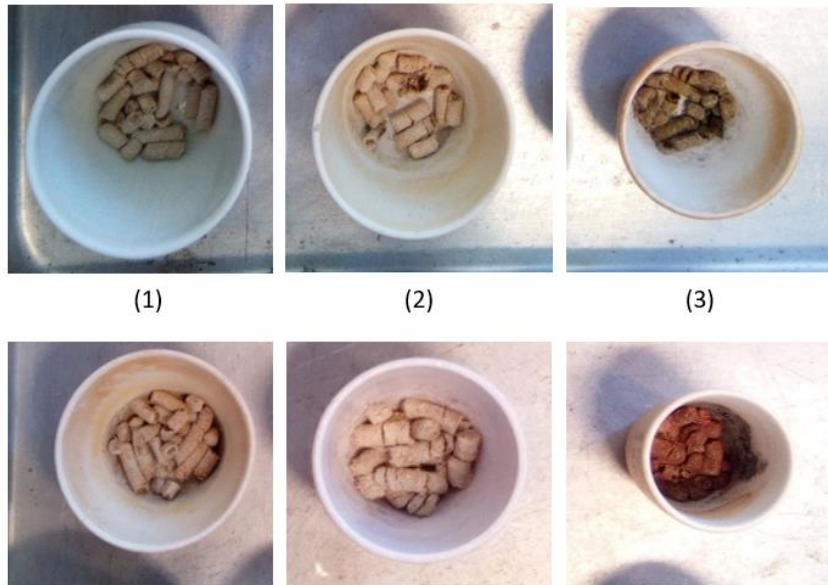
Figure 31. First analysis ash content.
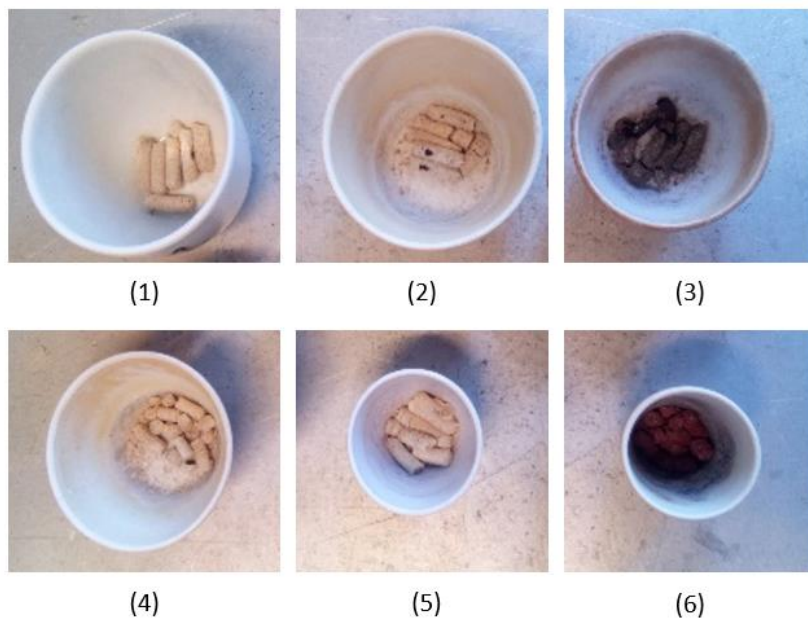
Figure 32. Second analysis ash content.

Table 11 shows the results of both analysis of ash content.

Table 11. Ash content analysis.

FIRST ANALYSIS					
Samples	Weight of crucible (g)	Total weight dry pellets (g)	Total weight with ash (g)	Moisture content (%)	Ash content (%)
1. Without Additive	35,14	42,25	35,20	4,02	0,83
2. Urea	23,85	29,44	23,89	3,81	0,72
3. $MnCO_3$	19,21	24,69	19,27	3,87	1,10
4. $(NH_4)_2SO_4$	19,65	26,71	19,71	3,60	0,82
5. TiO_2	9,91	15,18	9,98	3,01	1,31
6. Fe_2O_3	13,30	22,02	13,72	5,78	5,12
SECOND ANALYSIS					
1. Without Additive	35,14	38,61	35,17	4,26	0,80
2. Urea	23,85	27,35	23,87	4,12	0,71
3. $MnCO_3$	19,21	22,90	19,25	4,06	1,07
4. $(NH_4)_2SO_4$	19,65	23,34	19,68	3,56	0,82
5. TiO_2	9,91	13,73	9,96	3,04	1,29
6. Fe_2O_3	13,30	16,98	13,47	5,87	4,92

In order to maintain an overview of progress on the ash content, the following graphic presents the analysed samples at the laboratory.
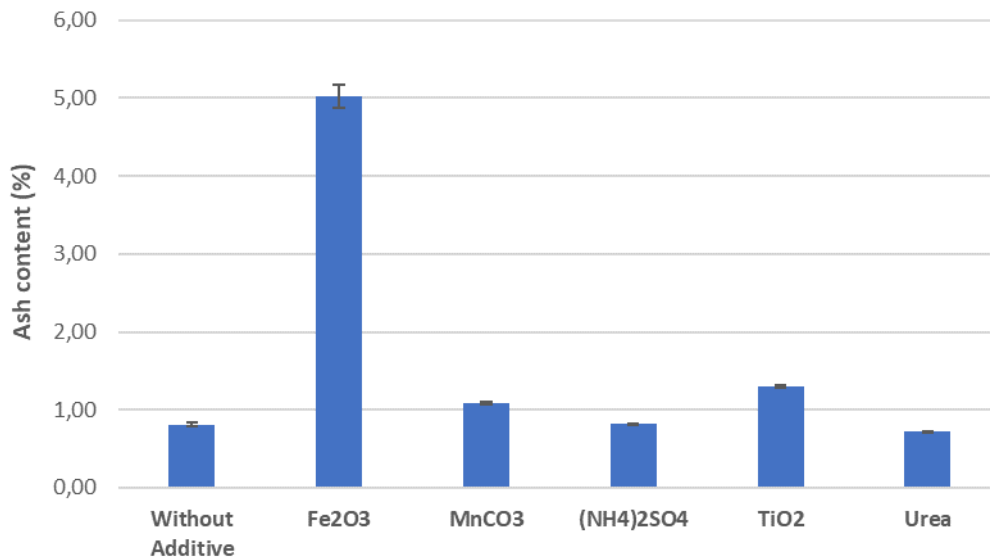
Figure 33. Percentage of ash content.

As displayed on the above graphic, the amount of ash content is between 0,8 % and 5,12 %. All results were more than 0,7 % required by DIN EN 18122. However, the mean value closer to 0,7% is the use of Urea with 0,72% ± 0,01. In case of Fe_2O_3, TiO_2 and $MnCO_3$, they are present as a part of the biomass elements (Si, Al, Fe, Ca, Mg, Mn, Na, K, P, S and Cl). These elements can be divided in two groups: particulate matter formation and ash formation.

The elements which are in lower concentrations in solid biomass such as Fe and Mn form mainly ash and are typically found only in the bottom ash [39]. The following figure shows a general scheme of particulate matter and ash formation of the biomass elements.
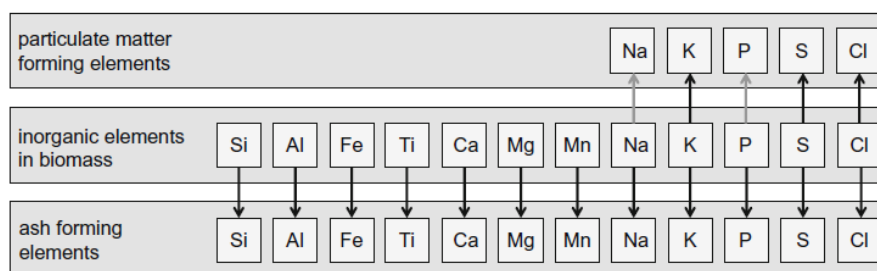
Figure 34. Scheme of particulate matter and ash formation.

However, despite Fe, Mn and Ti are ash forming elements, the value of ash content of Fe_2O_3 respect to $MnCO_3$ and TiO_2 is quite higher in comparison to the other two additives.

Consequently, the addition of these additives are increasing the ash content of pellets. Beech wood, urea and $(NH_4)_2SO_4$ have an ash content closer to the regulation establish by DIN EN 18122 norm. Its mean values are between 0,72% and 0,82%.

4.2.6 Summary results

The following table shows an overview of the analysis results. In general, the results are within the European Standard for solid biofuel. However, the conflict lies in abrasion resistance and ash content.

As mentioned in the previous sections, there are variable factors to be taken into account such as the correct utilisation of the feeding system or the use of the different matrices in which both requires experience. Nonetheless, the addition of urea provides the best results respect to the other additives.

Table 12. Pellet summary results.

	Diameter (mm)	Length (mm)	Bulk density (kg/m³)	Abrasion resistance (%)	Moisture content (%)	Ash content (%)
Norm DIN	6	3,15 <L ≤ 40	≥ 600	≥ 97,5	≤ 10	≤ 0,70
Without Additive	5,91 ± 0,02	17,82 ± 1,65	790,93 ± 17,26	95,33 ± 0,23	4,14 ± 0,17	0,81 ± 0,02
Fe_2O_3	5,97 ± 0,04	17,62 ± 2,35	760,57 ± 11,18	88,66 ± 1,62	5,83 ± 0,06	5,02 ± 0,14
MnCO3	5,95 ± 0,00	16,86 ± 1,59	791,02 ± 8,20	96,86 ± 1,14	3,96 ± 0,13	1,08 ± 0,02
$(NH_4)_2SO_4$	5,91 ± 0,02	18,38 ± 3,98	794,59 ± 9,30	91,18 ± 2,08	3,58 ± 0,03	0,82 ± 0,00
TiO_2	5,95 ± 0,04	17,87 ± 2,69	799,95 ± 10,74	92,52 ± 1,62	3,02 ± 0,02	1,30 ± 0,01
Urea	5,92 ± 0,03	18,59 ± 1,55	792,83 ± 6,20	97,13 ± 0,99	3,97 ± 0,22	0,72 ± 0,01

The next step to follow will be the reduction of NOx emissions on the basis of the pellets obtained.

4.3   Combustion of pellets

4.3.1   NOx emissions

In the following sections, the NOx emissions obtained during the combustion of the different pellets are presented.

4.3.1.1   Pellets without additive

The following graphic presents the first combustion of pellets without additive. As explained in section 3.5, there are three phases in the stove to take into account: ignition phase, heating mode and burner test or cleaning. The first phase is not represented in figure 35 because there were problems at the start of the programme *Wöhler A550 L* so the graphic below shows the combustion from the heating mode phase.

On the other side, the filters for the particulate matter measurement are represented in the following graphic. During the first combustion were performed filter 1 and filter 2. In the second combustion will be performed the filters 3 and 4.
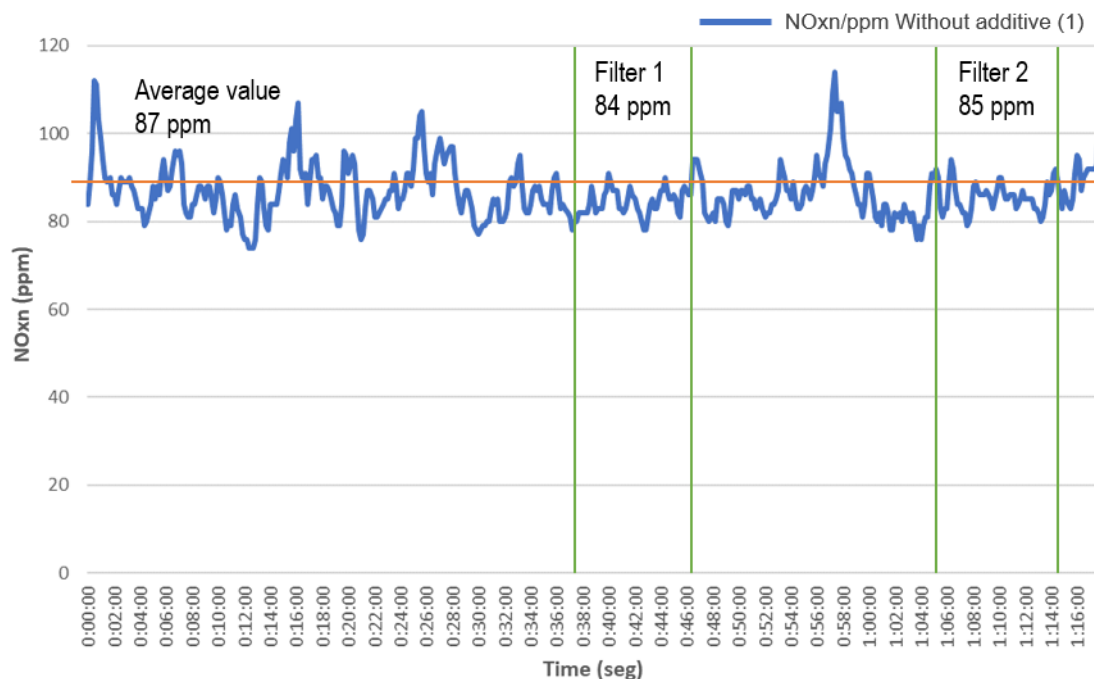
Figure 35. NOx emissions pellets without additive. First combustion.

Since the temperature inside the combustion device was below 1000°C, all the NOx emitted are too low for thermal and prompt NOX formation, so probably the NOx emissions measured come from fuel-N formation, in other words, from the nitrogen contained in the biomass.

On the other hand, the fact that the temperature is lower than 1000°C, favours greater formation of NOx in the exhaust gases. A possible measure to reduce the formation of NOx is to create an atmosphere with high temperature (more than 1000°C), in absence of oxygen and fuel

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particles from an incomplete combustion [23]. The objective would be an endothermic reaction. However, since this stove is for residential buildings, this measure would not be optimal. In this case the additivation of pellets will be performed in the following points.

Figure 36 shows the second combustion for pellets without additive. The average NOx value is 80 ppm and for the filters 3 and 4 are 80 ppm and 81 ppm respectively. Additionally, the ignition phase can be seen in the first five minutes.
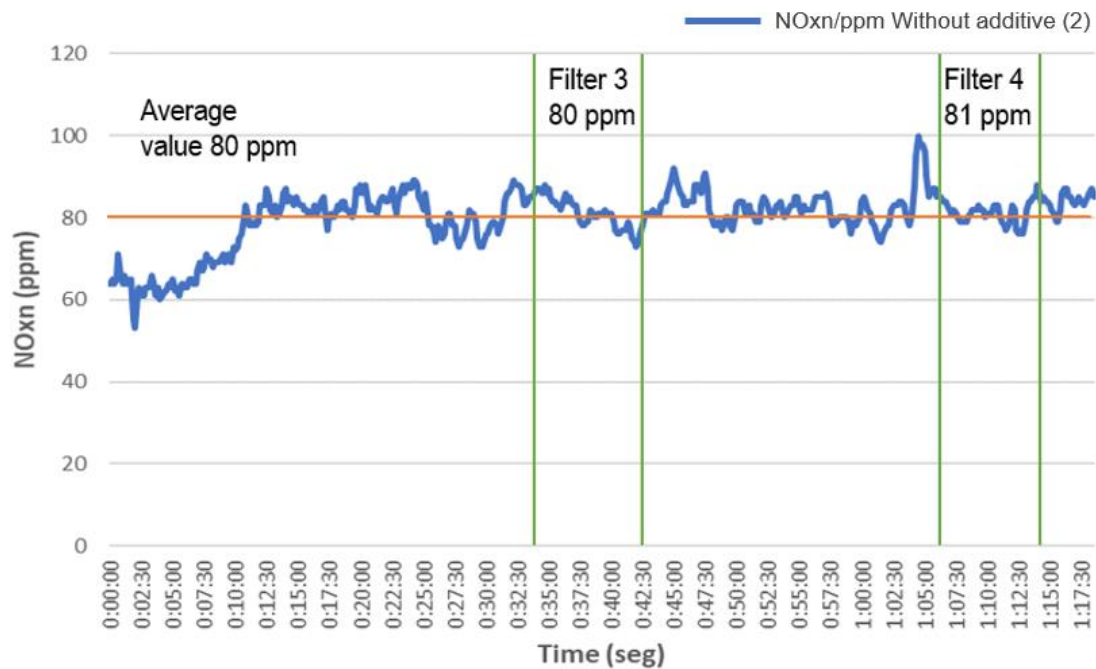
Figure 36. NOx emissions pellets without additive. Second combustion.

In this case, the NOx emissions are lower than the first combustion. A possible explanation for this could be the oxygen content inside the combustion chamber is lower than the first case. A lower amount of oxygen hinders the nitrogen oxidation reactions.

The values obtained from both combustions will serve as a starting point for the additives used to reduce the NOx formation. A comparison will be performed to know if the additives achieve a decrease of the NOx emissions or if, on the contrary, they increase such emissions.

4.3.1.2 Pellets with Fe_2O_3

The first additive used to reduce NOx emissions is Fe_2O_3. As explained in section 3.1, the use of Fe as well as Ca are beneficial to NOx reduction in the sintering process [30]. This process occurs when the bond between particles becomes stronger due to geometrical changes which appear when the temperature of a set of particles is elevated for an extended period of time [44].

The quantity added to the beech wood was 0,5% total mass, resulting 60 g in 12 kilograms of wood. The first measurement is shown in figure 37. Here the ignition phase can be seen in the first five minutes.

