Effects on the combustion properties of wheat straw after different thermobiological pretreatments

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Abstract

Wheat straw could be used for pellet production and therefore as solid fuel. However, it presents challenges due to its inferior combustion properties such as high ash content, low gross calorific value (GCV), and low ash melting temperature.
To evaluate its combustion properties and based on recent work that improved methane production, wheat straw was subjected to thermobiological pretreatments. Nine pretreated samples based on wheat straw and nine pretreated samples based on compost-wheat straw mixture were produced. In addition, due to the ability to remove minerals and decrease the ash content, a washing process with water as a solvent was used. Ash content, net calorific value (NCV) and ash melting temperatures were evaluated.

For the pretreated wheat straw (SW) samples, a 5,8% reduction in ash content was obtained due to the pretreatments when compared to untreated wheat straw. A 55% decrease in ash content was obtained when comparing the same materials before and after the washing process. No statistically significant changes in GCV were found. As for the ash melting temperatures, due to the incubation pretreatment, an average increase in the shrinkage starting temperature (SST) of 4,4% was obtained for anaerobic conditions and a decrease of 2,5% for aerobic conditions, compared to the same material without heat treatment. In addition, an increase in all ash melting temperatures was observed because of the washing process. It was possible to obtain a pellet complying with standard ISO 17225-6 that can be used in medium or large burners and significantly reduces the effort during combustion.

For samples pretreated with a homogeneous compost-wheat straw (SKW) mixture, an average ash content decrease of 27% was obtained after using autoclave pretreatment at 140°C, compared to the same material without thermal pretreatment. The biggest decrease was due to the washing process, reducing the ash content on average by 43% when comparing the same materials before and after washing. GCV were 13% lower than samples pretreated with wheat straw, due to the low calorific value and high ash content of the compost. During ash melting temperature tests, an average 60% increase in SST was observed compared to pretreated SW ashes due to the high melting temperature of compost. Results are considered satisfactory since pellets based on this mixture would not cause ash sintering or slagging. However, counter effects were observed as the addition of compost increased the ash content and decreased the GCV, not complying with ISO 17225-6 for non-woody pellets. To achieve a pellet based on a compost-wheat straw mixture that complies with the standards, it is recommended for future research to control the percentage of compost added to the mixture.

Keywords: wheat straw, compost, pellets, combustion, thermobiological pretreatment.

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Abbreviations

ANOVA	analysis of variance
DT	deformation temperature
FT	flow temperature
GCV	gross calorific value
HT	hemisphere temperature
kW_{th}	kilowatts thermal
NCV	net calorific value
RCF	relative centrifugal force
SKW	compost-wheat straw samples
SKW30_a120B	compost and wheat straw mixture pretreated with autoclave at 120 ºC and incubated for 15 days under anaerobic conditions at 55 ºC. Dry matter of 30%
SKW30_a140B	compost and wheat straw mixture pretreated with autoclave at 140ºC and incubated for 15 days under anaerobic conditions at 55 ºC. Dry matter of 30%
SKW30_a120Control	compost and wheat straw mixture pretreated with autoclave at 120 ºC. Dry matter of 30%
SKW30_a140Control	compost and wheat straw mixture pretreated with autoclave at 120 ºC. Dry matter of 30%
SKW30_a120I	compost and wheat straw mixture pretreated with autoclave at 120 ºC and incubated for 15 days under aerobic conditions at 25 ºC. Dry matter of 30%
SKW30_a140I	compost and wheat straw mixture pretreated with autoclave at 140 ºC and incubated for 15 days under aerobic conditions at 25 ºC. Dry matter of 30%
SKW30_B	compost and wheat straw mixture, incubated for 15 days under anerobic conditions at 55 ºC. Dry matter of 30%
SKW30_I	compost and wheat straw mixture, incubated for 15 days under aerobic conditions at 25 ºC. Dry matter of 30%
SKW30_Control	compost and wheat straw mixture, dry matter of 30%
SST	shrinkage starting temperature
SW	wheat straw-based samples
SW30_a120B	wheat straw pretreated with autoclave at 120 ºC and anaerobic incubation for 15 days at 55 ºC. Dry matter of 30%
SW30_a140B	wheat straw pretreated with autoclave at 140 ºC and anaerobic incubation for 15 days at 55 ºC. Dry matter of 30%

SWa30_120Control	wheat straw thermally pretreated with an autoclave for 20 minutes at 120 ºC. Dry matter of 30%
SWa30_140Control	wheat straw thermally pretreated with an autoclave for 20 minutes at 140 ºC. Dry matter of 30%
SW30_a120I	wheat straw pretreated with autoclave at 120 ºC and aerobic incubation for 15 days at 25 ºC. Dry matter of 30%
SW30_a140I	wheat straw pretreated with autoclave at 140 ºC and aerobic incubation for 15 days at 25 ºC. Dry matter of 30%
SW30_Control	wheat straw mixed with water, dry matter of 30%
SW30_B	wheat straw incubated for 15 days under anaerobic conditions at 55 ºC. Dry matter of 30%.
SW30_I	wheat straw incubated for 15 days under aerobic conditions at 25 ºC. Dry matter of 30%.
xg:	unit of relative centrifugal force, times gravity

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1. Introduction

The environmental impact caused by the emission of greenhouse gases is increased by the use of fossil fuels and their global prevalence. To overcome this situation, biogenic residues and waste materials, like by-products from agriculture such as wheat straw are gaining interest as potential raw materials that could serve as renewable energy sources [1]. Straw has been proposed as a source for bioenergy because it could intensify the economic benefit of agricultural land use since it is commonly eliminated by stubble burning, which also increases atmospheric pollution. Besides, the advantage of straw is its wide availability in almost all parts of the world, which is related to its low price [2]. Nevertheless, straw is known for its inferior combustion properties such as high ash content, low gross calorific value (GCV) and low melting temperature of ashes, which makes it difficult to use as a solid fuel [3], [4]. This can cause slagging, fouling and in some cases corrosion of boilers reducing the efficiency of combustion systems, incur additional cleaning and maintenance costs for boilers, and in some cases even prevent the use of it for combustion [5].

Beuel et al., [6] explored the effect of adding green waste compost in wheat straw for methane production. A thermobiological pre-treatment was carried out with a mixture of mechanically comminuted wheat straw and green waste compost as a substrate. The results revealed a lignocellulose degradation in all samples; besides, the use of compost ensured the growth of cellulose-degrading anaerobic microorganisms and the hydrolysis process, which is considered the rate-limiting step in anaerobic digestion, improving the process.
On the other hand, to improve combustive properties like the low melting temperature in herbaceous biomasses such as wheat straw in the form of solid fuel (e.g. pellets), the literature has recently proposed the use of additives such as Al-Si based, S-based, P-based, or Ca-based among others [7]. Various waste materials are of particular interest as additives, especially if they contain active chemical compositions for economically attractive costs [5]. However, compost as an additive has been scarcely studied. Due to this and the promising results obtained for thermobiological pretreated wheat straw in methane production, compost will be evaluated.

Also has been studied the effect of washing wheat straw using water as a solvent, due to its capacity to remove minerals that reduce the ash melting temperature and its capacity to significantly reduce the ash content [8]–[10]. This could mitigate ash deposition and emission problems during biomass combustion and be an alternative to improve the combustion properties of wheat straw [8]. Due to its benefits, low cost and short time required to perform this process, it has been decided to study it on a laboratory scale in this research.