The average value of NOx emissions is 71 ppm. On the other hand, the average values of NOx from the filters for the particulate matter measurement are also marked in the following graphic.
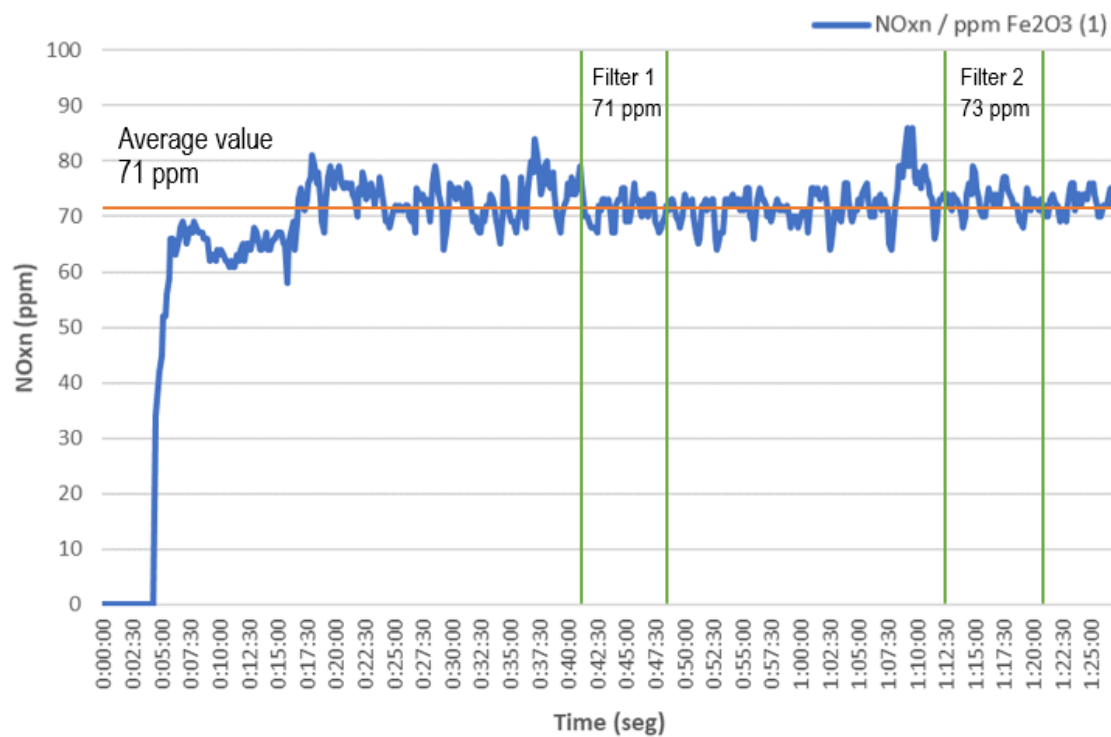
Figure 37. NOx emissions pellets Fe_2O_3. First combustion.

The emissions obtained are lower than pellets without additive. The reduction of the total average value of NOx emissions compared to the initial case without any type of additive, is 18,4%.

The use of Fe is present in chemical systems such as catalytic conversion. The catalytic conversion is based on the use of catalytically active materials to reduce the activation energy of the tar cracking and ammonia decomposition reactions. In the case of NOx in presence of NH_3 with Fe_2O_3 as catalyst potentially generates a reduction reaction which avoids the formation of NOx [45].

In case of sintering process, the NOx reduction ratio with 8% Ca-Fe oxides can achieve a reduction of 27,76% [30].

Another measurement was performed to compare the results with this additive. Figure 38 shows an average value of 72 ppm. The average values of NOx from the filters are also marked in the following graphic .

Figure 38. NOx emissions pellets Fe_2O_3. Second combustion.

The reduction of NOx respect to the second combustion of pellets without additive is 10 % less than the first case. It should be taken into account that the formation of NOx depends on the fuel and environmental conditions. Not all pellets have the same composition because some of them were produced manually and the oxygen content varied from the first combustion to the second.

It is true that, the use of Fe_2O_3 reduces the formation of NOx emissions. However, during the combustion the formation of CO was higher than without additive. This additive may lower the NOx but increases the CO formation.

On the other hand, it is important to take into account the results of section 4.2 which show that pellets with this additive do not have good resistance to the abrasion and the ash content is higher than the value indicated in the European norm.

4.3.1.3 Pellets with MnCO₃

The second additive used was $MnCO_3$. This compound is present in the biomass composition and it is one of the ash forming elements during the combustion [39] as will be shown in section 4.3.3.

This additive is used in SCR to reduce NOx emissions at low temperature. As shown in section 3.1, manganese catalysts, at moderate temperatures such as 523 K and 623 K, decrease the NOx conversion and increase the N_2 formation in selective catalytic reduction at low temperature [32].

The quantity added to the beech wood was 0,5% total mass, resulting 60 g in 12 kilograms of wood. Figure 39 shows the results obtained of NOx emissions during the combustion. The average value is 84 ppm and the average values of NOx from the filters 1 and 2 are 85 ppm and 82 ppm respectively. They are also marked in the following graphic.

Additionally, during the first five minutes are represented the ignition phase.
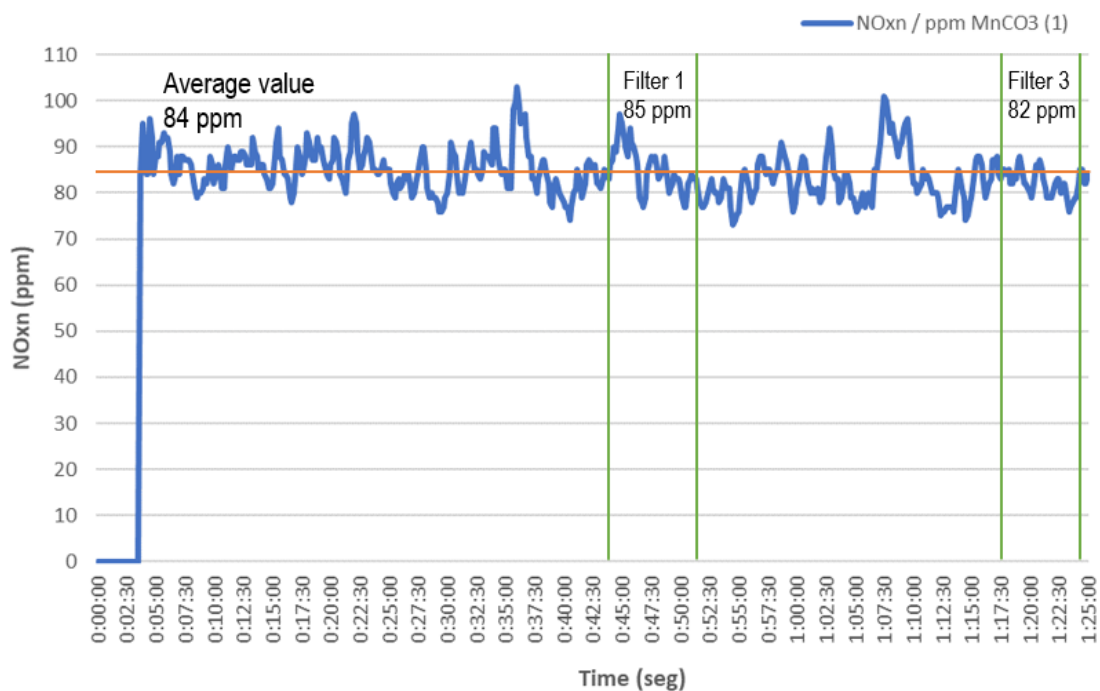
Figure 39. NOx emissions pellets $MnCO_3$. First combustion.

The reduction of NOx respect to the first combustion of pellets without additive is 3,4 %. This value is lower than the reduction obtained with Fe_2O_3. Although in SCR systems the use of manganese reduces significantly the NOx formation, the direct additivation with this element does not work so efficiently as catalyst.

The second measurement is shown in figure 40. The average value of NOx emissions is 83 ppm. The average values of NOx from the filters are also marked in the following graphic.
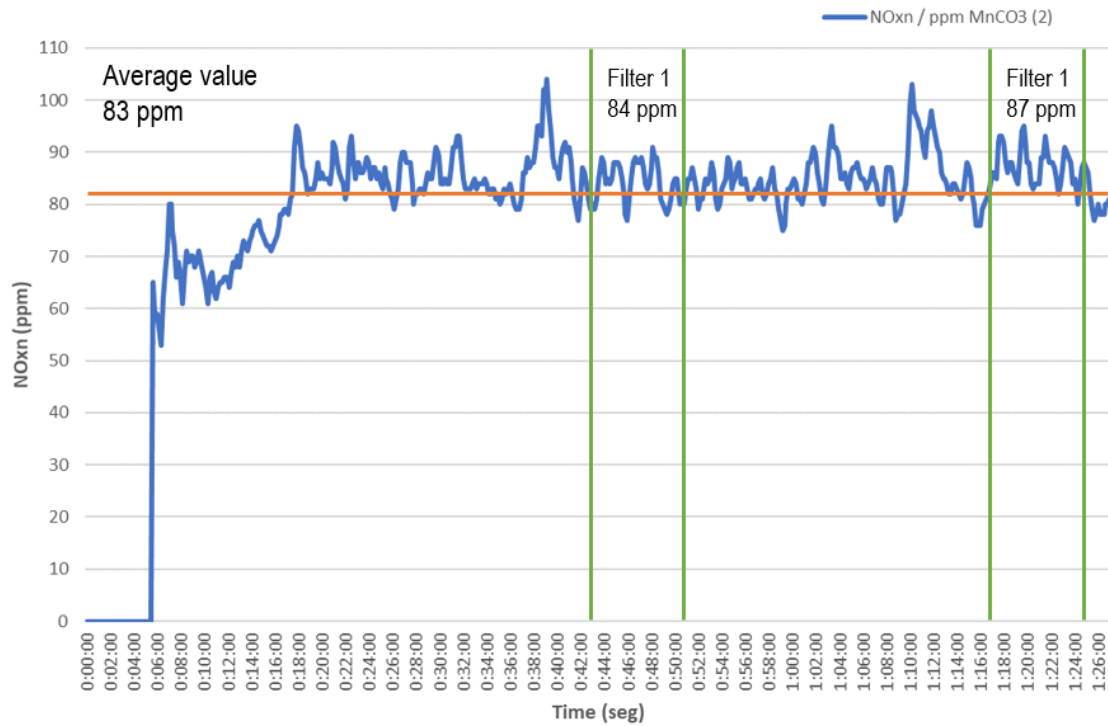
Figure 40. NOx emissions pellets MnCO$_3$. Second combustion.

Despite the characteristics obtained in section 4.2, which are better than Fe$_2$O$_3$, this additive not only do not reduce the NOx formation, but it also increases in 3,8% respect to the second combustion of pellets without additive. This variation of the values is probably due to the composition of pellets and the environmental conditions.

Additionally, there was an increase of CO formation during the combustion in comparison with pellets without additive.

This element is useful in SCR systems. During an investigation, the highest NOx reduction was observed over MnOx catalysts precipitated with sodium carbonate. MnCO$_3$ is not use directly as a catalyst, but it is a decomposed and amorphous structure of the MnOx catalysts [32].

The applicability of MnCO$_3$ is more suitable for the reduction of particulate matter (PM). In a recent study, the use of this compound as additive, shows a loss mass of the particulate matter forming elements but an incorporation of K in the ash [42].

4.3.1.4 Pellets with $(NH_4)_2SO_4$

The third additive was $(NH_4)_2SO_4$. One of its main uses is in SCNR systems to reduce NOx emissions and KCl during the combustion in a CFB boiler [25]. Another use is as fertilizer in the harvests or to reduce the sulphates in the soils of the forests [46]. In this case, it is added directly to the beech wood.

The quantity, as in the other cases, 0,5% total mass, resulting 60 g in 12 kilograms of wood. Figure 41 shows the results obtained of NOx emissions during the combustion. The average value is 111 ppm. There are two different graphics for filter 1 and 2 because filter 2 in the first combustion was destroyed by an accident. On the other hand, in both cases, the first five minutes correspond to the ignition phase.
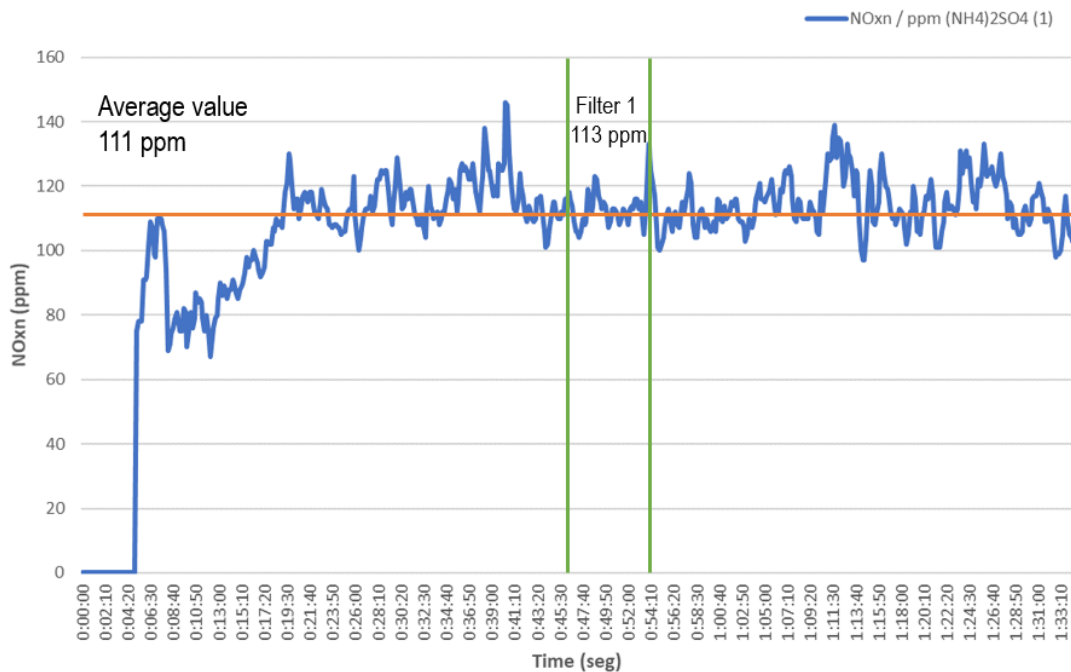
Figure 41. NOx emissions pellets $(NH_4)_2SO_4$. First combustion Filter 1.
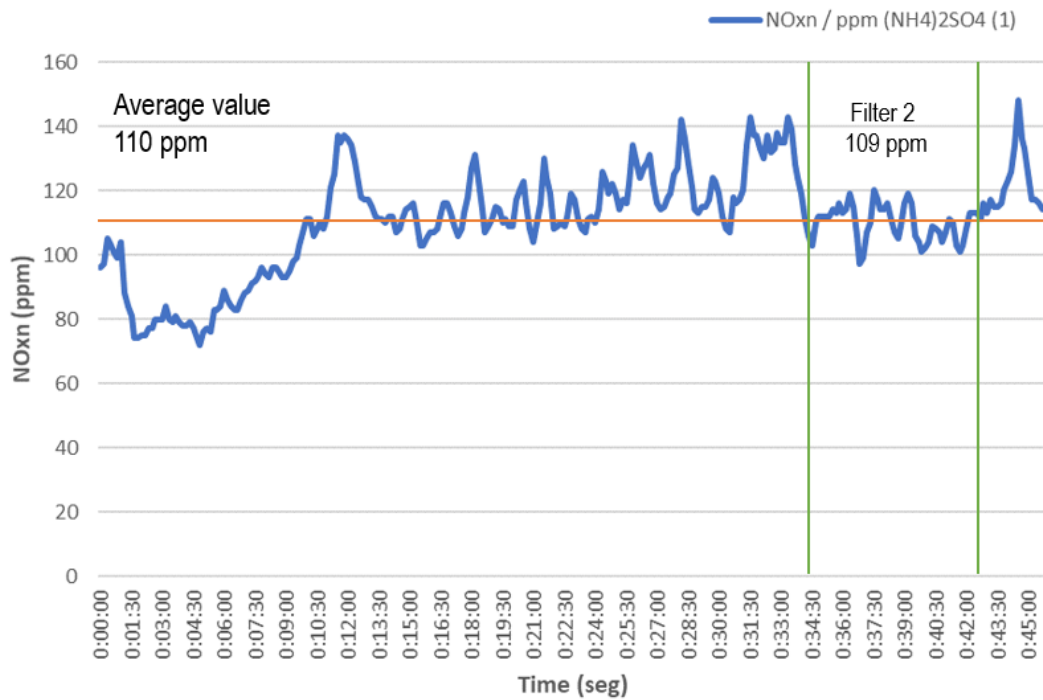
Figure 42. NOx emissions pellets $(NH_4)_2SO_4$. First combustion. Filter 2**.**

The average values for both filters are 113 ppm and 109 ppm respectively. This additive as well as $MnCO_3$ in the second case, do not reduce NOx emissions. Instead these emissions have raised by 27,6 %.

In a study about NOx emissions due to the use of fertilizers, $(NH_4)_2SO_4$ was used to mitigate the formation of NOx. However, the highest N_2O emissions were from the additive $(NH_4)_2SO_4$. This was presumably due to the quicker availability of NH_4 from $(NH_4)_2SO_4$, which ensured quicker nitrification and higher N_2O production [47].

The second measurement is shown in figure 43. The average value of NOx emissions is 116 ppm. The average values from filters 3 and 4 are 117 ppm and 116 ppm respectively. On the other hand, the first five minutes correspond to the ignition phase.
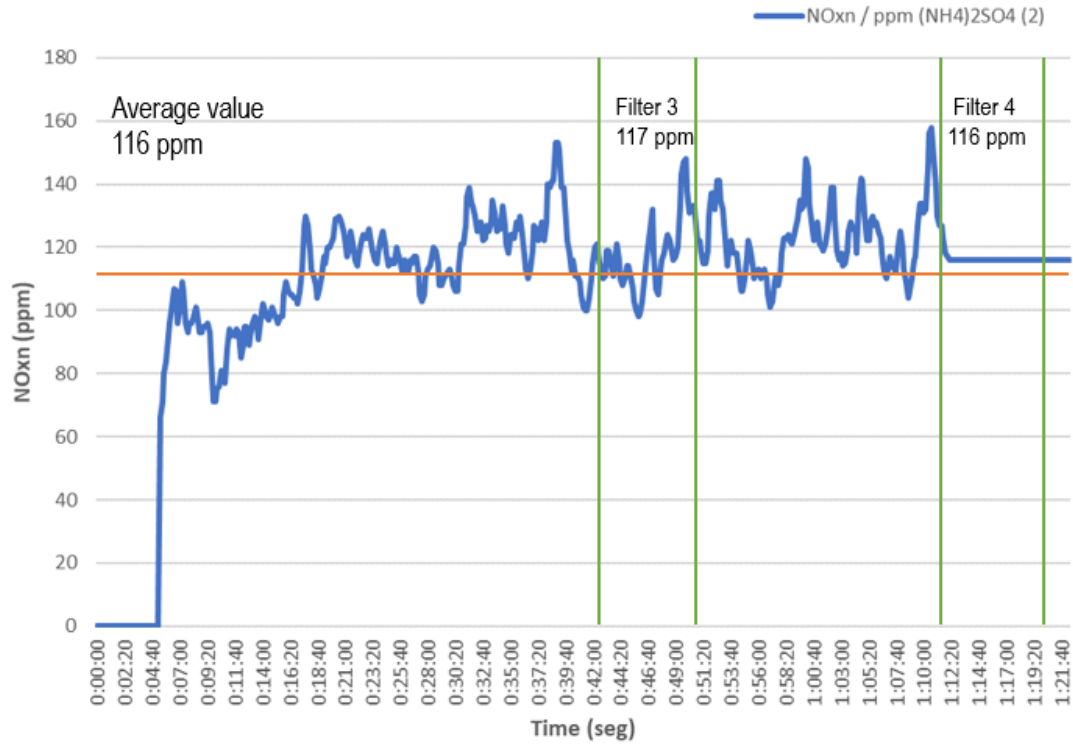
Figure 43. NOx emissions pellets $(NH_4)_2SO_4$. Second combustion**.**

The last part of the measurement which corresponds to filter 4 has not been implemented correctly. This is probably due to a connection failure of the sensor *Wöhler* to the computer. Nevertheless, in this second combustion not only the emissions were not reduced, but it also increases in 45% with respect to the second combustion of pellets without additive.

Despite the physical characteristics obtained during the analysis performed in section 4.2 which are also a little bit better than Fe_2O_3, it increases the NOx formation as well as CO emissions.

Therefore, the use of this additive is not suitable for the reduction of NOx emissions.

4.3.1.5   Pellets with TiO_2

The fourth additive added was TiO_2. Titanium is also an element contained naturally in biomass as manganese [39].

As explained in section 3.1, this additive is one of the main catalyst in SCR in combination with V_2O_5. It is used in practice as one of the best catalysts for the reduction of NOx by NH_3, because of its high activity at low temperature and of its high resistance to the poisoning by SOx [31].

The quantity added to the beech wood was 0,5% total mass, resulting 60 g in 12 kilograms of wood. Figure 44 shows the results obtained of NOx emissions during the combustion. The average value is 86 ppm and the average values of NOx from the filters 1 and 2 are 83 ppm and 86 ppm respectively. In the graphic is shown the ignition phase during the first five minutes as well.
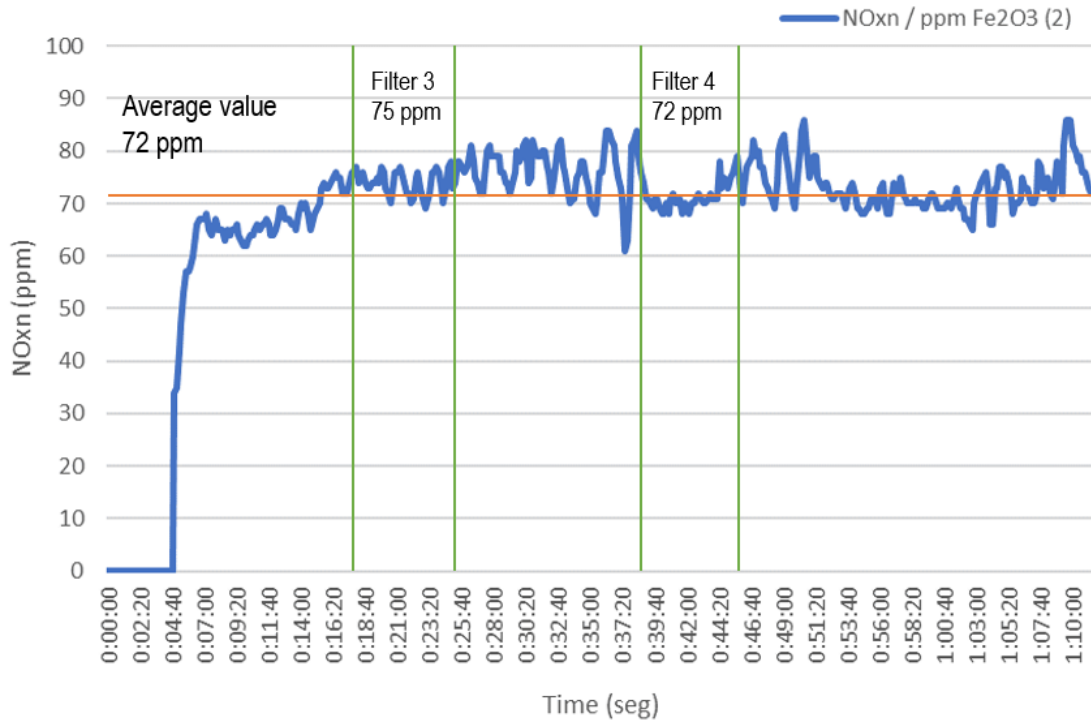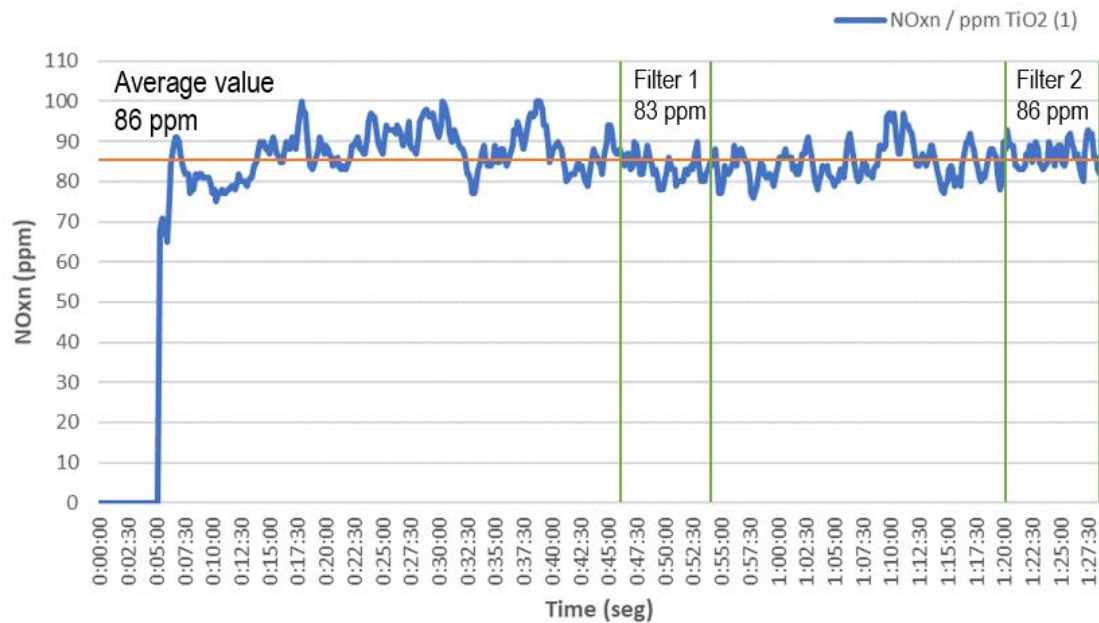

Figure 44. NOx emissions pellets TiO_2. First combustion.

The reduction of NOx respect to the first combustion of pellets without additive is 1,1 %. This value is also lower than the reduction obtained with Fe_2O_3. This case is quite similar to the additive $MnCO_3$. In SCR systems, TiO_2 is a good catalyst for the reduction reactions. However, when it is introduced in its solid form and manually it does not reduce the NOx as good as in SCR.

The second measurement is shown in figure 45. The average value of NOx emissions is 83 ppm and the average values from filters 3 and 4 are 85 ppm and 84 ppm respectively.
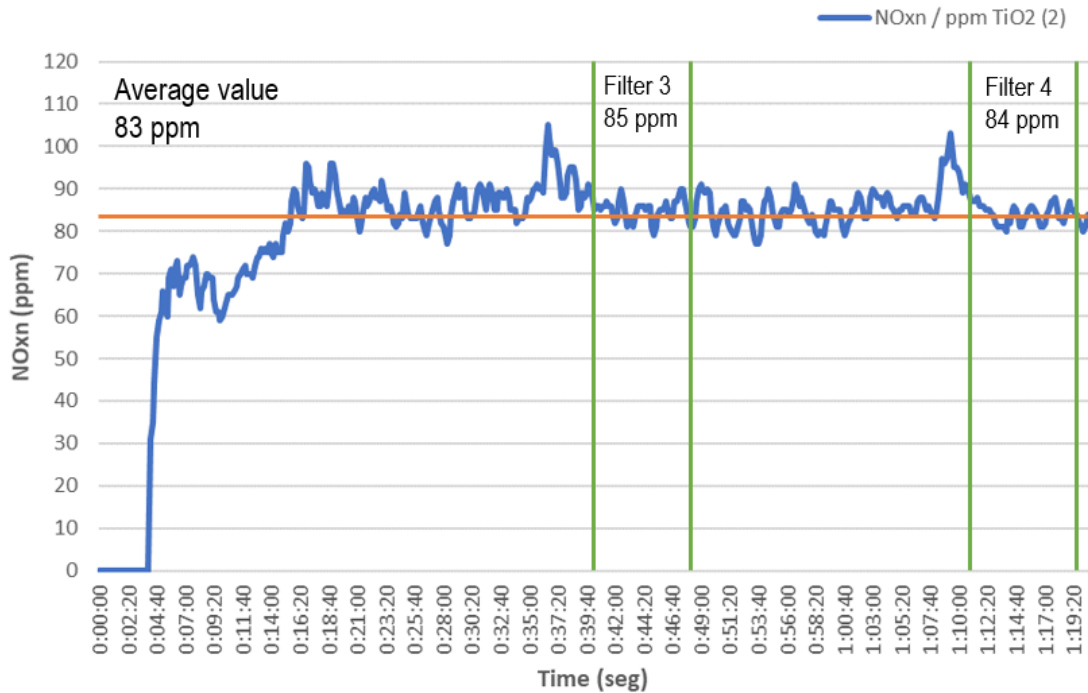
Figure 45. NOx emissions pellets TiO$_2$. Second combustion.

In this combustion, there is an increase in the NOx emissions respect to the first combustion. The formation of NOx has risen by 3,8 % in comparison to the second combustion of pellets without additive. On the other side, the values obtained in section 4.2 are quite similar to the additive MnCO$_3$ as well as its contribution to the formation of CO during the combustion.

This additive receives much attention for air purification applications especially for removal of air pollutants like NOx [48]. However, another use for this additive is by means of photocatalytic oxidation. This means that the catalyst is activated when it is exposed to the light.

A study proves that the TiO$_2$ photocatalyst exhibited significant improvement in NO oxidation and importantly in NOx removal [48]. Nevertheless, the additivation of pellets with this compound does not reduce the NOx emissions despite the fact that in other systems archived good results.

4.3.1.6   Pellets with Urea

The last additive was urea whose chemical formula is $CO(NH_2)_2$ [49]. This compound is very used in SNCR systems as well as ammonia. The efficiency of this substance in SNCR systems is around 44% in comparison to ammonia which reduces the NOX emissions around 84 % [49].

The quantity added, as in previous cases, is 0,5 % total mass of beech wood. Figure 46 shows the results obtained of NOx emissions during the combustion. The average value is 144 ppm and the average values of NOx from the filters 1 and 2 are 145 ppm and 159 ppm respectively. In the graphic is also shown the ignition phase during the first five minutes.
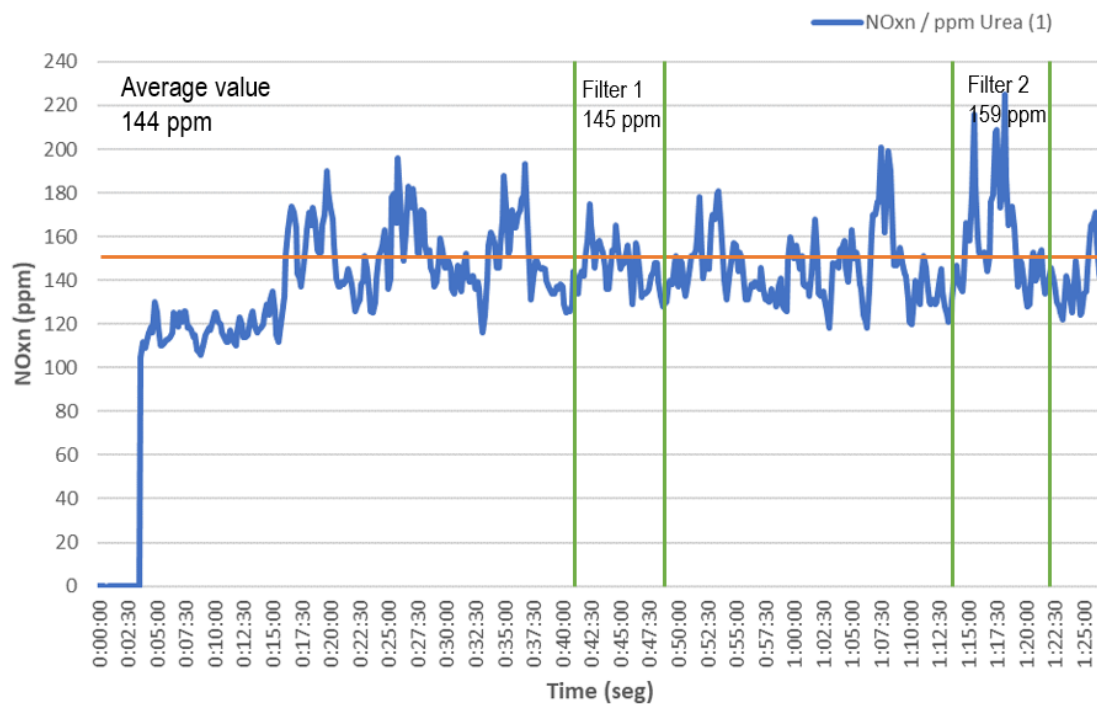
Figure 46. NOx emissions pellets Urea. First combustion.

The graphic illustrates an increase of NOx emissions respect to the first combustion of pellets without additive. This increase achieves a value of 31 %, so this substance is one of the additives that most rises the formation of NOx, despite the values obtained in section 4.2 are the closest to the European norm. On the other side, the CO emissions have been increased during the combustion as well.

The increase of the NOx emissions can be due to the union of the nitrogen from the urea and the content in the fuel. A study shows that urea in powder had an efficiency lower than in solution. An explanation for this was that the very low value obtained with powdered urea could moreover be due to the fact that the solid urea particles may not have sufficient residence time in the boiler to sublimate, reducing the effective time of contact with NOx [49].

Therefore, in this case the same may have happened. Urea has not reacted with NO probably due to the temperature conditions or because the mixture was not well realized. In any case it does not work adding it directly to the biomass.

The second measurement is shown in figure 47. The average value of NOx emissions is 148 ppm and the average values from filters 3 and 4 are 153 ppm and 139 ppm respectively. On the other hand, the first five minutes correspond to the ignition phase.
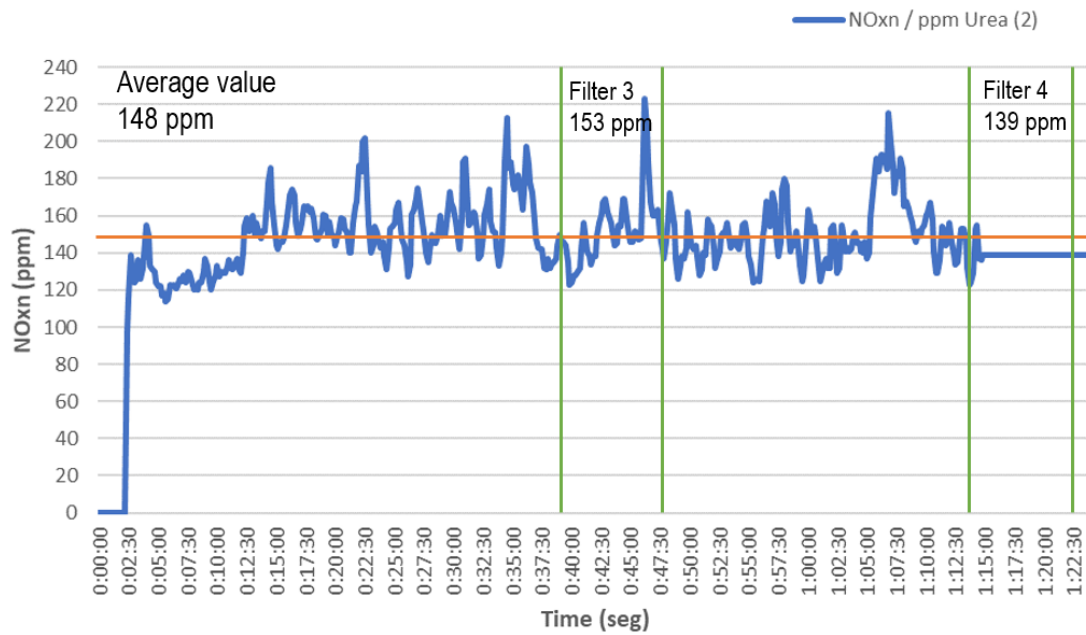
Figure 47. NOx emissions pellets Urea. Second combustion.

The last part of the measurement which corresponds to filter 4 has not been implemented correctly as the second combustion of $(NH_4)_2SO_4$. This is probably due to a connection failure of the sensor *Wöhler* to the computer. Nevertheless, in this second combustion not only the emissions were not reduced, but it also increases in 85% with respect to the second combustion of pellets without additive.

4.3.2 Summary results NOx emissions

Finally, after the measurements performed, Fe_2O_3 has been the only additive that has reduced the NOx emissions during the combustion. Nonetheless, as mentioned previously, it is important to take into account the results obtained after the analysis previous to the combustion.

$MnCO_3$ and TiO_2 have decreased the NOx formation in a small amount during the first combustion of pellets. However, it was not the same during the second combustion. In this case, these additives have increase the NOx emissions, in addition to contribute to the CO formation.

$(NH_4)_2SO_4$ and urea have not worked as efficient as hoped. Both have increased noticeably the formation of NOx and as the other additives, these have produced more CO emissions in comparison to the combustion of pellets without additives.

Table 13 shows a summary of the results obtained after the combustion and its contribution to the reduction or increment to the NOx formation.

Table 13. Summary results of NOx emissions.

		Average value (ppm)	Filter 1-3 (ppm)	Filter 2-4 (ppm)	Reduction/Increment %
Without Additive	Sample 1	87	84	85	-
	Sample 2	80	80	81	-
Fe_2O_3	Sample 1	71	71	73	18,4
	Sample 2	72	75	72	10,0
$MnCO_3$	Sample 1	84	85	82	3,4
	Sample 2	83	84	87	-3,8
$(NH_4)_2SO_4$	Sample 1	111	113	109	-27,6
	Sample 2	116	117	116	-45,0
TiO_2	Sample 1	86	83	86	1,1
	Sample 2	83	85	84	-3,8
Urea	Sample 1	114	145	159	-31,0
	Sample 2	148	153	139	-85,0

4.3.3 Particulate matter

This section shows the quantity of particulates emitted for each type of pellets during the combustion. The equations presented in section 3.5.2 for particulate matter have been applied to the different pellets. The results obtained are exposed in the following points.