Thus, the objective of this work is to study and improve the combustive properties of wheat straw through a thermobiological treatment. For this purpose, nine pretreated wheat straw and nine pretreated compost-wheat straw samples are produced and evaluated on three variables: ash content, calorific value and ash melting behavior.

Additionally, the impact of lignin degradation is studied in compost-wheat straw samples subjected to aerobic treatment. Due to the degradation and consequently lower content of this molecule, a decrease in the calorific value is expected due to the linear correlation between lignin and GCV [11]. It is also sought to elucidate the impact on anaerobic treatments.

Finally, it is expected to observe positive effects on the combustion characteristics studied due to the washing process and its ability to mineral remotion.

2. :metabolon and Lignobiol

All the scientific work developed here was performed at :metabolon as part of the Lignobiol project.

Opened in September 2011 in the state of North Rhine-Westphalia, Germany, :metabolon is a joint venture of the TH Köln – University of Applied Sciences and the Bergische Abfallwirtschaftsverband (BAV). The project focuses on the development of a thermochemical center at :metabolon research site. There, plants for pyrolysis and gasification processes are installed, which convert different waste-derived residual materials into materials or products that can be used in new ways. The three central, thematic pillars of :metabolon - the extracurricular learning landscape, the research community, and the Bergisch Energy Competence Center - are closely linked at many interfaces and, through the resulting network, they enable increasingly intensive work on the project-specific goals. The project intersects and bundles actors from the fields of education and research as well as companies and municipalities. In addition to a specialized audience, the declared goal is to address the general public with the :metabolon offerings [12]. The project is financially supported by the European Commission and the European Regional Development Fund (ERDF) under the slogan "Investing in our future" [12].

Within :metabolon is the Lignobiol subproject that aims to a cascading use of agricultural residues (straw) to generate mainly bioenergy and (1) improve the biodegradability of lignocellulosic materials, such as straw, through appropriate treatments (biological and thermal) to produce bioenergy; (2) estimate the biological potential of lignocellulosic biomass through thermal cogeneration; (3) evaluate the proposed process (cascade utilization) as a sustainable conversion of biomass for energy supply and (4) extend the use of the proposed process to other cellulosic materials in addition to straw [13].

Under Lignobiol, different processes and technologies are combined in innovative and integrated practices to ensure the sustainable and environmental development of bioenergy production from biogenic waste. The process can be used to produce biogas and solid fuel (e.g., pellets), expanding the efficiency in the use of waste materials. The sustainable development of the process is based on the cascading-multiple uses of waste and the innovative and efficient use of waste conversion [13].

3. Theoretical Framework

3.1 Biomass and straws

Biomass has been defined by the European Union [1] as the biologically decomposable part of products, waste and residual material based on agriculture and of biological origin (including animal-based and plant-based substances), from forestry, and form associated sectors of business, including fishing and aquaculture. Therefore, biomass is plants, constituent parts of plants and the energy sources produced from plants; waste and by products (of plant and animal origin) from agriculture, forestry, and fisheries; waste wood from forest-based industry; material from landscape conservation and various organic matter obtained by the maintenance of water bodies, including their banks; waste wood and municipal organic waste.

The term biomass includes the criteria of renewability [1], which means it can be renewed at once, or fast enough, by natural or managed processes that can be expected to continue indefinitely. One advantage of biomass from other renewable energies is its capability of being storable over longer periods (months or years) and can be made available or used for energy generation according to demand.

The global share of the total primary energy demand of biomass in 2019 was 4% as shown below [14]:

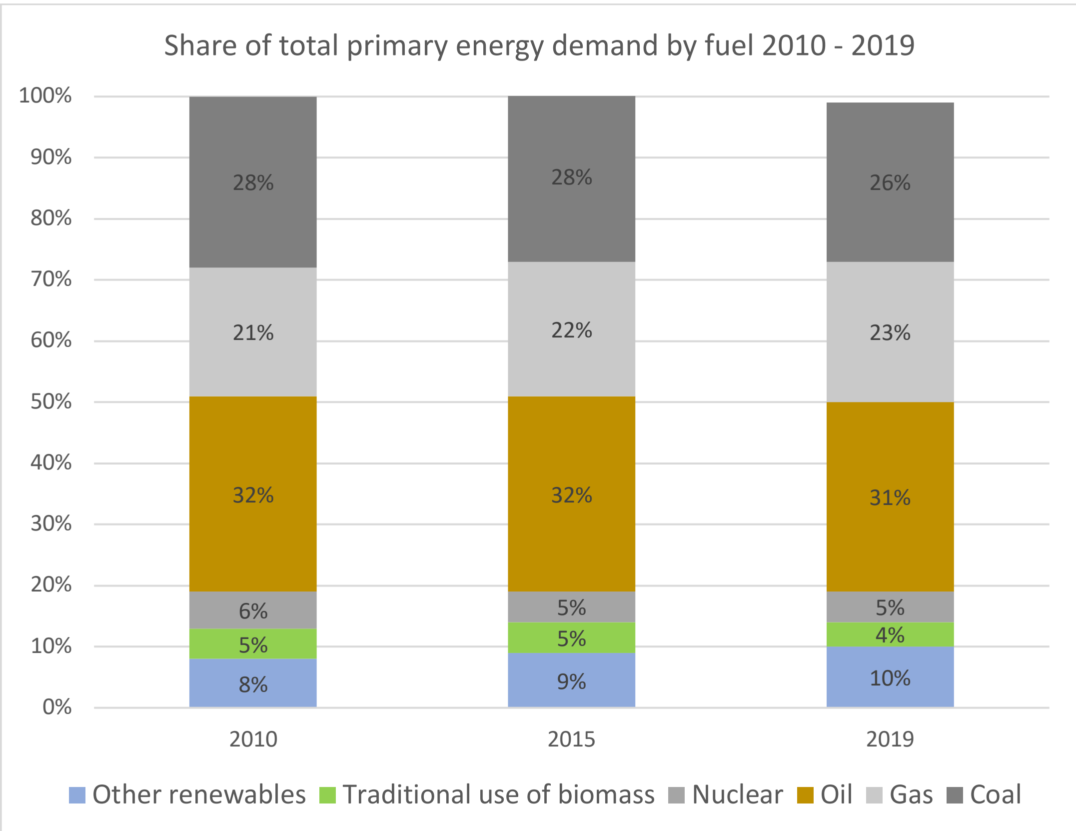

Fig. 1. Share of total primary energy demand by fuel 2010-2019.

In the forecast for renewable energies to 2024 made by the International Energy Agency (IEA) [15], the bioenergy global capacity expands from 130 GW in 2018 to 171 GW by 2024, increasing by 32%. While this accounts for just 3% of total renewable capacity growth, bioenergy is nevertheless responsible for 8% of renewable generation at the end of the forecast period, with China providing over 50% of new capacity, mainly in the form of solid biomass co-generation and energy-from-waste projects.

Straws are a type of biomass from agricultural by-products obtained after harvesting grains which have significant potential as a renewable energy source due to its availability and low commercial value [1]. In particular, the use of straws has been explored recently in form of solid biofuel for the production of pellets. A pellet is thus normally a small round mass, mostly made of compressed material, of a spherical or cylindrical shape. Various products and materials can be pelletised to be used thermally or for different purposes. Pellets for energetic utilisation can be made of wood, peat, herbaceous biomass or waste [16].

Straws are available in great amounts and are commonly eliminated by stubble burning, which increases atmospheric pollution and therefore generates contamination problems; moreover, in most cases, straws are not used to generate added-value products. Due to this, the production of biofuel pellets from agro-industrial residues has gained attention in the scientific community [2], [17].

If managed efficiently, straws can be used as energy feedstock and contribute to reducing dependence on fossil fuels. For example, in China alone, it is estimated 400 million tons of straw – in case all straw from the country could be used- could generate 291 TWh electricity which is equivalent to an annual substitution for 200 million tons of coal, approx. 7,5% of China's total consumption in 2008 [18].

3.2 Wheat straw characteristics

Wheat straw is the agricultural by-product obtained from different parts of the wheat plant like stem or leaves. According to the guideline ISO 17225-1, wheat straw is classified as herbaceous and agricultural biomass, which is a type of biomass that comes from plants that have a non-woody stem and which die back at the end of the growing season. This classification incorporates straws, grasses, cereals and fruits [19].

Wheat growing is abundant worldwide, and straw is gradually being used for heat production by the combustion of pellets produced from it [20]. However, to be used as a solid fuel, it presents challenges in its combustion properties addressed in this work, which will be described below:

3.2.1 Ash content

The ash content or ash yield of biomass is understood as the measured quantity of the incombustible inorganic residue resulting from the complete combustion of biomass, mainly at 500-600 ºC under laboratory conditions. Major and minor ash-forming elements in biomass ashes, in decreasing order of abundance, are: O > Ca > K > Si > Mg > Al > Cl > P > Fe > Na > S > Mn > Ti [21].

The ash yield normally decreases in order : animal biomass > aquatic biomass > contamined biomass > herbaceous and agricultural biomass > wood and woody biomass [3]. Therefore, wheat straw has a higher ash content than biomass from wood but lower than contamined biomass. Furthermore, the ash content is an important parameter for estimation of [21]:

- organic and inorganic matter,
- possible contamination of biomass,
- predominant affinity of elements and compounds to inorganic or organic matter and
- different technological and environmental problems

The low ash content of biomass is more desirable and has benefits in achieving better fuel quality mainly due to: (1) increased calorific value, (2) easier thermochemical and biochemical conversions, (3) less fouling, deposition, agglomeration, slagging, corrosion and erosion problems, (4) decreasing operating costs concerning biomass harvesting, transport and processing, gas-cleaning technologies, as well as ash transport, disposal and utilization; among others benefits [20].

Low ash content in pellets also means benefits for small furnace users (up to 100 kW_{th}) because it means longer emptying intervals for the ash box, therefore, better comfort [16]. If the pellets are to be used in medium- or large-scale furnaces, such low ash contents are not necessary because bigger installations are usually built more robustly and are typically equipped with sophisticated combustion and control systems [19].

For wheat straw pellets mixed with papermaking sludge as an additive, Matúš et al., [20], mention that ash contents up to 19% (dry basis) can be used in small burners, however, and according to the ISO 17225-6 to satisfy the residential, small commercial and public building applications it should not exceed 10% (dry basis) [19]. Besides, the ISO 17225-1 [22] shows the typical values for the ash content of materials based on wheat, rye, or barley straw. Table 1 below summarizes this information:

Table 1. Typical values for the ash content of materials based on wheat, rye, or barley straw (ISO 17225-1) and value required for pellets (ISO 17225-6)

Source	Parameter	Unit	Straw from wheat, rye, barley	
			Typical value	Typical variation
ISO 17225-1	Ash content	w-%dry	5	2 to 10
	Value required for pellets			
ISO 17225-6	Ash content 10 w-%dry			

Lastly, an extended overview by Vassilev et al., [21] of the ash content and ash-forming elements of different biomasses indicates that typical value for wheat straw pellets is 8%. This value falls within the range given in Table 1.

3.2.2 Gross calorific value (GCV) and Net calorific value (NCV)

The calorific value is the energy amount per unit of mass or volume released from complete combustion [16]. Besides, there are two types of calorific value described below:

The gross calorific value (GCV) is a measured value of the specific energy of combustion for a mass unit of a fuel burned in oxygen in a bomb calorimeter under specified conditions. The GCV of raw material should be as high as possible concerning the energy density of the pellets. It is purely dependent on the material used, i.e., the chemical composition of the raw material and can therefore not be influenced. The old term is "higher heating value" (HHV), this definition was adapted from ISO 1928:1995 [16].

The net calorific value (NCV) is a calculated value of the energy of combustion for a mass unit of a fuel burned in oxygen in a bomb calorimeter under such conditions that all the water of the reaction products remains water vapour at 0.1 MPa [16]. The NCV depends mainly on the gross calorific value, the moisture content, and the content of hydrogen in the fuel. Other parameters such as nitrogen, oxygen or ash content have a minor influence [16]. The NCV can be calculated from the GCV, and the equation is provided by ISO 18125 [23], which is described in section 4.3.5. The old term is "lower heating value" (LHV) and it is adapted from ISO 1928:1995 [16].

The wheat straw understood as herbaceous biomass, has a lower GCV than woody biomass since the concentrations of carbon and hydrogen in herbaceous biomasses are lower than those of woody biomass [16].

Carbon, hydrogen, and oxygen are the main components of biomass fuels (since cellulose, hemicellulose and lignin consist of these elements), whereby carbon and hydrogen are the main elements responsible for the energy content due to the exothermic reaction to CO_2, respectively H_2O, during combustion. The oxygen bound in organic material covers part of the oxygen needed for the combustion; the rest oxygen needed for complete combustion has to be supplied by air [16].

Woody biomass has commonly higher NCV values. These values range between 18 to 19 MJ/kg [22]. NCV values for wheat straw are shown in Table 2.

Lastly, ISO 17225-1 provides typical calorific values for materials based on wheat, rye or barley straw [22]. In addition, to satisfy the residential, small commercial and public building applications according to the ISO 17225-6, wheat straw pellets should have a NCV greater than 14,5 MJ/kg [19]:

Table 2. Typical values of GCV and NCV for materials based on wheat, rye, or barley straw (ISO 17225-1) and value required (ISO 17225-6)

Source	Parameter	Unit	Straw from wheat, rye, barley	
			Typical value	Typical variation
ISO 17225-1	GCV	MJ/kg	18,8	16,6 to 20,1
	NCV	MJ/kg	17,6	15,8 to 19,1
	Value required for pellets			
ISO 17225-6	NCV 14,5 MJ/kg			

3.2.3 Ash melting behavior

Ash melting behavior is a characteristic physical state of the ash obtained by heating under specific conditions and it is either determined under oxidizing or reducing conditions [16]. It is widely accepted that the high concentrations of K, Si, P, S, Fe, Na and Mg containing minerals (excluding the highly enriched in Si biomass varieties) and low contents of Ca, Al and Ti bearing minerals are commonly responsible for decreased ash-fusion temperatures of biomass [24]. Furthermore, most of the serious slagging and fouling problems during biomass combustion resulted from the low ash-melting temperatures [25].

The low ash fusion biomass varieties generally have a high slagging propensity due to the occurrence of low-temperature melts and their subsequent intensive melt crystallization followed by abrupt glass formation during cooling at relatively lower temperatures. On the other hand, biomass varieties with high ash fusion temperatures commonly show lower slagging propensity because their ash fusion temperatures are high, and the processes above are less intensive during combustion. For example, the medium to high contents of Si and K in biomass (excluding some highly enriched in Si varieties) greatly contribute to extremely low ash fusion temperatures. It seems that the combination of such concentrations for Si and K in the biomass ash system (represented mostly as K silicates and inorganic amorphous matter) has a leading role in the formation of some low-temperature eutectics that strongly influence ash fusion behavior [24].