4.3.3.1 Pellets without additive

Filters with a diameter of 45 mm are used for the capture of particulate material. An example of these filters are presented in figure 48 before the analysis.

Figure 48. Filters 45 mm without particles.

Figure 49 shows the filters obtained during the combustion of pellets without additive. Two combustions were performed for each type of pellet. The first two filters correspond to the first combustion and the second filters to the second combustion.

In order to maintain an overview of the particles emitted, the first step was to weigh the filters before and after the combustion. Table 14 shows the values obtained, the pump run time and the difference in mass of the particles.
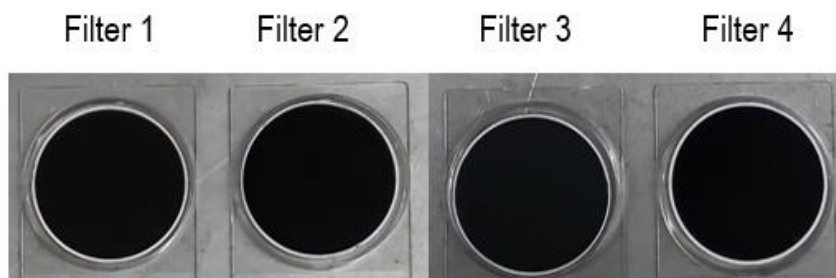
Figure 49. Particulate matter filter without additive.

Table 14. Weight of the filters without additive.

	Before (g)	After (g)	Pump run time (min)	Difference (g)
Filter 1	0,1545	0,1638	8,51	0,0093
Filter 2	0,1533	0,1622	8,32	0,0089
Filter 3	0,1518	0,1597	7,40	0,0079
Filter 4	0,1537	0,1616	7,42	0,0079

The pump time from the first two filters was too high in comparison with the second filters. This is partly due to the inexperience with the regulation of the pump. The optimal time is 7 minutes and 30 seconds.

Apart from the weight of the filters, it is necessary to know the mass of the particles contained in the probe after its cleaning and the water content in silica gel for the calculation of the equations. In table 15 these values are presented.

Table 15. Particles contained in the probe and water content in silica gel pellets without additive.

NUMBER OF COMBUSTION		Particles contained in the probe (g)	Water content in silica gel (g)
1	Before (g)	35,9352	1176,56
	After (g)	35,9360	1188,92
	Difference (g)	0,0008	12,36
2	Before (g)	19,5598	1181,90
	After (g)	19,5606	1192,02
	Difference (g)	0,0008	10,12

The results from the particulate matter measurement are summarized in table 16.

Table 16. Particulate matter without additive analysis.

	Filter 2	Filter 3	Filter 4	Filter 5
m_{PM} (mg)	9,60	9,18	8,32	8,32
p_{ap} (Pa)	101900	101900	101200	101200
T_{GM} (K)	297,42	297,74	299,72	299,83
V_{GM} (m3)	0,125	0,125	0,125	0,125
V_N (m3)	0,12	0,12	0,11	0,11
$m_{PM,N}$ (mg)	83,17	79,61	73,21	73,23
c_{O2} (%)	14,00	14,15	13,29	13,22
$m_{PM,N,13\%}$ (mg)	95,05	92,98	75,95	75,31
c_{H2O} (%)	0,0625	0,0625	0,0525	0,0525
$m_{PM,N,13\%,dry}$ (mg)	95,11	93,04	75,99	75,35

The range of values oscillate between 75,35 mg and 95,11 mg on dry basis with an average value of 84,26 ± 10,77 mg. These values will serve as baseline data for pellets with additives to observe if the additives used have an impact on the particulate matter formation apart from the NOx reduction.

4.3.3.2 Pellets with Fe_2O_3

Figure 50 shows the filters obtained with Fe_2O_3 during both combustions. On the other hand, in table 17 are presented the values of the weights of the filters before and after the process.

Figure 50. Particulate matter filter with Fe_2O_3.

Table 17. Weight of the filters with Fe_2O_3.

	Before (g)	After (g)	Pump run time (min)	Difference (g)
Filter 1	0,1522	0,1608	7,25	0,0086
Filter 2	0,1514	0,1590	7,39	0,0076
Filter 3	0,1538	0,1632	7,29	0,0094
Filter 4	0,1547	0,1645	7,38	0,0098

In this case, the difference in mass are higher than pellets without additive. It is difficult to know the size of the particles by only weighting the filters. The increase of the mass may be due to the existence of big particles (PM10) or a larger amount of smaller particles with this additive.

Moreover, there is not a relation between the pump run time and the difference in mass. For example, there is a difference between filter 2 and filter 3 that, despite the high time of filter 2, it has the smallest mass in comparison to the other filters. A possible explanation for this is the combinations of big and small particles captured in the filters.

On the other hand, table 18 shows the particles contained in the probe and the water content in silica gel.

Table 18. Particles contained in the probe and water content in silica gel, Fe_2O_3.

NUMBER OF COMBUSTION		Particles contained in the probe (g)	Water content in silica gel (g)
1	Before (g)	36,3194	1281,95
	After (g)	36,3197	1293,89
	Difference (g)	0,0003	11,94
2	Before (g)	36,9364	1274,05
	After (g)	36,9375	1283,85
	Difference (g)	0,0011	9,80

The results from the particulate matter measurement are summarized in table 19.

Table 19. Particulate matter Fe_2O_3 analysis.

	Filter 1	Filter 2	Filter 3	Filter 4
m_{PM} (mg)	8,75	7,75	9,95	10,35
p_{ap} (Pa)	101400	101400	101600	101600
T_{GM} (K)	298,10	298,62	298,66	299,12
V_{GM} (m3)	0,125	0,125	0,125	0,125
V_N (m3)	0,11	0,11	0,11	0,11
$m_{PM,N}$ (mg)	76,38	67,77	86,85	90,48
c_{O2} (%)	13,06	13,23	14,85	13,85
$m_{PM,N,13\%}$ (mg)	76,96	69,77	112,97	101,23
c_{H2O} (%)	0,0609	0,0610	0,0505	0,0506
$m_{PM,N,13\%,dry}$ (mg)	77,00	69,82	113,03	101,28

The mass of the particulate matter on dry basis are quite similar to the results from pellets without additive with an average value of 88,57 ± 20,28. As stated in section 4.2.5, the elements contained in solid biomass can be divided into particulate matter and ash-forming elements [39]. Iron is a constituent of ash-forming so does not increase the particulate matter formation.

4.3.3.3 Pellets with MnCO₃

Another additive used for the potential reduction of NOx emissions is $MnCO_3$. Figure 51 shows the filters obtained during the combustions and in table 20 are presented the values of the weights of the filters before and after the process.

Figure 51. Particulate matter filter with $MnCO_3$.

Table 20. Weight of the filter with MnCO₃.

	Before (g)	After (g)	Pump run time (min)	Difference (g)
Filter 1	0,15554	0,1643	7,59	0,0088
Filter 2	0,1554	0,1635	7,29	0,0081
Filter 3	0,1573	0,1625	7,27	0,0052
Filter 4	0,1546	0,1665	7,31	0,0119

The results are within a wider range of values. The difference in mass is between 0,0052 g and 0,0119 g. As explained in previous sections, it may be due to the size of the particulate matter which it is not possible to know with the weight of the filters.

On the other side, the results from particles contained in the probe and the water content are quite similar to pellets without additive and Fe_2O_3. In table 21 are exposed these values.

Table 21. Particles contained in the probe and water content in silica gel pellets with $MnCO_3$.

NUMBER OF COMBUSTION		Particles contained in the probe (g)	Water content in silica gel (g)
1	Before (g)	36,348	1289,94
	After (g)	36,3486	1300,33
	Difference (g)	0,0006	10,39
2	Before (g)	36,1362	1324,41
	After (g)	36,1373	1335,16
	Difference (g)	0,0011	10,75

The results from the particulate matter measurement are summarized in table 22.

Table 22. Particulate matter $MnCO_3$ analysis.

	Filter 1	Filter 2	Filter 3	Filter 4
m_{PM} (mg)	9,06	8,40	5,75	12,45
p_{ap} (Pa)	101400	101400	101400	101400
T_{GM} (K)	295,14	295,37	294,72	295,10
V_{GM} (m3)	0,125	0,125	0,125	0,125
V_N (m3)	0,12	0,12	0,12	0,12
$m_{PM,N}$ (mg)	78,30	72,65	49,62	107,58
c_{O2} (%)	14,02	13,00	13,62	13,93
$m_{PM,N,13\%}$ (mg)	89,74	72,63	53,82	121,77
c_{H2O} (%)	0,0529	0,0530	0,0546	0,0546
$m_{PM,N,13\%,dry}$ (mg)	89,79	72,66	53,85	121,84

The average value of the particulate matter on dry basis is 80,89 ± 28,88 mg. Manganese is also a constituent of ash-forming so does not increase the particulate matter formation. In comparison with previous pellets, it has a lower influence in particulate matter formation.

Manganese together with iron are present as minor elements contained naturally in wood. They are present in small concentrations as inorganic compounds or dissolved ions in biomass [39].

4.3.3.4 Pellets with $(NH_4)_2SO_4$

The third additive used is $(NH_4)_2SO_4$. Figure 52 shows the filters obtained during the combustions and in table 23 are presented the values of the weights of the filters before and after the process.

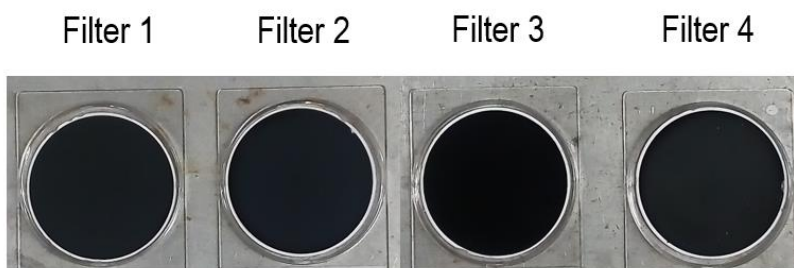**Figure 52.** Particulate matter filter with $(NH_4)2SO_4$.

Table 23. Weight of the filter with $(NH_4)2SO_4$.

	Before (g)	After (g)	Pump run time (min)	Difference (g)
Filter 1	0,1544	0,1654	7,50	0,0110
Filter 2	0,1541	0,1665	7,49	0,0124
Filter 3	0,1543	0,1640	7,50	0,0097
Filter 4	0,1543	0,1640	7,44	0,0097

In this case, the difference in mass is higher than in the other situations. The range of values are between 0,0097 g and 0,0124 g. However, there are less particles contained in the probe than with the other additives. The values of water content in the exhaust gases are similar to the other pellets.

Table 24. Particles contained in the probe and water content in silica gel pellets with $(NH_4)2SO_4$.

NUMBER OF COMBUSTION		Particles contained in the probe (g)	Water content in silica gel (g)
1	Before (g)	36,0464	1220,83
	After (g)	36,0467	1231,47
	Difference (g)	0,0003	10,64
2	Before (g)	113,0156	1260,63
	After (g)	113,0157	1270,28
	Difference (g)	0,00004	9,65

The results from the particulate matter measurement are summarized in table 25.

Table 25. Particulate matter $(NH_4)_2SO_4$ analysis.

	Filter 1	**Filter 2**	**Filter 3**	**Filter 4**
m_{PM} (mg)	11,00	12,70	9,77	9,75
p_{ap} (Pa)	101500	101200	101500	101500
T_{GM} (K)	297,27	300,62	297,96	298,66
V_{GM} (m3)	0,125	0,125	0,125	0,125
V_N (m3)	0,11	0,11	0,11	0,11
$m_{PM,N}$ (mg)	95,66	112,02	85,16	85,18
c_{O2} (%)	13,38	12,29	13,40	12,22
$m_{PM,N,13\%}$ (mg)	100,47	102,92	89,58	77,62
c_{H2O} (%)	0,0544	0,0584	0,0497	0,0498
$m_{PM,N,13\%,dry}$ (mg)	100,52	102,98	89,63	77,66

The average value of the particulate matter on dry basis is 92,13 ± 11,59 mg. The use of this additive contains sulphur which apart from being an ash former, is one of the particulate matter forming element together with Na, K, P and Cl [39].

On the other hand, sulphur is contained naturally in wood such as minor element. However, in this case, it increases the formation of particulate matter.

4.3.3.5 Pellets with TiO_2

The fourth additive used is TiO_2. Figure 53 shows the filters obtained during the combustions and in table 26 are presented the values of the weights of the filters before and after the process.
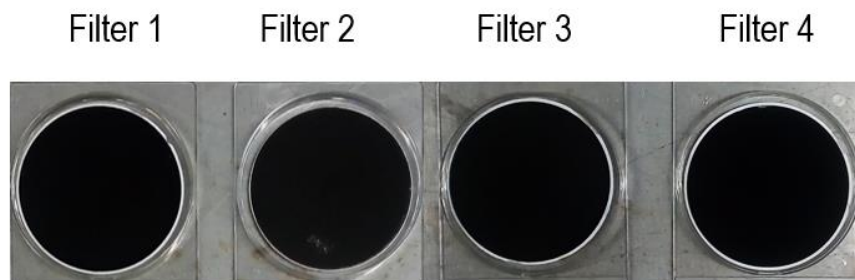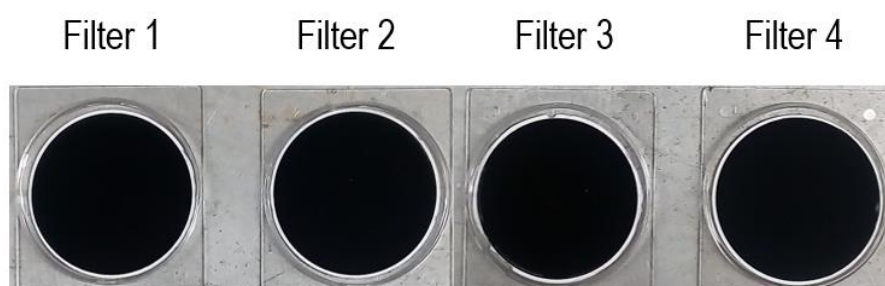

Figure 53. Particulate matte filter with TiO_2.

Table 26. Weight of the filter TiO_2.

	Before (g)	**After (g)**	**Pump run time (min)**	**Difference (g)**
Filter 1	0,1533	0,1606	7,44	0,0073
Filter 2	0,1538	0,1599	7,33	0,0061
Filter 3	0,1537	0,1571	7,38	0,0034
Filter 4	0,1531	0,1589	7,35	0,0058

The mass contained in the filters are lower than in the other cases. The range of values are between 0,0034 g and 0,0073 g. Moreover, the particles contained in the probe are practically negligible. The water content in the exhaust gases is similar to the other additives.

Table 27. Particles contained in the probe and water content in silica gel pellets with TiO_2.

NUMBER OF COMBUSTION		Particles contained in the probe (g)	Water content in silica gel (g)
1	Before (g)	36,8575	1246,66
	After (g)	36,8579	1257,84
	Difference (g)	0,0004	11,18
2	Before (g)	36,313	1228,94
	After (g)	36,313	1238,65
	Difference (g)	0	9,71

The results from the particulate matter measurement are summarized in table 28.

Table 28. Particulate matter TiO_2 analysis.

	Filter 1	Filter 2	Filter 3	Filter 4
m_{PM} (mg)	7,50	6,30	3,40	5,80
p_{ap} (Pa)	101800	101800	101800	101800
T_{GM} (K)	295,89	297,33	297,71	297,85
V_{GM} (m3)	0,125	0,125	0,125	0,125
V_N (m3)	0,12	0,12	0,12	0,12
$m_{PM,N}$ (mg)	64,73	54,64	29,52	50,39
c_{O2} (%)	13,30	13,67	13,31	13,23
$m_{PM,N,13\%}$ (mg)	67,22	59,61	30,72	51,86
c_{H2O} (%)	0,0566	0,0569	0,0498	0,0499
$m_{PM,N,13\%,dry}$ (mg)	67,26	59,65	30,74	51,88

The average value of the particulate matter on dry basis is 50,29 ± 15,74 mg. This additive reduces the formation of particulate matter in relation with the values obtained from pellets without additive. The element titanium as well as iron and manganese are part of the ash forming elements. These inorganic compounds are chemically transformed to other compounds and are deposited in the ash [39].

4.3.3.6 Pellets with Urea

The fifth additive used is urea. Figure 54 shows the filters obtained during the combustions and in table 29 are presented the values of the weights of the filters before and after the process.
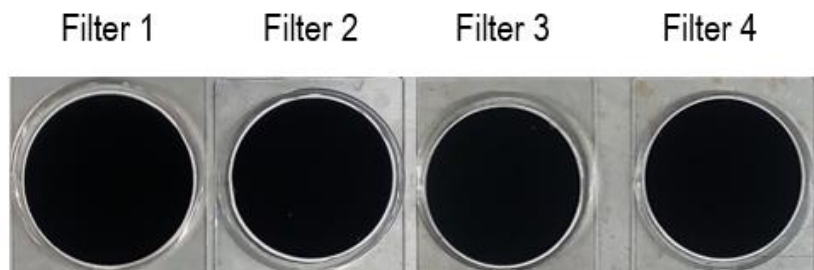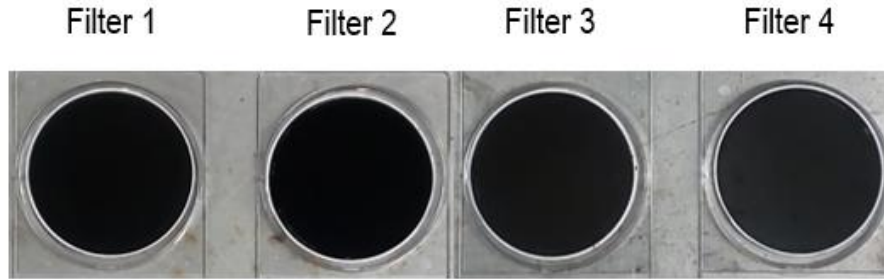

Figure 54. Particulate matter with Urea.

Table 29. Weight of the filter Urea.

	Before (g)	After (g)	Pump run time (min)	Difference (g)
Filter 1	0,15398	0,1652	6,50	0,01122
Filter 2	0,15389	0,1644	7,34	0,01051
Filter 3	0,15447	0,1626	7,44	0,00813
Filter 4	0,1525	0,1611	7,30	0,00860

In this case, the difference in mass is the highest. The range of values are between 0,00813 g and 0,01122 g. On the other side, the results from particles contained in the probe and the water content are quite similar to the rest of pellets.