Herbaceous biomasses present low fusion temperatures and high corrosion potential compared to traditional woody biomass [4], and particularly straw due to its high content of ashes, K, Cl and Si and low content of Al, Ca, Fe, Mg, Mn, Na, P, S, Ti [21]. Typical mineral concentration in straws are shown in Table 3 [16], [27]:

Table 3. Typical minerals content in straws.

Element	Straw (wheat, rye) wt.% (d.b)
K	10.0 – 16.0
Cl	0,1 – 2,1
Si	16,0 – 30,0
Na	0,2 – 1,0
S	0,1 – 0,35
Ca	4,5 – 8,0
Mg	1,1 – 2,7

Table 4. below summarizes the effects of relevant minerals in the straw ash melting process:

Table 4. Minerals influencing the straw ash melting process.

Element	Effect	Description
Potassium (K)	negative	Decrease the ash melting point. Lead to: (1) decreased ash melting temperatures, which can cause high rates of fouling and slagging; (2) rise the amount of aerosols and fine particulate emissions; (3) corrosion and other problems [21]. May also cause ash melting problems by the formation of phosphates [16].
Chlorine (Cl)	negative	It is perhaps the most problematic of elements found in biomass fuels with respect to deposition, corrosion and fouling of combustion units [21]. Cl has a major role in corrosion because it boost the emissions of Hydrochloric acid (HCl), furthermore corrosive effects are of great relevance concerning deposit formation [16].
Silicon (Si)	negative	It is one of the main ashes forming elements (together with Ca, Mg and K). Si also influences the ash melting behavior as low melting potassium silicates may be formed [16]. However, Si could have a positive effect reacting with Ca, causing formation of calcium silicates that have higher melting temperatures than potassium silicates [4].
Sodium (Na)	negative	Na in combination with Cl and S, plays a major role in corrosion mechanisms. These elements partly evaporate during the combustion process by forming alkali chlorides, which condense on the heat exchanger surfaces and react with the flue gas by forming sulphates and releasing chlorine [28]. However, there is extremely low content of this mineral in straws [21] .
Sulfur (S)	negative / positive	It boost the emissions of sulfur oxides (SOx) and has corrosive effects [16]. However as additive, the main effect is to convert the gaseous alkali chlorides in the flue gas to alkali sulfates, which are less harmful with respect to ash deposition and corrosion. A typical S-based additive is ammonium sulfate, which can not only convert the gaseous alkali chlorides to sulfates but also reduce the NOx concentration in the flue gas [7].
Calcium (Ca)	positive	Ca and Mg normally increase the melting temperature of ashes [28]. Si will react with Ca with formation of calcium silicates that have higher melting temperatures than potassium silicates [4]. Normally there is low content of this mineral in straws [21].
Magnesium (Mg)	positive	Ca and Mg normally increase the melting temperature of ashes [28]. Furthermore, magnesium oxide (MgO) Prevents ash sintering up to 1100 °C, forms higher-melting compounds and binds $SO_4{}^{2-}$achieving the formation of MgSO4 (melting point=1124 °C) [4]. Normally there is low content of this mineral in straws [21].
Aluminum (Al)	positive	By reacting with KCl, it forms higher-melting compounds, according to the reaction: 2 KCl+H2O(g)+Al2O3→2 KAlO2+HCl(g) [4]. Normally there is low content of this mineral in straws [21].

Thus, scientific literature reveals that a beneficial approach for problematic low ash fusion biofuels is to use additives, namely kaolinite, mullite, clinochlore, bentonite, K feldspar, plagioclase, olivine, quartz, lime, bauxite, gibbsite, diaspore, corundum, hematite, calcite, dolomite, magnesite, ankerite, sand, high alumina sand, limestone, diatomaceous earth, dicalcium phosphate, chalk, elemental S, peat and coal fly ash. The application of such additives is to prevent the agglomeration, sintering and slagging tendencies by achieving higher ash melting temperatures [24]. The usable additives can be approximately categorized as Al-Si based (e.g. kaolinite), S-based (e.g. ammonium sulphate), P-based (usually refer to Ca-phosphates), or Ca-based according to the major elements present in the additives [7].

Recent literature similar to this work has focused on trying to increase the ash temperatures by means of different additives. For example, the behavior of herbaceous biomass ash has been studied mixed with elements rich in calcium, magnesium or aluminium such as eggshells, CaO, MgO or Al_2O_3 [4]. Wheat straw has been studied with additives such as papermaking sludge, a waste by-product of the paper recycling process, which contains a high proportion of mineral fillers such as kaolin, calcium oxide and others [5], [20] or has also been studied with other biomass blends, such as wood and reed [26]. Related to cost, availability and functionality at low concentrations, the use of calcium-based additives is particularly interesting [4].

For wheat straw pellets, according to the ISO 17225-6 to satisfy the residential, small commercial and public building applications there are no specific or required characteristic temperatures. However, the guideline recommends that all characteristic temperatures: shrinkage starting temperature (SST), deformation temperature (DT), hemisphere temperature (HT) and flow temperature (FT) in oxidizing conditions should be stated using the guideline CEN/TS 15370-1 [19], which was used for this work. For more information about the guidelines see section 4.3.6.
Typical values for wheat straw found in the literature are shown below [27]:

Table 5. Typical values for straw ash melting temperatures.

SST	DT	HT	FT
848 ºC	956 ºC	1107 ºC	1241 ºC

Additionally, a recent study of wheat straw pellets mixed with paper sludge was conducted by Matúš et al., [20] applying the guideline CEN/TS 15370-1. The paper stated that a temperature equivalent to SST higher than 1080 ºC is an appropriate range for producing quality wheat composite pellets and avoiding combustion problems due to low ash melting temperature.

3.3 Green waste compost and its interaction with straw

Green waste understood as biowaste consists of tree wood and bark, pruning from young trees and scrubs, dead and green leaves, grass clippings and solid, and originates from municipal parks, gardens, reserves, and domestic dwellings among others. Because of this, the green waste composition is highly variable and depends on the predominant source vegetation, the season of the year, and the local collection policies, among others [29].

In an extended review on the composting of green waste, Reyes-Torres et al., [29] indicates that despite the reported heterogeneity, green waste is characterized by low content of essential nutrients such as K and very low heavy metal content. Besides, the study reported low content of minerals that are relevant for the ash melting point process (as explained in section 3.2.3) as shown in Table 6 below:

Table 6. Relevant ash melting point minerals commonly find in green waste. Percentages based on dry matter basis.

Mineral	Range value (%)	Average value (%)
Potassium (K)	0,26 – 1,56	0,58
Sulfur (S)	0,12 – 6,13	2,23
Calcium (Ca)	0,15 – 3,00	1,06
Magnesium (Mg)	0,10 – 0,75	0,38

Other studies also report this heterogeneity in the ash content of green waste compost. Generally in the literature ash content values above 60% have been reported [30], [31], but also values as low as 7% have been found [6].

Regarding composting, it is defined as a process of biological oxidation, in which oxygen is used by microorganisms as the final acceptor of electrons for aerobic respiration; under these conditions, the transformation of substrates is characterized by the consumption of oxygen and the generation of CO_2, water and heat. Due to the continuous decrease in oxygen concentration during the process, the air supply is necessary to maintain metabolic activities [29].

The C and N are essential for microorganisms because they are structural elements and sources of energy. Heterotrophic microorganisms use C as a source of energy and for the synthesis of cellular constituents; N is a component of the proteins, nucleic acids, amino acids, enzymes, and coenzymes necessary for the growth and functioning of cells. The generally recommended value of the (total) C / N ratio in substrates is between 25 and 30.

Furthermore, the pH of the substrate and the production of acids at the beginning of the process is important to maintain certain microbial groups during the transformation of organic matter, and the pH also is one indicator of the maturity of the final product. PH in mature compost must be in a neutral range [29].

Composting is a suitable method for the recycling of green waste, since the compost obtained is a useful organic amendment and/or organic substrate that can be reincorporated into the economic system, helping to solve the disposal problem and to reduce emissions of greenhouse gases [29].

On the other hand, straw is mainly composed of cellulose (30–50 %), hemicellulose (20–35 %), and lignin (15–20 %) [6]. However, the biodegradability of such valuable biomasses is still restricted due to the high content of lignocellulose fibers, which counteracts their use to achieve complete digestion during fermentative processes like anaerobic digestion [6]. Therein, different studies that used a pretreatment similar to the one used in this research [6], [32], demonstrated that the enhancement of the biodegradability of lignocellulose feedstocks using compost as a natural source of microorganisms could improve methane production:

Bursche et al., [32] described a paradigm shift in the degradation of the lignocellulose material in wheat straw for methane production because compost is a source of microorganisms (bacteria and fungi), which may degrade structural carbohydrates of biomasses. The investigation showed that the use of green compost seemed to improve, at lower levels, the methane potential of straw when a thermobiological pre-treatment was carried for less than 56 days since storage.

Beuel et al., [6] further explored these concepts and the effect of adding green waste compost as a biological pretreatment for improving the biogenic catalysis of wheat straw to enhance the use of lignocellulose biomasses for a biorefinery concept. A thermobiological pre-treatment was carried out with a mixture of mechanically comminuted wheat straw and green waste compost as a substrate and the results revealed a lignocellulose degradation in all samples. The use of compost ensured the growth of cellulose-degrading anaerobic microorganisms under thermophilic conditions. Due to the sugar compounds released during the biogenic catalysis, the hydrolysis process, which is considered the rate-limiting step in anaerobic digestion, was improved.

Nevertheless, the effects of mixing wheat straw with compost as an additive for use as a solid fuel in pellets have been scarcely investigated and more information are expected to be elucidated in this study.

3.3.1 Lignin influence on biomass combustion and its degradation using green waste compost.

Lignin (e.g. $C_{40}H_{44}O_{14}$) is a high molecular mass complex non-sugar polymer that gives strength to the wood fiber [28]. As described previously, wheat straw is composed of cellulose (30-50%), hemicellulose (20-35%) and lignin (15-20%) [6].

Lignin in biomass combustion has been investigated [33], the results show that it appears that lignin-deficient biomass samples are inherently more reactive with lower activation energy and ignition points, and thus might be expected to burn more efficiently in a power

station. On the contrary, lignin-rich samples are known to produce higher thick-walled char yield. This suggests that samples of this nature are less suited for combustion processes.
It has also been found that the higher the lignin content, the higher the GCV and vice versa [11]. There is a highly significant linear correlation between the GCV of the biomass fuel and the lignin content. Besides, three mathematical equations have been developed to calculate the GCV of various lignocellulosic fuels from their lignin content: a general model for all fuel samples, for wood samples, and for non-wood samples (like wheat straw). These models, especially the general model, have been often cited [34] and the results developed show excellent agreement with experimental results for the used samples [11].

Furthermore, in a study for a biorefinery concept, Beuel et al., [6] conducted samples similar to those studied in this work, namely, pretreated wheat straw with green waste compost. Because of the green waste compost on wheat straw samples, lignin degradation was described and occurred when the samples were kept under aerobic conditions. Lignin degradation around 30% for the straw-compost sample (SCWa-I) and 37% for the straw-compost-liquid digested sample (SCDa-I) was achieved.
On the other hand, the same study shows a favorable effect on methane production when compost is used as a natural source of microorganisms (which can degrade lignocellulose feedstocks) under anaerobic incubation. Digestion time of samples pretreated with compost is shortened by 35–91% compared to the untreated wheat straw fermentation. For the straw-compost sample (SCWa-B), more than 84% of methane production from wheat straw was already formed during biological pretreatment of anaerobic samples at 55 ºC, suggesting that pretreating wheat straw with compost has great potential to improve anaerobic fermentation efficiency [6].

Therefore, a similar phenomenon is expected in this research: the wheat straw-compost samples that are conducted under aerobic conditions should show degradation of their lignin content. In addition, due to the degradation of lignin and consequently a lower amount of this non-sugar polymer, a lower calorific value is expected in straw-compost samples than in straw-only samples. Other possible effects on the behavior of wheat straw-compost samples under aerobic and anaerobic conditions will be investigated.

3.4 Effect of water washing on wheat straw

Water washing on biomass has been shown to reduce the ash deposition and air-borne emissions because washing removes minerals like K, Cl, Na, S, Ca, Mg, Fe, and P from the biomass, furthermore removal of S and Cl reduce acid gases formation and hence corrosion in boilers and associated environmental impact. As result, a washing pre-treatment mitigate the ash and allows to upgrade of low-grade biomass for a heat-electricity generation [8].

According to the literature reviewed [8]–[10], water is used as a solvent during the process, but there is no standardized process. For example, in one study, water was used at room temperature and wheat straw of size 1-3 cm was stirred for 20 hours, obtaining the removal of 54% K, 94% Na, 100% Cl, 12% Ca, 32% Mg, among others [9].
Another study used water at 30 ºC, 60 ºC and 90 ºC on the wheat straw of size 280 - 450 μm for 3 hours [10]. The study shows that the increase in water temperature benefits ash removal, obtaining a reduction of 55 to 75%. Among the results, removal of <90% K, 70 - 85% Cl, 85 - 95% S, is achieved.

Lastly, in a review of the mitigation of deposition and emission problems during biomass combustion through washing pre-treatment, Deng et al., [8], concludes among other findings that (1) washing with water at ambient temperature reduces the ash content of the fuel, (2) the impact of washing is minimal on GCV. However, ash content tends to reduce significantly, hence reducing the tendency of fouling and slagging to occur in boilers and furnaces, (3) removal of S and Cl reduce acid gases formation and hence corrosion in boilers and associated environmental impact.

Consequently, in this study, it is expected to observe a reduction of ashes in the washed wheat straw samples and the effect of washing on the wheat straw-compost samples will be investigated. In addition, due to the removal of minerals that negatively affect the melting temperature, such as K, Cl or Na, it is expected to observe an increase in ash melting temperatures in wheat straw samples, as in wheat straw samples with compost.

3.5 Statistical tools

3.5.1 The analysis of variance, two-way ANOVA

To evaluate the impact of pretreatments on combustion results, it was decided to use the analysis of variance (ANOVA) tool. ANOVA is a statistical method used to test differences between two or more means [35].
If an experiment has a quantitative outcome and two categorical explanatory variables (factors), then the most common analysis method is two-way ANOVA [35]. This study uses an experiment with two factors. The pre-treatment applied in this study was conducted using three types of incubation (without incubation, aerobic at 25 ºC, and anaerobic at 55 ºC) and different autoclave temperatures (without autoclave, at 120 ºC, and 140 ºC). The factors would be types of incubation and autoclave temperatures. Types of incubation would have three levels and autoclave temperatures would have another three levels. Besides, a two-way ANOVA allows a test of the interaction between the variables, e.g., the interaction between types of incubation and autoclave temperatures.