Table 30. Particles contained in the probe and water content in silica gel pellets with Urea.

NUMBER OF COMBUSTION		Particles contained in the probe (g)	Water content in silica gel (g)
1	Before (g)	16,76395	1305,86
	After (g)	16,7653	1315,74
	Difference (g)	0,00135	9,88
2	Before (g)	36,4072	1238,44
	After (g)	36,4157	1247,93
	Difference (g)	0,0085	9,49

The results from the particulate matter measurement are summarized in table 31.

Table 31. Particulate matter Urea analysis.

	Filter 1	**Filter 2**	**Filter 3**	**Filter 4**
m_{PM} (mg)	11,89	11,18	12,38	12,85
p_{ap} (Pa)	101300	101300	101400	101400
T_{GM} (K)	296,24	295,41	297,38	297,40
V_{GM} (m3)	0,125	0,125	0,125	0,125
V_N (m3)	0,12	0,12	0,11	0,11
$m_{PM,N}$ (mg)	103,29	96,85	107,80	111,91
c_{O2} (%)	13,84	14,46	14,04	12,29
$m_{PM,N,13\%}$ (mg)	115,42	118,47	123,91	102,77
c_{H2O} (%)	0,0507	0,0505	0,0489	0,0489
$m_{PM,N,13\%,dry}$ (mg)	115,48	118,53	123,97	102,82

The average value of the particulate matter on dry basis is 114,93 ± 8,97 mg. This additive increases the formation of particulate matter in relation with the values obtained from pellets without additive.

Urea is a crystalline and colourless chemical compound whose formula is $CO(NH_2)_2$. Its components are the mayor elements contained in biomass [39]. The increase of particulate matter may be due to an incomplete combustion so these elements are present as particulate matter in conjunction with other inorganic elements and not in the ashes.

4.3.4 Summary results particulate matter

The following figure shows an overview of the analysis results. There are two main primary sources for particulate matter formation in biomass combustion [43]:

- Incomplete combustion, which originates soot and unburned char.
- The inorganic matter that constitutes the ash content of the biomass.

As mentioned in previous sections, the use of urea increases the particulate matter formation. In studies performed in a small-scale pellet boiler was shown that total particulate matter emissions may be dominated by elemental carbon due to disturbances in the fuel bed [43].

On the other hand, particulate emissions are significantly affected by the type of biomass fuel. It was observed that biomass fuels with higher Si content in the ash produced the lowest total particulate matter emissions [43]. In this case, the lowest concentration of particulate matter comes from the use of TiO_2 as an additive.
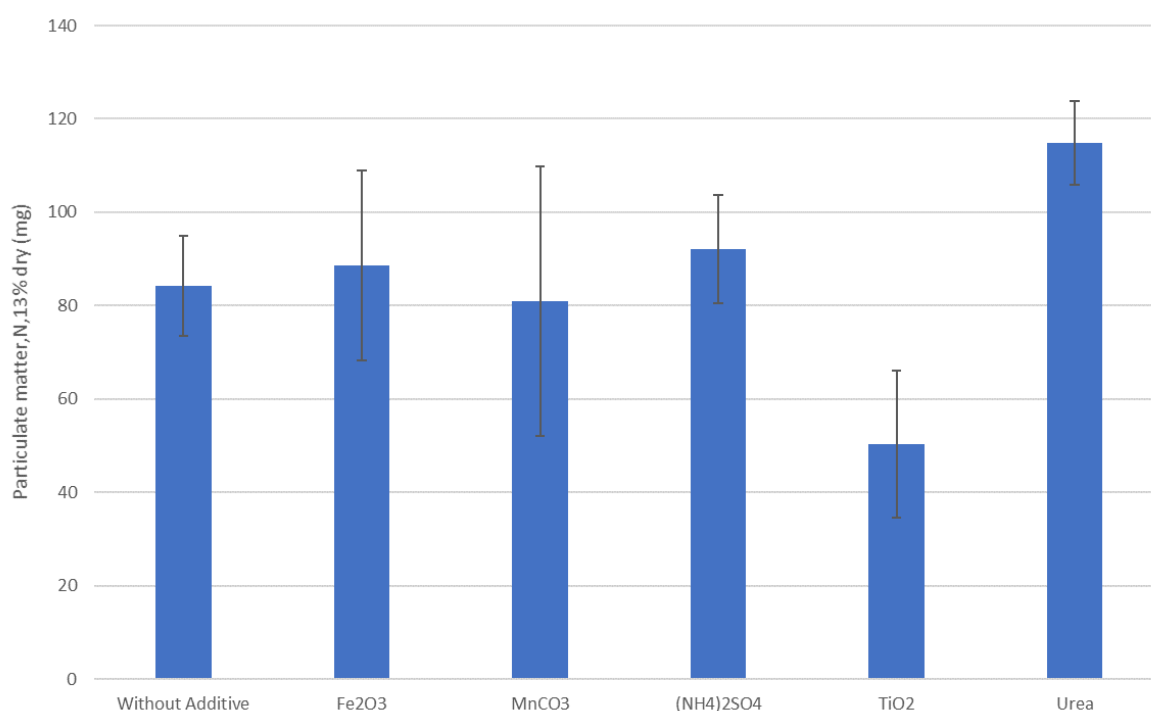
Figure 55. Summary results of particulate matter.

Table 32 presents the summary results of particulate matter on dry basis.

Table 32. Summary results of particulate matter.

	Without Additive	Fe_2O_3	$MnCO_3$	$(NH_4)2SO_4$	TiO_2	Urea
$m_{PM,N,13\%,dry}$ (mg)	84,26 ± 10,77	80,89 ± 20,28	80,89 ± 28,88	92,13 ± 11,59	50,29 ± 15,74	114,93 ± 8,97

4.4 X-ray diffraction results (XRD)

In the following the x-ray diffraction results are presented for the various pellets.

4.4.1 Pellets without additive

After the combustion, the ashes of each sample were analyse by x-ray diffraction to determine crystalline structures. As explained in section 3.5.3, during the analysis, different crystalline phases were stored in a database, allowing the ashes to obtain its composition.

The crystalline structures of pellets without additive are mainly CaO, MgO and $CaCO_3$. These species can be seen on the diagrams obtained after the analysis in figures 57 and 58 in Annex 8. This structures form part of the general composition of biomass which is shown in figure 56.
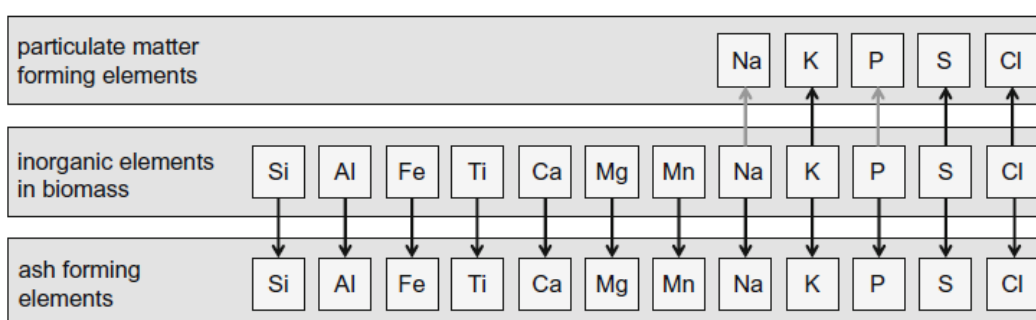
Figure 56. General composition of biomass without additive.

However, there are other structures in both combustions to a lesser extend which can be seen on table 36 (Annex 8). There are traces of chloride, phosphate and alkali metals such as potassium and sodium which can cause problems of slag because of the low melting point of the biomass ash [50]. Ash is a serious concern in biomass combustion, for it causes slagging, bed agglomeration, fouling, and corrosion in the combustion device, which degrade its performance and severely damage the firing equipment [51].

In order to maintain an overview of how the ash-forming elements are combined, below is shown how these species behave during the combustion without any type of additive [51]:

- Sulphur (S) occurs in two different forms: as sulphates in salts, or as reduced sulphur in various organic compounds. In this case there is not sulphur in the composition of the ashes.
- Chlorine (Cl) is present as chloride in soluble salts.
- Phosphorus (P) occurs as phosphate, either in inorganic salts or in organic compounds such as esters and pyrophosphates.
- Silicon (Si) is present in oxidized form as silica.
- Metals such as aluminium (Al), iron (Fe), calcium (Ca), magnesium (Mg), manganese (Mn), sodium (Na), and potassium (K) occur as positive metal ions. These can be present in minerals and precipitated salts and can occur in solution as free ions or complexes.

4.4.2 Pellets with Fe_2O_3

The crystalline structures of pellets with Fe_2O_3 are mainly Fe_3O_4, $Na_4CaSi_3O_9$ and $MgFe_2O_4$. These species can be seen on the diagrams obtained after the analysis in figures 59 and 60 in Annex 8. Table 36 from Annex 8 shows the rest of the crystalline structures obtained during the analysis.

Apart from these structures, predominant elements from other species have been calcium, silicon, sodium and phosphorus. In case of calcium is easily combined with the oxygen, forming elements such as CaO and $CaCO_3$ which are present in these ashes.

Silica as exposed in previous section, is found as silica in solid biomass. In combination with Ca can form Ca silicates [39] as $CaFeSi_2O_6$ present in these ashes as well.

On the other hand, sodium (Na) is present in the ash mostly compounds and it is one of the producers of particulate matter. These three ash-forming compounds have formed different salts and have been oxidized in the presence of CO, CO_2 and H_2O [39].

Phosphorus (P) can exist in various oxidation states, depending on the conditions within a specific combustion [39]. The different oxidized P compounds are extremely volatile [39], so in this case the content of P which was registered as $Na_2Ca_4(PO_4)_2SiO_4$ was small respect to the other elements. The rest of this compound probably has passed into the gas phase during combustion and has been released with the exhaust gas flow into the environment.

Finally, the results of the x-ray diffraction show that Fe has been captured by Mg and Ca and thanks to the oxygen affinity of these elements has been possible the reduction of the NOx emissions. This additive is the most promising one because it has been the only that has reduced the NOx emissions during the combustion.

It is important to know that this additive contains 5,02% of ash content. This means that it will be probably deposited in the lower part of the boiler, contributing to slag formation and the corrosion in incinerators, so it is important to know the amount of ash contained in a fuel.

4.4.3 Pellets with $MnCO_3$

The ash of this second additive contains mainly $CaMnO_3$/$CaO·MnO_2$, $Ca_3(AlO_3)_2$ and Mg_6MnO_8. These species can be seen on the diagrams obtained after the analysis in figures 61 and 62 in Annex 8. Table 36 from Annex 8 shows the rest of the crystalline structures obtained during the analysis.

Manganese (Mn) is one of the ash-forming element contained in biomass [39][51]. However, considering the reactions responsible for ash-related operational problems during combustion, Fe and Mn may be excluded [52]. The reason for this is that these metals often appear as individual oxides, with limited interaction with the other main ash-forming elements in biomass [52].

It is mainly combined with calcium, magnesium and oxygen obtaining two of the principal crystalline structures exposed previously. In case of calcium reacts easily in contact with air obtaining, a part from the principal compounds, $CaSO_4$, $Ca_2MgSi_2O_7$, $Ca_2MgSi_2O_6$ and $CaMn_2O_4$.

Magnesium (Mg) as alkali earth, is practically always present in residual ashes of woody fuels [52]. Moreover, this element is found with silicon, forming earth alkali silicates ($Ca_2MgSi_2O_7$, $Ca_2MgSi_2O_6$) which are relatively refractory and are supposed to contribute to decreased slagging tendencies [52]. Furthermore, in contact with oxygen is oxidized and reacted with manganese forming Mg_6MnO_8 [53].

There is another element which has appeared in a small portion and is aluminium (Al) forming $Ca_3(AlO_3)_2$. This element is also an ash-forming element in biomass and is a minor element contained naturally in wood [39].

In spite of the oxidation of the compounds that form the ashes, barely achieved a reduction of NOx emissions. Probably the oxygen content of the structures was lower in comparison to the structures from Fe_2O_3, so the nitrogen has been able to oxidize. Nonetheless, this additive contains 1,08 % of ash content being its contribution to slag formation and corrosion lower than the additive Fe_2O_3.

4.4.4   Pellets with $(NH_4)_2SO_4$

The ash contains mainly CaO, K_2SO_4 and $Mg_2P_2O_7$. These species can be seen on the diagrams obtained after the analysis in figures 63 and 64 in Annex 8. Table 36 from Annex 8 shows the rest of the crystalline structures obtained during the analysis.

This additive was the second most polluting together with the Urea. In its composition, nitrogen is found which had probably helped to increase the NOx emissions.

On the basis of the results obtained, the additive may have been separated in two parts. Possibly $(NH_4)_2$ has passed into the gas phase during the combustion and has released with the exhaust gas flow into the environment and SO_4 has combined with the elements from the biomass obtaining K_2SO_4 and Na_2CS_4.

Apart from the principal structures, there are other elements in the crystalline structures from the ashes such as calcium, magnesium, potassium, sodium, phosphorus and iron. Calcium, as aforementioned, is easily combined with the oxygen, forming elements such as CaO and $CaCO_3$ which are present in these ashes.

Magnesium, besides being an ash forming element, in contact with oxygen is oxidized forming mainly MgO. This structure is furthermore combined with phosphorus obtaining $Mg_2P_2O_7$. Since phosphorus is a volatile element [39], it will, in the case of biomass incineration, inevitably end up in the atmosphere. That is why, it is only found in one component.

Potassium (K) is the key element for the formation of particulate matter emission [39]. In most of the biomass potassium is expected to occur in the form of chloride, sulphates, carbonates and phosphate salts [54]. In this case, potassium has been combined with sulphur obtaining K_2SO_4. This salt has low melting point and can be carried out of the furnace by the gas stream together with the solid-particles generated during the combustion [39].

Another element which has appeared in a small portion is iron (Fe). This element is also an ash-forming element in biomass and is a minor element contained naturally in wood [39].

Finally, in spite of the increase of NOx emissions, this additive contains 0,82 % of ash content being its contribution to slag formation and corrosion lower than the other additives.

4.4.5 Pellets with TiO_2

The crystalline structures of ash from pellets with TiO_2 are mainly $Ca_3Al_2O_6$, $CaTiO_3$/$CaO \cdot TiO_2$ and $CaSO_4$. These species can be seen on the diagrams obtained after the analysis in figures 65 and 66 in Annex 8. Table 36 from Annex 8 shows the rest of the crystalline structures obtained during the analysis.

Titanium (Ti), besides being an ash forming element, is a refractory material in biomass [55]. This property refers to the capacity of certain materials to resist high temperatures without decomposing. A study suggested that titanium in rice straw is completely soluble in water, unlike titanium in any other biomass (or fossil) fuel [55]. Consequently, Ti resides within the bottom ash as $CaTiO_3$. This crystalline structure comes from the oxidation of the titanium in TiO_2, which together with the oxidation of calcium (CaO), it is produced $CaTiO_3$.

Apart from the principal structures, there are other elements in the crystalline structures from the ashes such as magnesium, aluminium and phosphorus. Magnesium, as commented on previously, in contact with oxygen is oxidized forming mainly MgO.

Another element which has appeared in a small portion and is aluminium (Al) forming $Ca_3(AlO_3)_2$ just as with the additive $MnCO_3$. This element is also an ash-forming element in biomass and is a minor element contained naturally in wood [39].

Finally, sulphur was registered as $CaSO_4$ which concentration was small respect to the other elements. As indicated in the above section, the rest of this compound probably has passed into the gas phase during combustion and has been released with the exhaust gas flow into the environment.

The behaviour of this additive was quite similar to $MnCO_3$. It barely achieved a reduction of NOx emissions. Probably the oxygen content of the structures was also lower in comparison to the structures from Fe_2O_3. Nonetheless, this additive contains 1,30 % of ash content, being its contribution to slag formation and corrosion lower than the additive Fe_2O_3.

4.4.6 Pellets with Urea

The last additive is urea whose chemical formula is $CO(NH_2)_2$ [49]. The crystalline ash structures are mainly CaO, Mn_3N_2 and MgO. These species can be seen on the diagrams obtained after the analysis in figures 67 and 68 in Annex 8. Table 36 from Annex 8 shows the rest of the crystalline structures obtained during the analysis.

This additive was the most polluting in comparison to the others. Its behaviour is quite similar to the additive $(NH_4)_2SO_4$. The results obtained show that the additive may have also been separated in two parts. Possibly CO has passed into the gas phase during the combustion and has released with the exhaust gases increasing the CO emissions and $(NH_2)_2$ has joined to the nitrogen contained in the air as well as in the biomass.

Calcium, magnesium and manganese are the principal elements in the crystalline structures. Nonetheless, there are other elements such as, potassium, silicon, sodium, phosphorus, iron, zinc and sulphur contained in the ashes.

As was mentioned in the preceding sections, potassium, sodium, phosphorus and sulphur are particulate matter forming elements as well as ash forming elements [39]. These elements have formed structures such as KO_2, $K_2Ca(CO_3)_2$, $K_2Mn_2(SO_4)_3$, $Na_2Fe_2Al(PO_4)_3$ and $NaMg(PO_4)$.

Silicon also appears in combination with calcium and zinc (Zn) forming $2Ca_2SiO_4$ and ZnO_3 respectively. In some cases, zinc is used as an additive to reduce the particulate matter during the combustion. When it is oxidized forming ZnO, its vapour pressure is very low, consequently, it is practically supersaturated [42]. The result of the behaviour of Zn is a condensation of higher vapour pressure species, like K2SO4 or KCl and an associated mass reduction of particulate matter [42].

On the other hand, iron has also appeared in a small portion in combination with sodium and phosphorus forming $Na_2Fe_2Al(PO_4)_3$. This element is also an ash-forming element in biomass and is a minor element contained naturally in wood [39].

Finally, in spite of the increase of NOx emissions, this additive contains 0,72 % being the additive the closest to the European norm and therefore, its contribution to slag formation and corrosion is lower than the other additives.

5 Timetable

Table 33 presents the progression of the master thesis during the weeks as well as the works steps followed from beginning to end.

Table 33. Progress of the master thesis.

Work steps	Week	April				May					June				July				August		
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Research		█	█	█	█																
Pellets Production					█	█	█	█	█	█	█	█									
Analysis of the pellets													█	█	█	█					
Combustion pellet stove														█	█	█	█				
XRD analysis																	█	█			
Redaction and correction										█	█	█	█	█	█	█	█	█	█	█	█

6   Conclusions

The objective of this master thesis was to produce pellets with different additives to reduce the NOx emissions and compare the results to find which additive or additives achieved this purpose. From the results of the analysis according to the norm EN 17225-2, pellets produced were in general within the European Standard for solid biofuel. However, the conflict lay in abrasion resistance and ash content.

Abrasion resistance as well as ash content reflect the quality of pellets and its possible contribution to slag formation and corrosion in incinerators. When observing the pellet properties, the addition of urea provided the best results respect to the other additives being the closest to the European norm. Unlike Fe_2O_3, which has the lowest value of abrasion resistance and the highest value in ash content. The addition of Fe_2O_3 weakened the pellets making them more porous reducing its mechanical strength and since Fe is an ash forming element of the biomass, contributed to the ash formation. The values of other additives were between Fe_2O_3 and urea.

Nevertheless, after the combustion the results of Fe_2O_3 and urea were invested being Fe_2O_3 the only additive which reduced the NOx emissions during the combustion. The reduction was 18,4% and 10% respect to the first and second combustion of pellets without additive. In contrast to urea, which increased the NOx emissions up to 85% during the second combustion. $MnCO_3$ and TiO_2 decreased the NOx formation in a small amount during the first combustion of pellets. However, it was not the same during the second combustion. In this case, these additives increased the NOx emissions. $(NH_4)_2SO_4$ did not work as efficient as hoped; increasing noticeably the formation of NOx together with urea. On the other hand, all the additives increased CO emissions in comparison to pellets without additives. Probably it was due to a lower concentration of oxygen during the combustion or the appearance of unburned fuel.

During the combustion, another measurement was performed: particulate matter emissions. There are two main primary sources for particulate matter formation in biomass combustion which are incomplete combustion and the inorganic matter that constitutes the ash content of the biomass. The use of urea increased the particulate matter formation with respect to pellets without additive, unlike TiO_2 which produced the lowest concentration of particulate matter. In case of the other additives did not have a big influence in particulate matter formation. Its values are quite similar to the values obtained in pellets without additive.

Finally, x-ray diffraction analysis showed the crystalline structures of the ashes after the combustion of the different pellets. The results show that the ash structures had principally elements such as calcium, potassium, magnesium and sodium being all of them ash forming elements. The two most common compounds are CaO ang MgO which have a high affinity with oxygen and form secondary compounds such as $CaCO_3$ or Mg_6MnO_8 among other structures.

Summarizing, the analysis showed that, despite the additive Fe_2O_3 had the worst characteristics, was the only which reduced the NOx emissions during the combustion. However, its physical properties must be improved in addition to control the formation of CO in the combustion.

7   Bibliography

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8 Annexes

8.1 Results of the analysis in tables

8.1.1 Physical properties of pellets

Table 34. Diameter measurement of pellets.

N° pellets	Without Additive (mm)	Fe_2O_3 (mm)	$MnCO_3$ (mm)	$(NH_4)2SO_4$ (mm)	TiO_2 (mm)	Urea (mm)
1	5,95	5,95	5,95	5,9	5,9	5,95
2	5,9	6	5,95	5,95	5,9	5,9
3	5,9	6	5,95	5,9	5,95	5,95
4	5,9	5,9	5,95	5,9	5,95	5,95
5	5,95	6	5,95	5,9	5,9	5,85
6	5,9	5,95	5,95	5,95	6	5,9
7	5,9	6	5,95	5,9	6	5,95
8	5,9	5,9	5,95	5,95	5,95	5,9
9	5,9	6	5,95	5,9	5,95	5,95
10	5,95	6	5,95	5,9	6	5,9
Mean value	5,91	5,97	5,95	5,91	5,95	5,92
Standard deviation	0,02	0,04	0,00	0,02	0,04	0,03

Table 35. Length measurement of pellets.

N° pellets	Without Additive (mm)	Fe$_2$O$_3$ (mm)	MnCO$_3$ (mm)	(NH$_4$)2SO$_4$ (mm)	TiO$_2$ (mm)	Urea (mm)
1	1,83	1,93	1,69	2,49	1,925	1,96
2	1,54	1,69	1,57	2,29	1,31	1,9
3	1,64	2,4	1,72	1,78	2,17	1,94
4	1,83	1,4	1,9	2,23	1,95	2
5	1,93	2,1	1,74	2,56	2,355	1,8
6	1,9	1,9	1,73	2,75	2,27	2
7	2	1,4	1,66	2,24	1,53	1,76
8	1,64	1,3	1,6	2,8	1,66	1,7
9	2,05	1,5	2,2	2	1,66	1,88
10	1,8	1,5	1,57	2,1	2,22	1,96
11	1,8	1,82	1,77	1,83	1,4	1,89
12	1,73	2,25	1,8	1,8	1,79	2
13	1,83	1,8	1,7	2,1	2,12	1,82
14	2,06	1,75	1,76	2,1	2	2
15	1,97	2	1,66	1,5	1,38	1,96
16	1,98	1,72	1,83	2	1,56	1,97
17	1,67	1,75	1,78	1,7	2,2	1,88
18	1,57	1,6	1,74	2,17	1,98	1,81
19	1,86	1,44	1,37	1,6	1,5	1,96
20	2,08	1,76	1,66	1,9	1,8	2,22
21	1,66	1,65	1,6	2,18	1,74	1,85
22	1,85	1,98	1,6	2,22	1,58	1,53
23	1,9	1,6	1,51	2	1,8	1,98
24	1,75	1,76	1,76	1,66	1,5	1,96
25	1,64	1,37	1,54	1,13	1,9	1,9
26	1,83	1,68	1,88	1,91	2,1	1,82
27	1,94	1,75	1,86	1,64	1,77	1,6
28	2,03	1,84	1,5	1,44	1,73	1,9
29	1,88	1,88	1,68	1,6	1,7	1,83
30	1,74	1,8	1,5	1,74	1,6	1,56
31	1,55	2	1,47	1,72	1,96	2,06
32	1,78	1,81	1,4	1,74	1,65	1,87
33	1,66	1,72	1,68	1,65	1,6	1,9
34	1,8	1,76	1,75	1,95	1,44	1,95
35	1,79	1,79	1,56	1,8	2,11	1,97
36	1,9	2,05	1,83	1,1	2,06	1,8
37	1,52	2,1	1,98	1,66	2	1,83
38	1,4	1,83	1,72	1,35	1,9	1,37
39	1,65	1,8	1,8	1,5	1,63	1,83
40	1,61	1,9	1,66	1,24	1,7	1,7
Mean value	17,82	17,62	16,86	18,38	17,87	18,59
Standard deviation	1,65	2,35	1,59	3,98	2,69	1,55

8.2   X-Ray diffraction results. XRD analysis

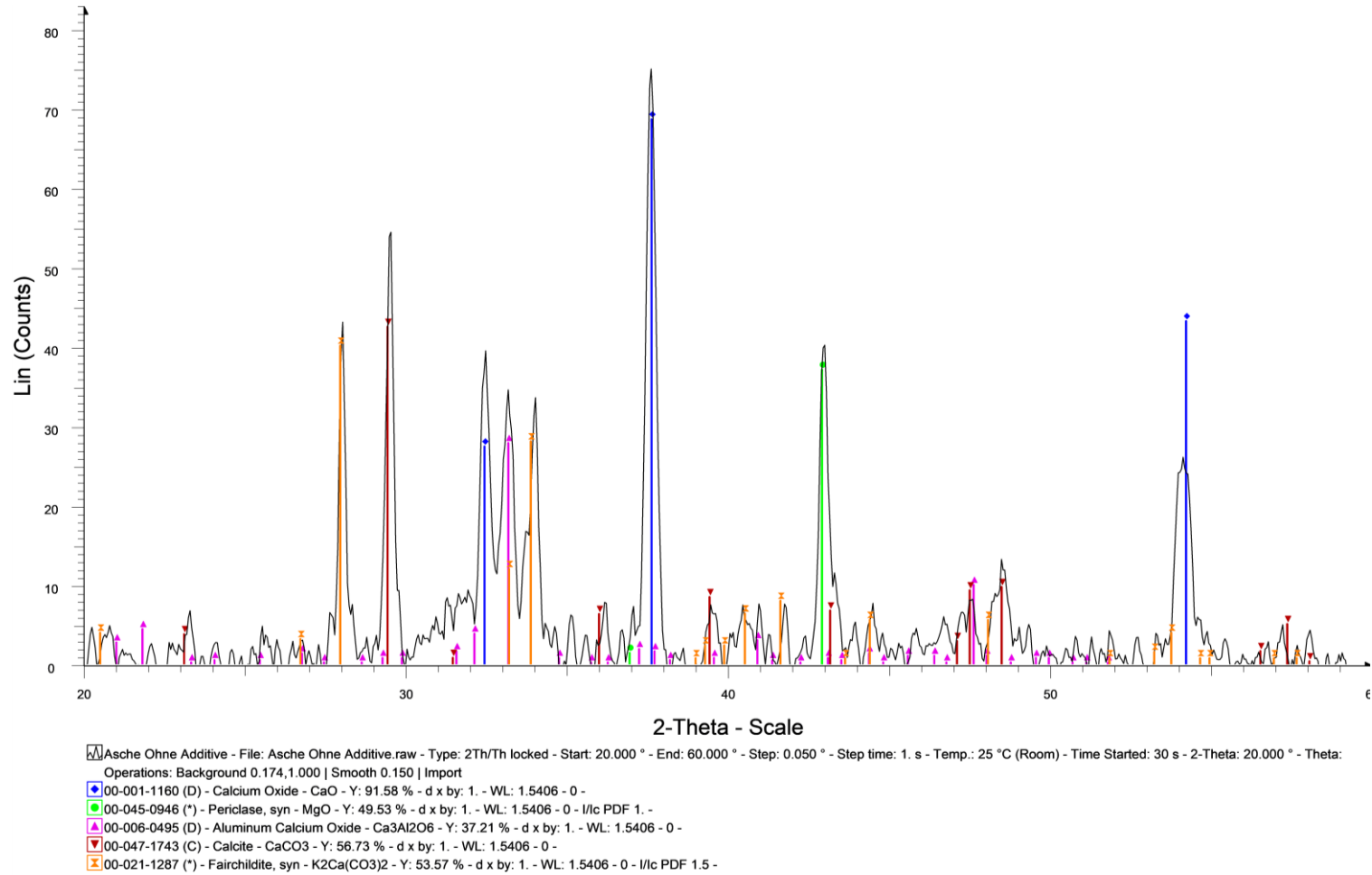### 8.2.1   Pellets without additive first combustion

Figure 57. XRD pellets without additive. First combustion.

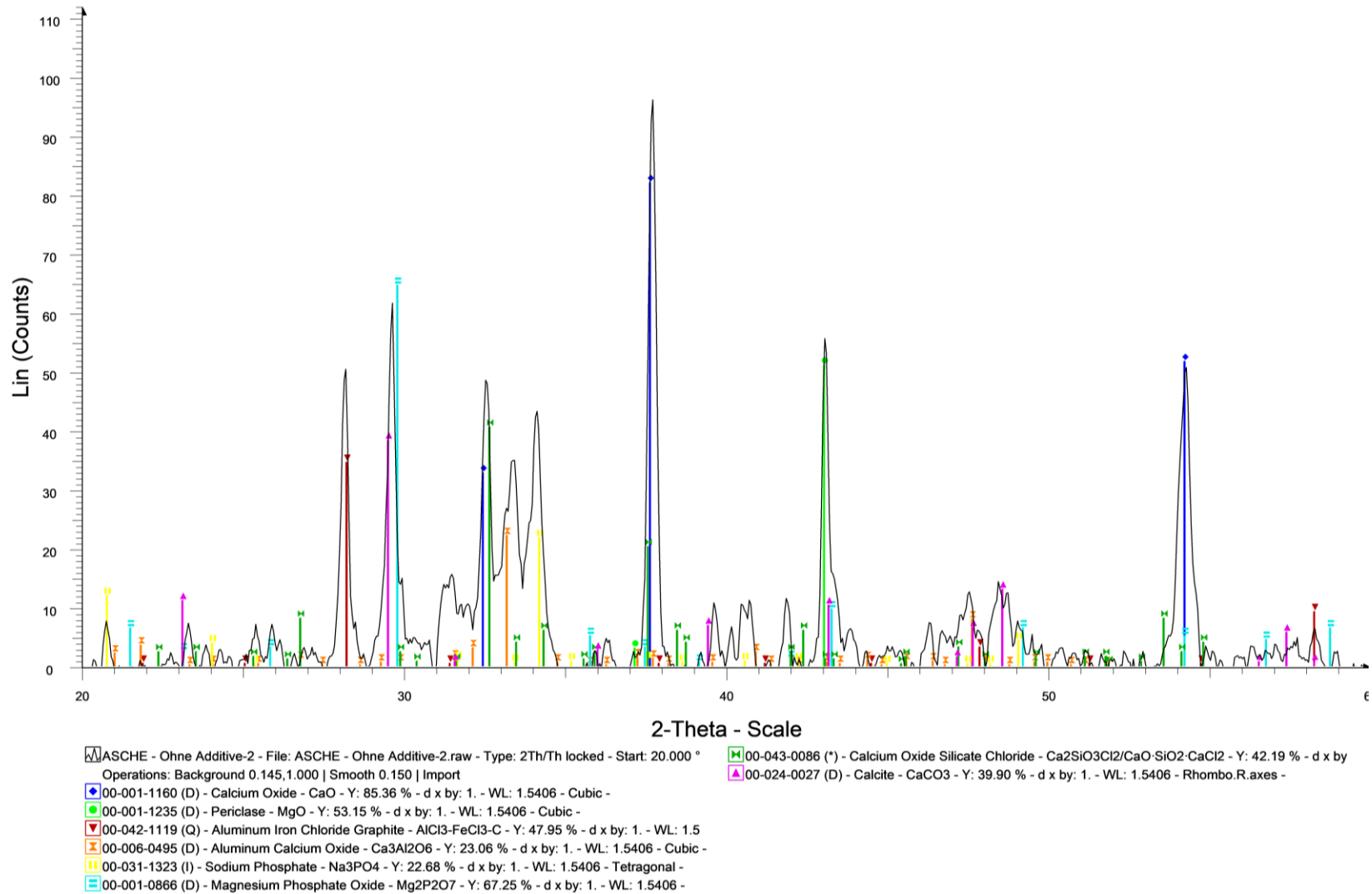## 8.2.2   Pellets without additive second combustion

Figure 58. XRD pellets without additive. Second combustion.
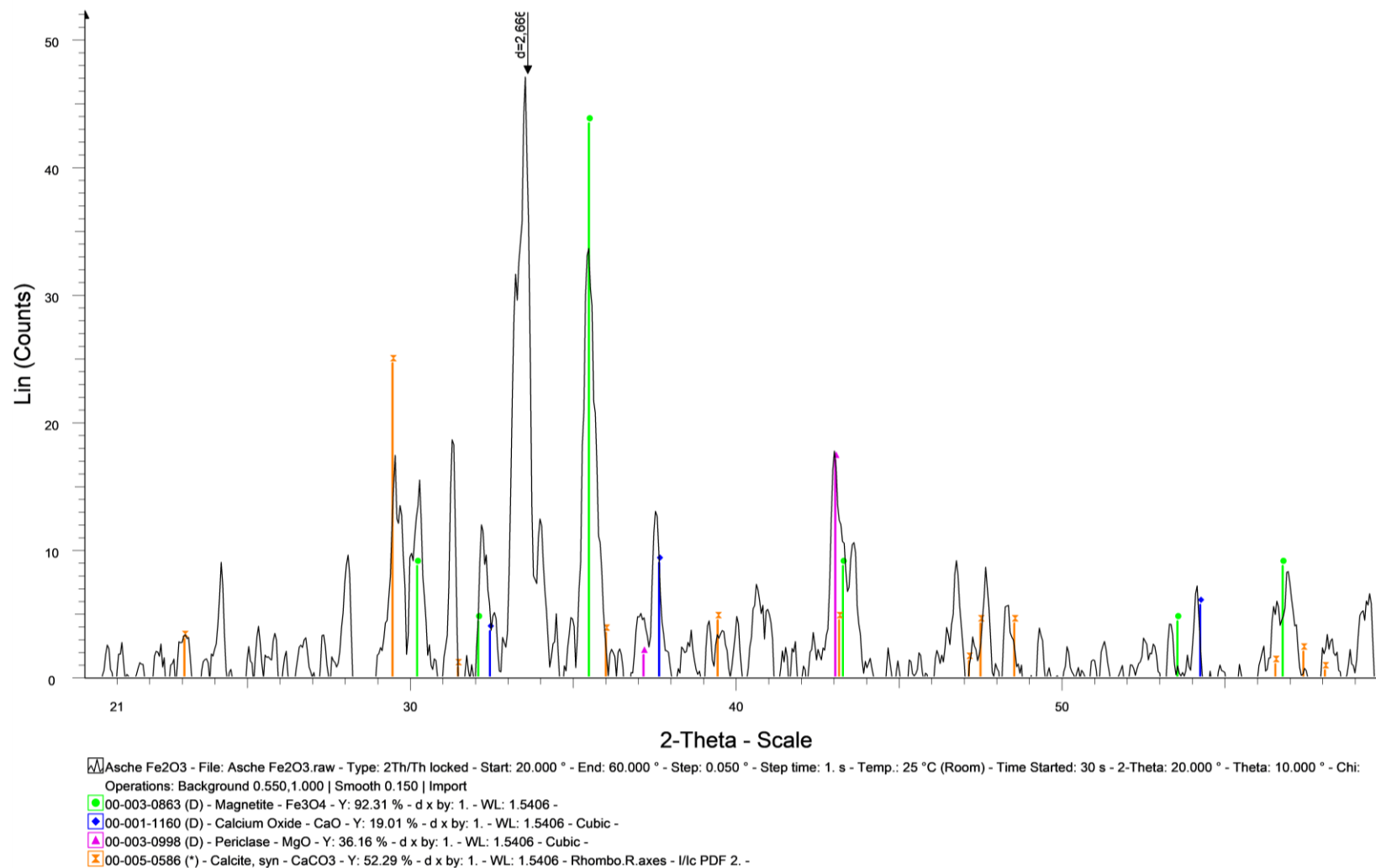
8.2.3 Pellets with Fe₂O₃ first combustion

Figure 59. XRD pellets with Fe₂O₃. First combustion.