In general, a two-factor factorial experiment will appear as in Table 7. The order in which the *abn* observations are taken is selected at random so that this design is a completely randomized design [35]:

Table 7. General arrangement for a two-factor factorial design [35].

		Factor B			
		1	2	$\ldots$	b
Factor A	1	$y_{111}, y_{112}, \ldots, y_{11n}$	$y_{121}, y_{122}, \ldots, y_{12n}$		$y_{1b1}, y_{1b2}, \ldots, y_{1bn}$
	2	$y_{211}, y_{212}, \ldots, y_{21n}$	$y_{221}, y_{222}, \ldots, y_{22n}$		$y_{2b1}, y_{2b2}, \ldots, y_{2bn}$
	$\vdots$				
	a	$y_{a11}, y_{a12}, \ldots, y_{a1n}$	$y_{a21}, y_{a22}, \ldots, y_{a2n}$		$y_{ab1}, y_{ab2}, \ldots, y_{abn}$

For the two-factor ANOVA model, we have $\mu_{ij} = \mu + \tau_i + \beta_j + (\tau\beta)_{ij}$ [35] where,
μ_{ij} is the mean of the *ij*th,
μ is the overall mean effect,
τ_i is the main effect of Factor A,
B_j is the main effect of Factor B,
$(\tau\beta)_{ij}$ is the interaction effect between A and B.

In the two-factor ANOVA we are interested in testing hypotheses about the equality of row treatments effects [35], say

$$H_0: \tau_1 = \tau_2 = \cdots = \tau_a = 0$$
$$H_1: at\ least\ one\ \tau_i \neq 0$$

and the equality of column treatment effects [35], say

$$H_0: \beta_1 = \beta_2 = \cdots = \beta_b = 0$$
$$H_1: at\ least\ one\ \beta_j \neq 0$$

We are also interested in determining whether row and column treatments interact. Thus, we also wish to test

$$H_0: (\tau\beta)_{ij} = 0\ \ for\ all\ i, j$$
$$H_1: at\ least\ one\ (\tau\beta)_{ij} \neq 0$$

Thus, we speak of testing the equality of treatment means or testing that the treatment effects $(\tau_i, \beta_i, (\tau\beta)_{ij})$ are zero [35].

Computationally, we almost always employ a statistical software package to conduct an ANOVA. The test procedure is usually summarized in an analysis of variance table, as shown in Table 8 [35]:

Table 8. Analysis of variance table for the two-factor factorial model [35].

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F_0
A treatments	SS_A	$a-1$	$MS_A = \frac{SS_A}{a-1}$	$F_0 = \frac{MS_A}{MS_E}$
B treatments	SS_B	$b-1$	$MS_B = \frac{SS_B}{b-1}$	$F_0 = \frac{MS_B}{MS_E}$
Interaction	SS_{AB}	$(a-1)(b-1)$	$MS_{AB} = \frac{SS_{AB}}{(a-1)(b-1)}$	$F_0 = \frac{MS_{AB}}{MS_E}$
Error	SS_E	$ab(n-1)$	$MS_E = \frac{SS_E}{ab(n-1)}$	
Total	SS_T	$abn-1$		

After conducting the experiment, performing the statistical analysis, and investigating the underlying assumptions, the experimenter is ready to draw practical conclusions about the problem he or she is studying [35].

3.5.2 Two sample t-Test

The two-sample t-test is used to determine if two population means are equal. A common application is to test if a new process or treatment is superior to a current process or treatment [36].

If we assume that μ_1 and μ_2 represent the means of the two treatments of interest, the null hypothesis for comparing the two means is $H_0: \mu_1 = \mu_2$. The alternative hypothesis can be any one of [36]:

Two-sided $H_1: \mu_1 \neq \mu_2$.

Upper one-sided $H_1: \mu_1 > \mu_2$.

Lower one-sided $H_1: \mu_1 < \mu_2$.

depending upon the desire of the researcher or the protocol instructions. A suitable Type I error probability (α) is chosen for the test, the data is collected, and a t-statistic is generated using the formula [36]:

$$t = \frac{\overline{x_1} - \overline{x_2}}{\sqrt{\frac{(n_1 - 1) * S_1^2 + (n_1 - 1) * S_2^2}{n_1 + n_2 - 2} * (\frac{1}{n_1} + \frac{1}{n_2})}}$$

where,

$\overline{x_1}$ and $\overline{x_2}$, are the sample means,

n_1 and n_2, are the sample sizes,

S_1 and S_2, are the sample variances.

This t-statistic follows a t-distribution with $n_1 + n_2 - 2$ degrees of freedom. The null hypothesis is rejected in favor of the alternative if [36],

for $H_1: \mu_1 \neq \mu_2$,

$$t < t_{\alpha/2}\, or\; t > t_{\alpha/2}\,,$$

for $H_1: \mu_1 > \mu_2$,

$$t > t_{1-\alpha}\,,$$

or, for $H_1: \mu_1 < \mu_2$.

$$t < t_{\alpha}\,.$$

Comparing the t-statics to the cut-off t-value is equivalent to comparing the p-value to α, where α is the probability of obtaining a false positive with the statistical test. That is, it is the probability of rejecting a true null hypothesis. The null hypothesis is usually that the parameters of interest (means, proportions, etc.) are equal. Since Alpha is a probability, it is bounded by 0 and 1. Commonly, it is between 0,001 and 0,10. Alpha is often set to 0,05 for two-sided tests and to 0,025 for one-sided tests [36].

4. Material and methods

4.1 Wheat and compost used

Wheat straw was used as a substrate and was obtained from a farm close to Cologne in Germany. Compost used during the biological pretreatment was obtained from the green waste composting plant in the Leppe waste disposal center in Lindlar, Germany.

4.2 Mechanical and thermobiological pretreatment

To obtain the 20 samples to be subjected to the combustion tests studied in this report, the corresponding thermobiological pretreatments were first carried out. Fig. 2 shows the procedure followed for wheat straw-based (SW) samples. As a result of this procedure, 10 samples are obtained:

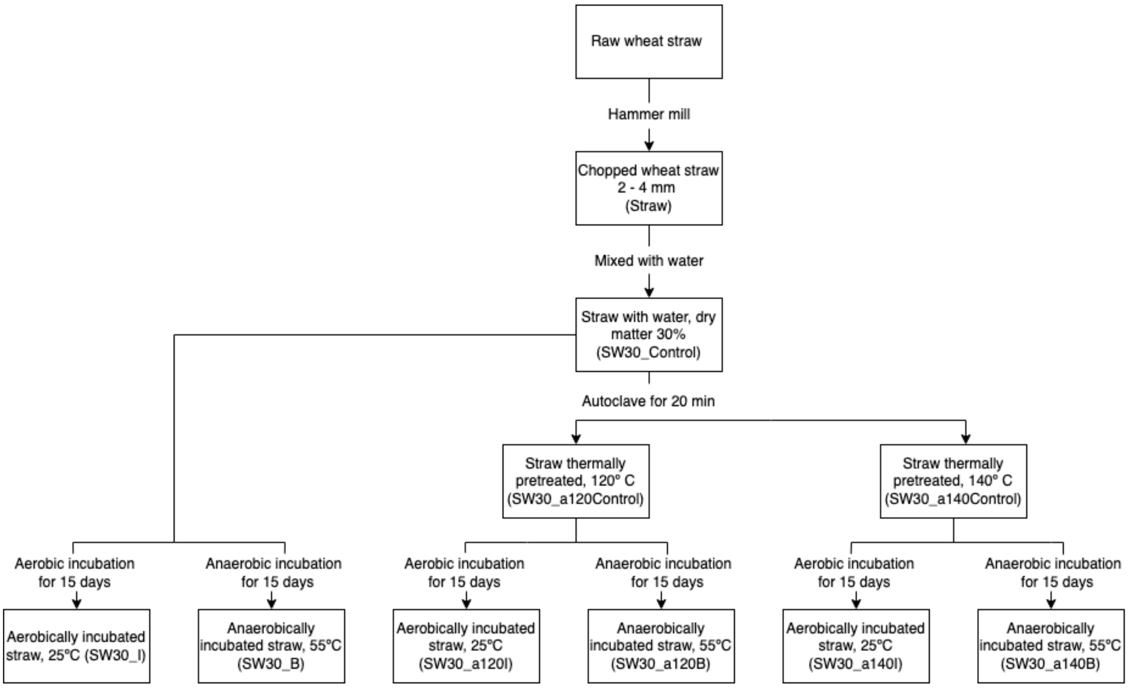

Fig. 2. Sequence of thermobiological pretreatment of wheat straw-based (SW) samples. The ten samples are named in parentheses.

For the preparation of SW samples, raw wheat straw is chopped using a hammermill Mütek Systemtechnik Type MPZ 600 with 22kW. A portion of the chopped wheat straw is separated and not subjected to pretreatment for later comparison of its combustion values. Another portion of the chopped wheat straw (Straw) is mixed with water to obtain a dry matter of 30% (SW30_Control). Then the sample is incubated for 15 days under aerobic conditions at 25 °C (SW30_I) and anaerobic conditions at 55 °C (SW30_B). In parallel, SW30_Control is thermally pretreated with an autoclave for 20 minutes at 120 °C (SWa30_120Control) and 140 °C (SW30_a140Control). Next, these two samples are pretreated for 15 days with aerobic incubation at 25 °C (SW30_a120I and SW30_a140I), as well as an anaerobic incubation at 55 °C (SW30_a120B and SW30_a140B).

On the other hand, Fig. 3 details the sequence followed for the pretreatment of the material based on compost-wheat straw (SKW) samples. As a result of this procedure, another 10 samples are obtained:

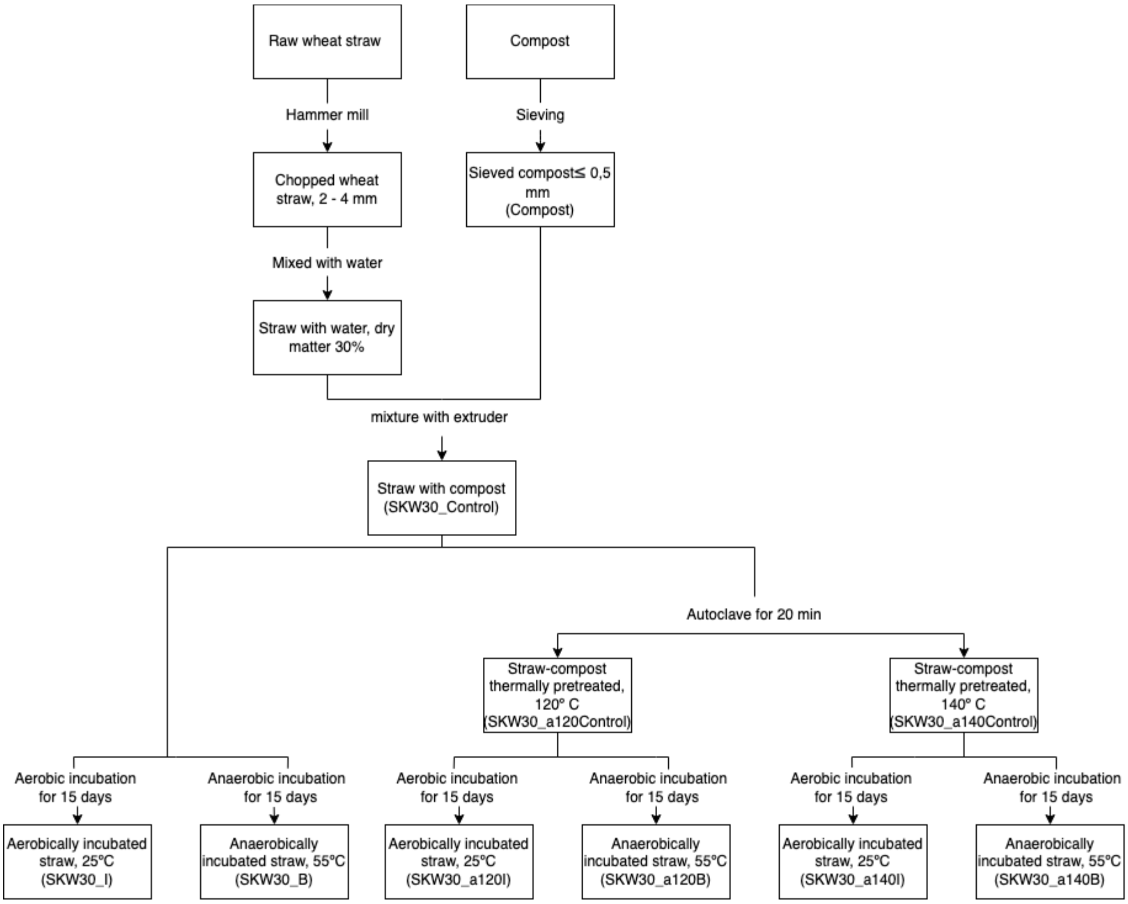

Fig. 3. Sequence of thermobiologial pretreatment of compost – wheat straw (SKW) samples. The ten samples are named in parentheses.

The compost was sieved to remove large fractions of material before carrying out the thermomechanical pretreatment using a sieve shaker Retsch AS 400. Piles of sieves were used to achieve a filtered compost with particles ≤ 0,5 mm. In addition, the compost as a single sample was not subjected to pretreatment to compare its combustion characteristics with the SKW samples.

To achieve homogenization of the wheat straw with compost is used a twin-screw extruder from Lehmann Maschinenbau GmbH. Thus, sieved green waste compost (Compost) is mixed with wheat straw with 30% dry matter. A homogeneous mixture of compost and wheat straw is obtained (SKW30_Control). Then the sample is incubated for 15 days under aerobic conditions at 25 ºC (SKW30_I) and anaerobic conditions at 55 ºC (SKW30_B). In parallel, SKW30_control is thermally pretreated with an autoclave for 20 minutes at 120 ºC (SKW30_a120Control) and 140 ºC (SKW30_a140Control). Next, these two samples are pretreated for 15 days with aerobic incubation at 25 ºC (SKW30_a120I and SKW30_a140I), as well as an anaerobic incubation at 55 ºC (SKW30_a120B and SKW30_a140B).

Lastly, Fig. 4 shows the equipment used for chopping, sieving and mixing:

Fig. 4. Up: hammermill Mütek Systemtechnik MPZ 600 chopping wheat straw. Low-left: sieve shaker Retsch AS 400 sieving compost. Low-right: twin-screw extruder Lehmann mixing homogeneously wheat straw – compost.