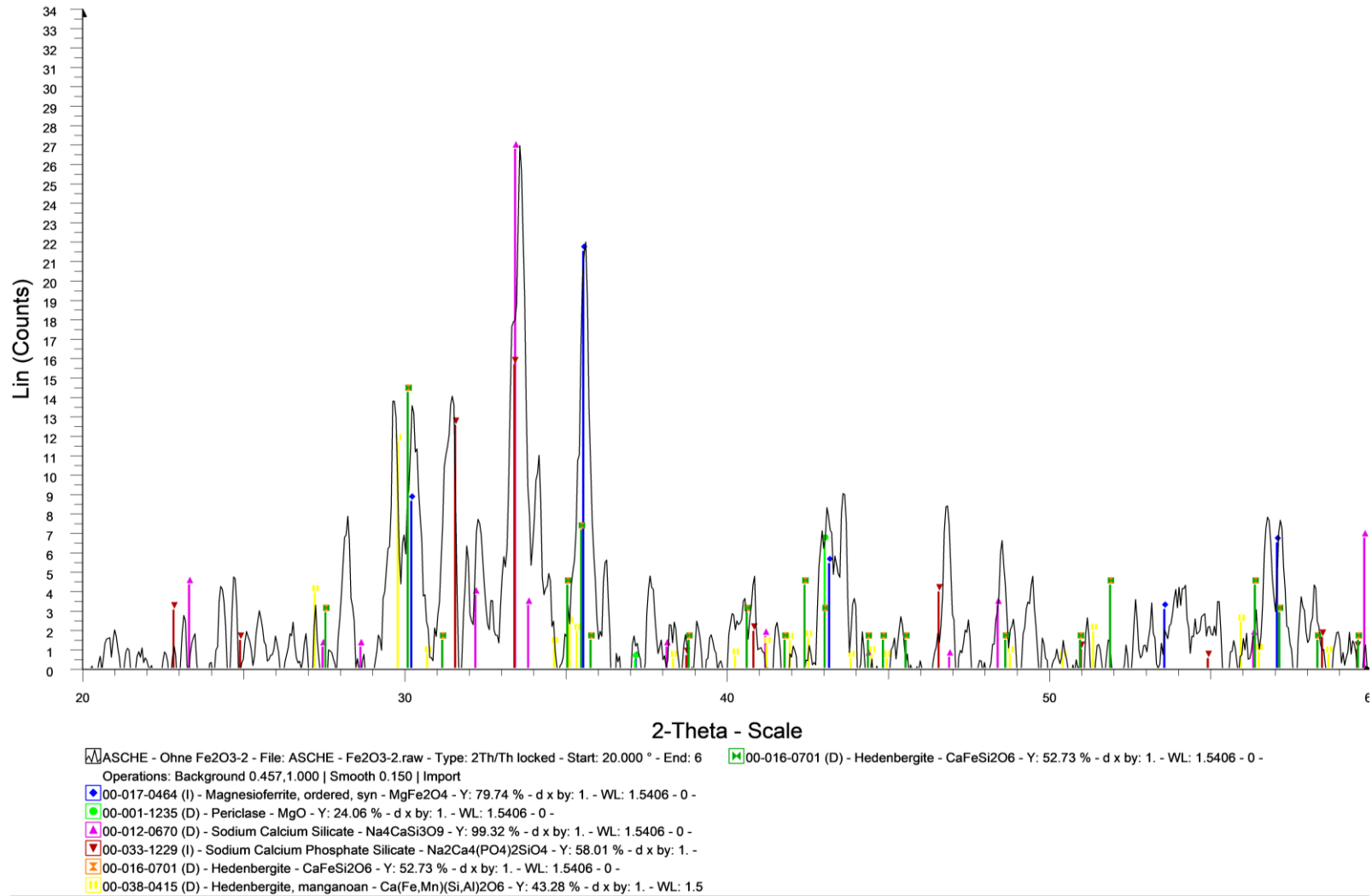### 8.2.4 Pellets with Fe₂O₃ second combustion

Figure 60. XRD pellets with Fe₂O₃. Second combustion.

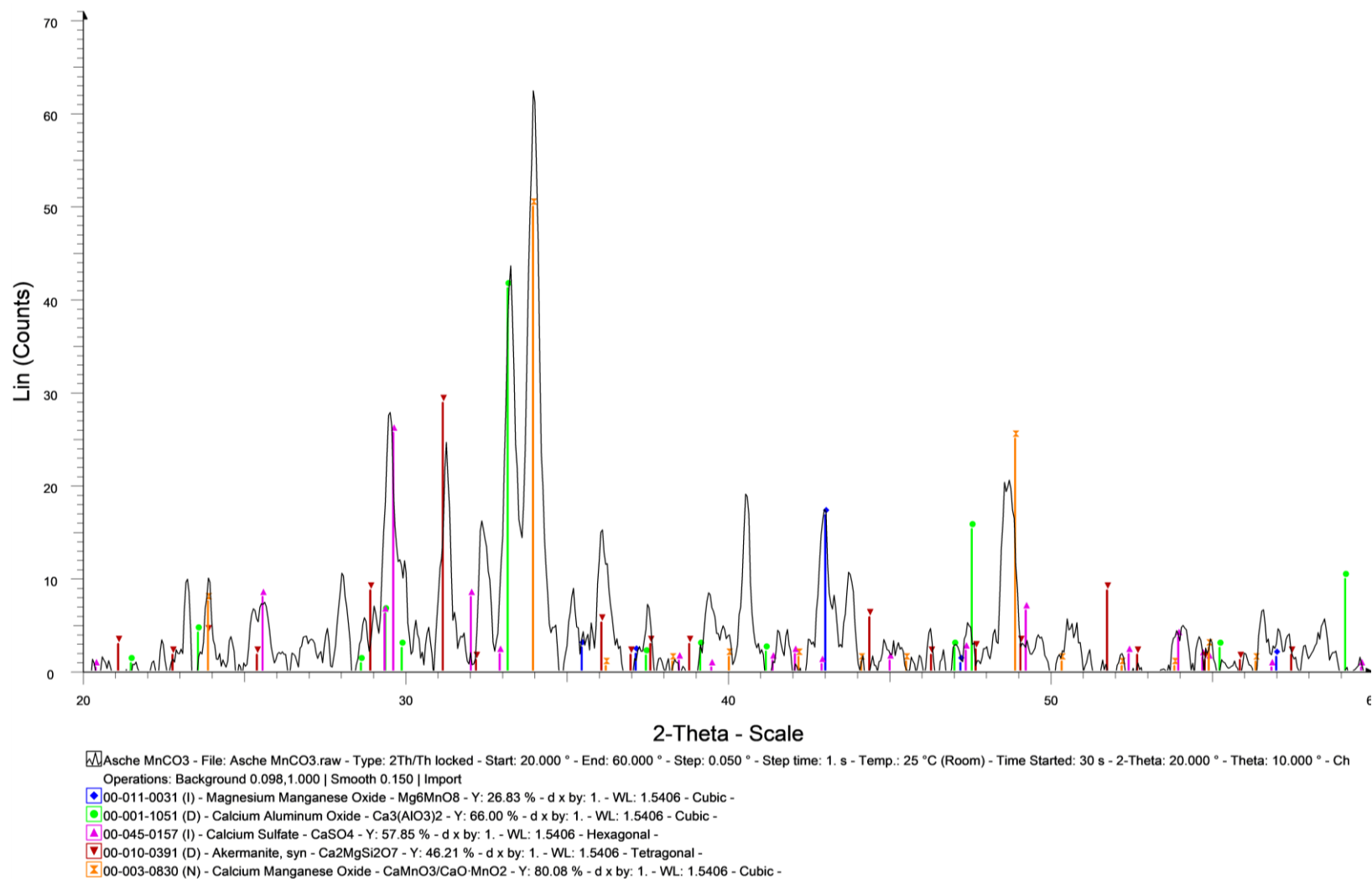## 8.2.5 Pellets with MnCO₃ first combustion

Figure 61. XRD pellets with MnCO₃. First combustion.
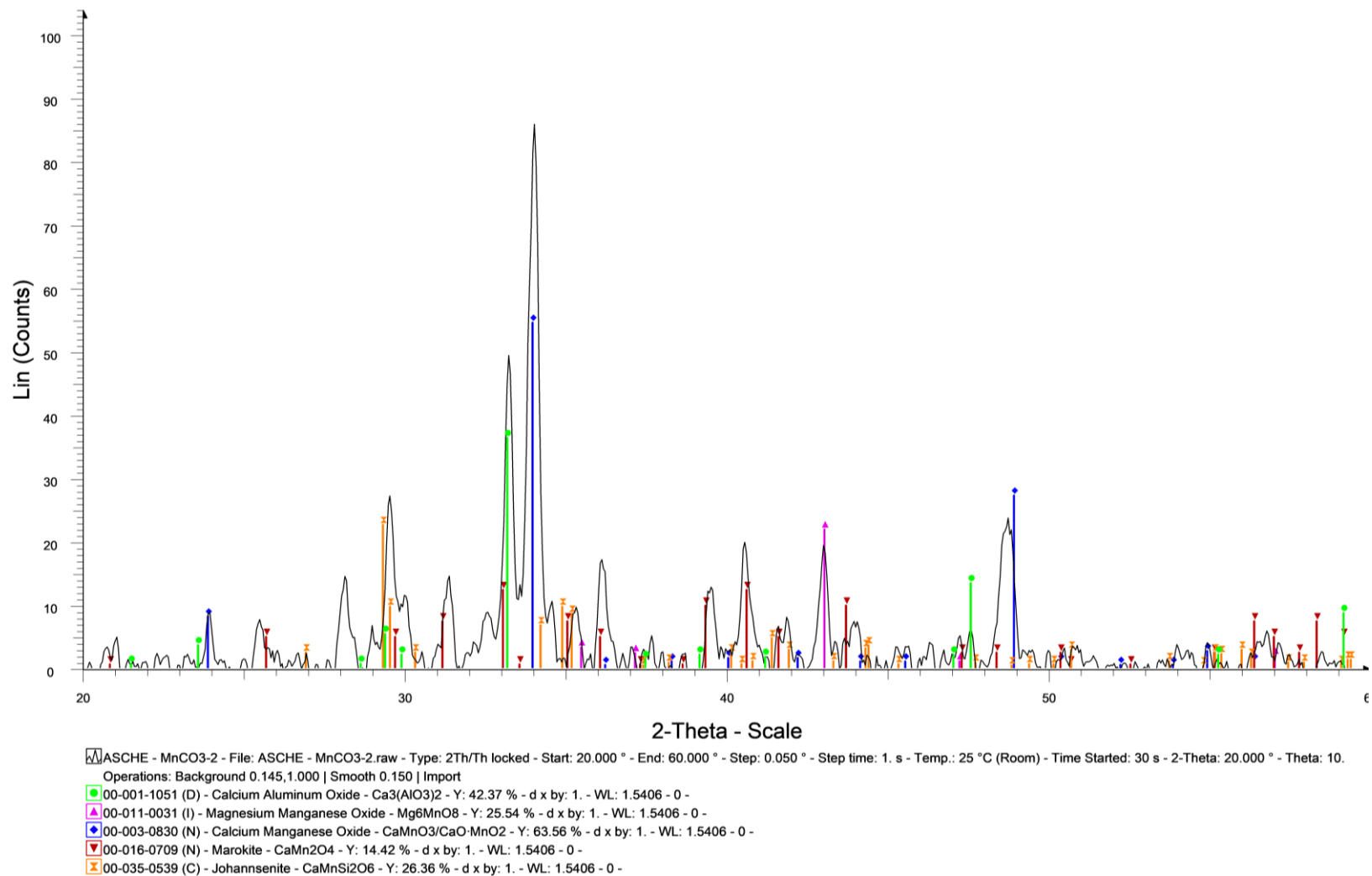
8.2.6 Pellets with MnCO₃ second combustion

Figure 62. XRD pellets with MnCO₃. Second combustion.
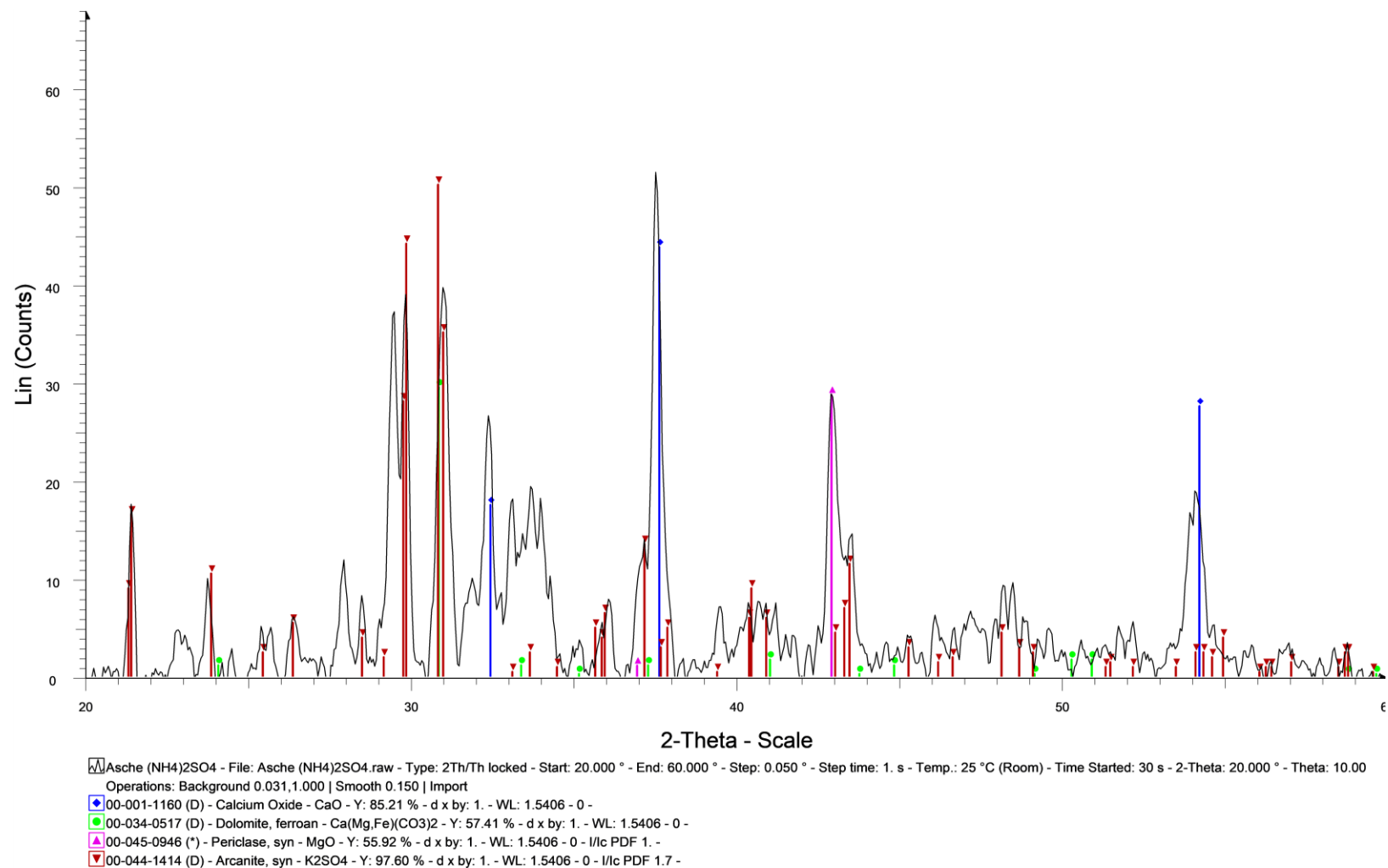
8.2.7 Pellets with (NH₄)₂SO₄ first combustion

Figure 63. XRD pellets with (NH₄)₂SO₄. First combustion.
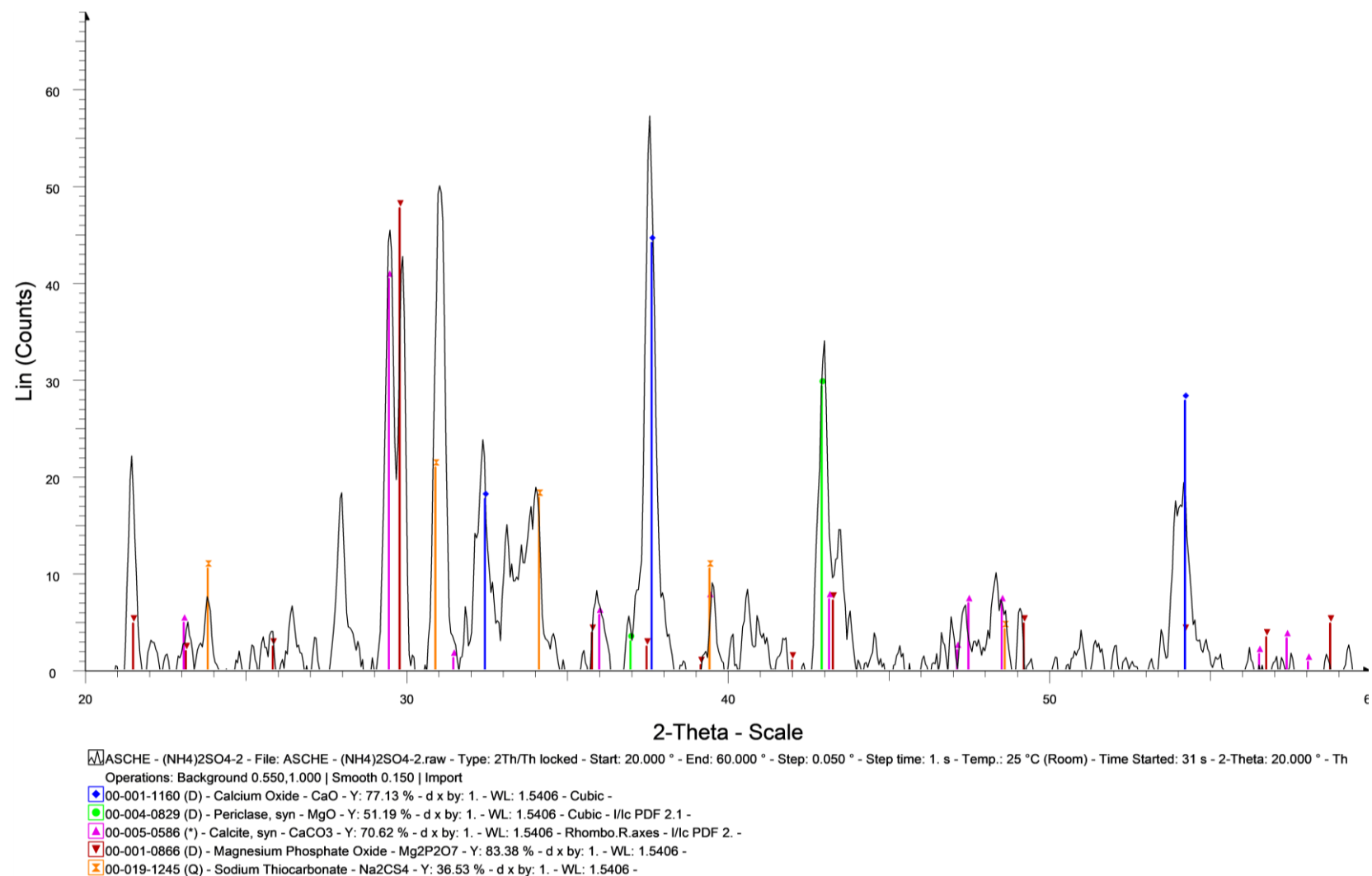
8.2.8   Pellets with (NH₄)₂SO₄ second combustion

Figure 64. XRD pellets with (NH₄)₂SO₄. Second combustion.

8.2.9 Pellets with TiO₂ first combustion
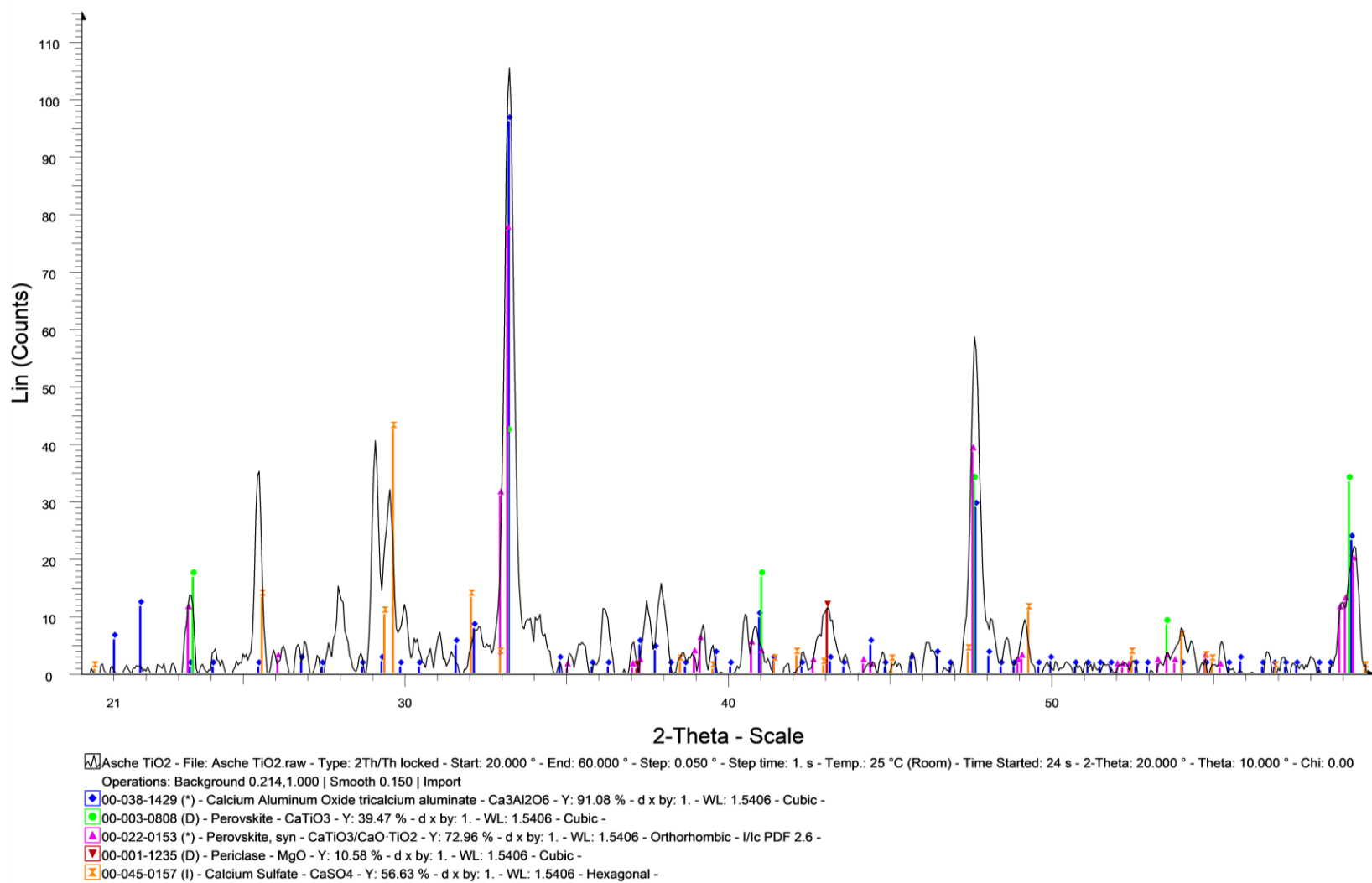

Figure 65. XRD pellets with TiO₂. First combustion.

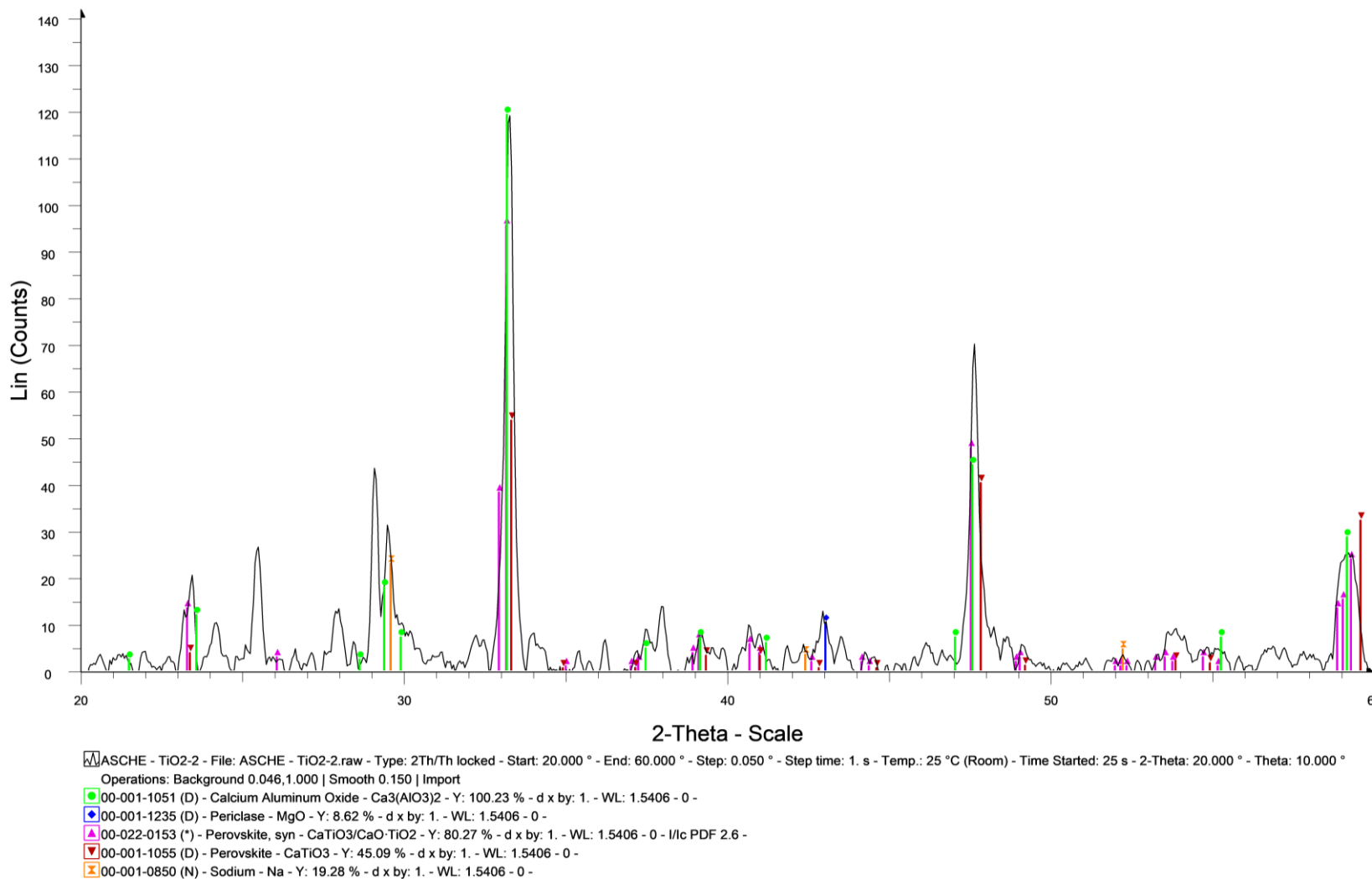## 8.2.10 Pellets with TiO₂ second combustion

Figure 66. XRD pellets with TiO₂. Second combustion

8.2.11 Pellets with Urea first combustion
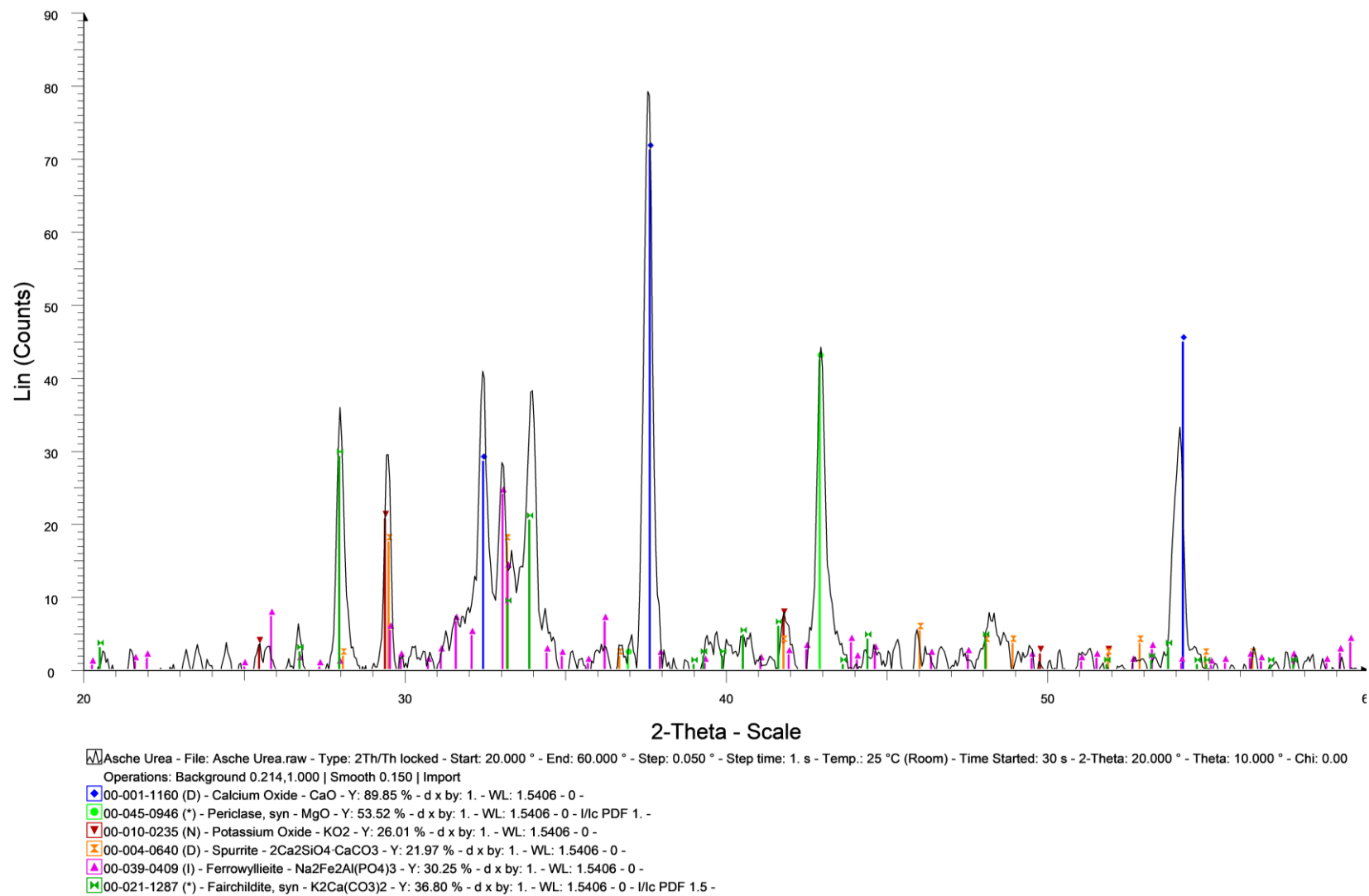

Figure 67. XRD pellets with Urea. First combustion.
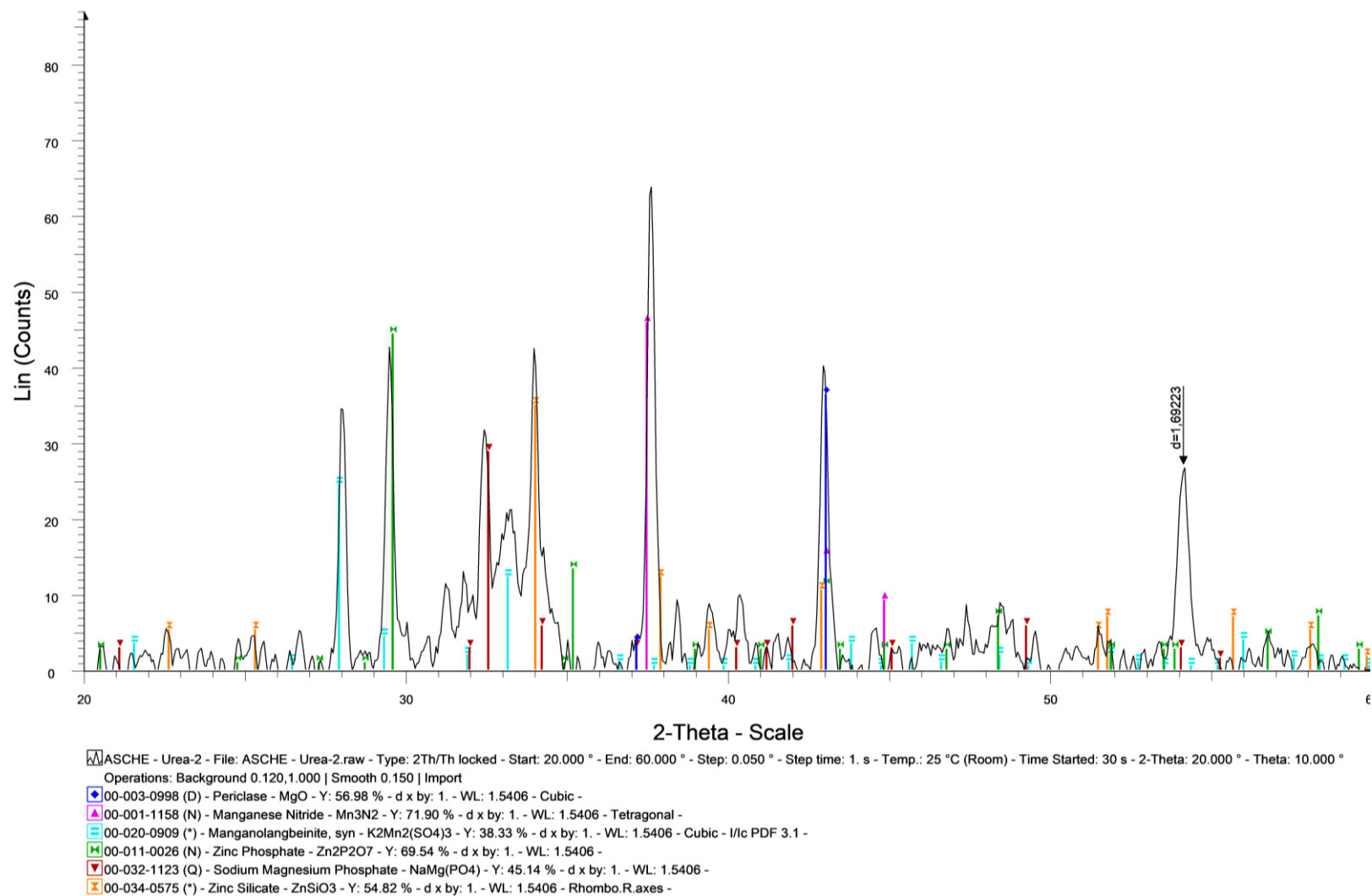
8.2.12 Pellets with Urea second combustion

Figure 68. XRD pellets with Urea. Second combustion.

8.3 Summary results XRD

Table 36. XRD summary results ashes.

	Without Additive		Fe$_2$O$_3$		MnCO$_3$		(NH$_4$)$_2$SO$_4$		TiO$_2$		Urea	
	1	2	1	2	1	2	1	2	1	2	1	2
AlCl$_3$-FeCl$_3$-C		x										
2Ca$_2$SiO$_4$-CaCO$_3$											x	
CaO	x	x	x				x	x			x	
CaCO$_3$	x		x					x				
Ca$_3$Al$_2$O$_6$	x	x							x	x		
CaFeSi$_2$O$_6$				x								
Ca(Fe,Mn)(Si,Al)$_2$O$_6$				x								
Ca$_3$Al$_2$O$_2$					x	x						
CaSO$_4$					x				x			
Ca$_2$MgSi$_2$O$_7$					x							
CaMnO$_3$/CaO - MnO$_2$					x	x						
CaMn$_2$O$_4$						x						
CaMnSi$_2$O$_6$						x						
Ca(Mg,Fe)(CO$_3$)$_2$							x					
CaTiO$_3$									x	x		
CaTiO$_3$/CaO-TiO$_2$									x			
Fe$_3$O$_4$			x									
KO$_2$											x	
K$_2$Ca(CO$_3$)$_2$	x											
K$_2$SO$_4$							x					
K$_2$Ca(CO$_3$)$_2$											x	
K$_2$Mn$_2$(SO$_4$)$_3$												x
MgO	x	x	x	x			x	x	x	x	x	x
Mg$_2$P$_2$O$_7$		x						x				
MgFe$_2$O$_4$				x								
Mg$_6$MnO$_8$					x	x						
Mn$_3$N$_2$												x
Na$_3$PO$_4$		x										
Na$_4$CaSiO$_3$O$_9$				x								
Na$_2$Ca$_4$(PO$_4$)$_2$SiO$_4$				x								
Na$_2$CS$_4$								x				
Na										x		
Na$_2$Fe$_2$Al(PO$_4$)$_3$											x	
NaMg(PO$_4$)												x
Zn$_2$P$_2$O$_7$												x
ZnSiO$_3$												x