4.3 Sequence preparation of pretreated samples for testing

Once the 20 pretreated samples are obtained as explained in section 4.2, they are prepared for calorimeter, ash content and ash melting behavior tests. The test sequence conducted for 19 samples, except for Compost is shown in Fig. 5 below:

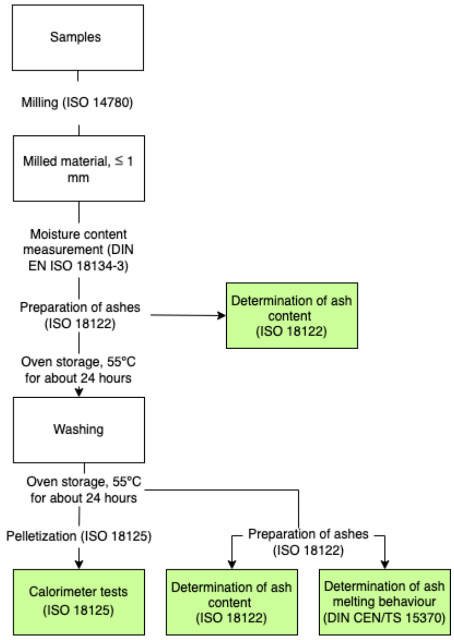

Fig. 5. Preparation of 19 pretreated samples nine wheat straw-based (SW) samples, nine the compost-wheat straw (SKW) and Straw for tests. The combustion tests conducted are shown in green.

The 19 samples pretreated are initially subjected to milling and then stored before the moisture content measurement. Once the moisture content is determined, the ashes are prepared, and the ash content is determined according to ISO 18122. In Fig. 5 the ash content is determined twice before and after the washing process to compare the values. Next, the samples are stored for 24 hours in an oven at 55 ºC to dry them until they reach equilibrium with the temperature and humidity of the laboratory. Then the washing process is conducted for nine SW samples and nine SKW samples and stored in an oven for 24 hours at 55 ºC again. Finally, three tests are performed: calorimeter, ash content and ash melting behavior. The results are obtained.

On the other hand, as shown in Fig. 6, it was considered that sieved compost (Compost) due to the shape of the material (particle size < 1 mm), there was no need to mill it. In addition, it would not be subjected to the washing procedure to have comparison patterns and not alter their initial composition:

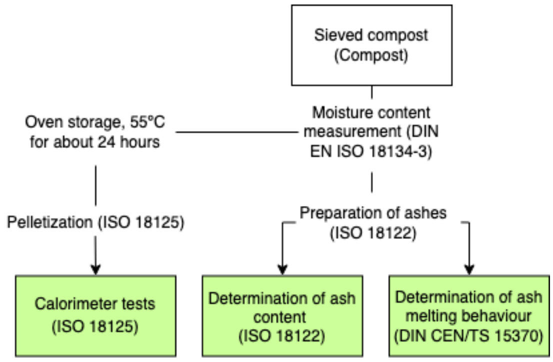

Fig. 6. Preparation of Compost for tests. The combustion tests conducted are shown in green.

The preparation of pretreated samples for testing was followed according to the corresponding standards as indicated in Fig. 5 and Fig. 6, and each test is carried out in duplicate. The details of each step are explained in further detail in this chapter.

4.3.1 Milling

The samples are prepared following ISO 14780 and have a nominal particle top size of 1 mm or less [37]. To achieve this, it is used an Ultra Centrifugal Mill Retsch ZM 200. All the materials are milled, except for the sieved compost (Compost), as it has already a particle size of less than 1 mm. An example of the straw before and after milling is shown below:

Fig. 7. Left: chopped wheat straw (2-4 mm) before milling. Right: straw after milling (≤1mm).

After the milling process, the samples are dried to determine their moisture content.

4.3.2 Determination of moisture content

As shown in Fig. 5 and Fig. 6 the total moisture content is determined for all test samples. To accomplish this, the materials were dried in a laboratory oven at 105 ºC in air atmosphere for 24 hours until constant mass is achieved, following the guideline DIN EN ISO 18134-3 [38].

The total moisture content is calculated on a wet basis by the following formula:

$$M_{ad} = \frac{(m_2 - m_3)}{(m_2 - m_1)} * 100$$

where,

m_1 is the mass in grams of the empty dish plus lid;

m_2 is the mass in grams of the dish plus lid plus test portion before drying;

m_3 is the mass in grams of the dish plus lid plus test portion after drying.

The results once obtained shall be calculated to two decimal places and the mean value of both determinations shall be rounded to the nearest 0,1% for reporting [38].

Once this process is completed, the ash content of the samples is determined.

4.3.3 Determination of ash content

The method of determination of ash content is described in ISO 18122 [39] and it is used in this research. The ash content is determined by calculation the mass of the residue remaining after the sample is heated in air under rigidly controlled conditions of time, sample weight and equipment specifications to a controlled temperature of 550 ± 10 °C. It is used an automatic oven Nabertherm with a range capacity of 30 - 3000 °C.

The test is conducted in duplicates. About 1 gram of milled sample weighed in duplicate, brought to incineration through three steps: 105, 250 and 550 °C, in an oxidizing atmosphere reaching a constant weight. The remaining mass after the process represents the inorganic fraction of the starting material.

The ash content on dry basis, A_d, of the sample expressed as a percentage by mass on a dry basis is calculated using the formula provided in ISO 18122 [39]:

$$A_d = \frac{(m_3 - m_1)}{(m_2 - m_1)} * 100 * \frac{100}{100 - M_{ad}}$$

where,

m_1 = is the mass in g of empty dish;

m_2 = is the mass in g of the dish plus the test portion;

m_3 = is the mass in g of the dish plus ash;

M_{ad} = is the % moisture content of the test portion used for determination;

The results once obtained shall be calculated to two decimal places and the mean value shall be rounded to the nearest 0,1% for reporting [39].

4.3.4 Water washing

For the washing process, distilled water is used as a solvent in a ratio material-water of 1:7 grams. Each material, except for Compost and Straw, was placed in a bag, and then distilled water is added. Next, every mixture is homogenized for 4 minutes using a bag mixer with a double paddle system, to efficiently mix the samples, avoiding the risk of cross-contamination. Moreover, during this process, sugar components dissolve and pass into the liquid. Once homogenization has been completed, the liquid is separated (the transfer of the hydrophilic sugar components into the liquid allows the potential for biogas and bioethanol production to be determined) from the solid material manually using a filter and funnel. Subsequently, the process continues with centrifugation.

For the centrifugation process, a Hermle Z 326K centrifuge with a rotor with a maximum radius of 10,3 cm is used. A setting of 12500 rpm for 15 minutes is selected, which achieves a relative centrifugal force (RCF) of 17993 xg. As consequence, test samples are dewatered due to the centrifugal force. Fig. 8 below illustrates the description of the process:

Fig. 8. Description of the washing process: (1) Bag mixer with double pedal and material in a bag on the right; (2) samples after manually liquid separation; (3) centrifugation with a centrifuge Hermle Z 326K; (4) dewatered material after centrifugation.

Once this process is completed, the material is stabilized in an oven at a constant temperature at 55 °C for about 24 hours to then determine its calorific value.

4.3.5 Pelletization and determination of calorific values

The guideline ISO 18125 [23] is followed to determine the calorific value. According to this document and due to the low density of solid biofuels, they shall be tested in a pellet form. As a test portion, a pellet of mass 1,0 ± 0,2 g is pressed with a suitable force to produce a compact, unbreakable test piece. To achieve this, a hand-operated press IKA from Werke GmbH & Co. is used, as shown in Fig. 9 below:

Fig. 9. Pelletization process. Left: hand press IKA and sample. Right: pellets prior to be tested in the calorimeter.

The pellet once obtained, is tested in the calorimeter. The tests are conducted in duplicate. The calorimeter used corresponds to an IKA C200.

The experiment consists of carrying out quantitatively a combustion reaction (in high-pressure oxygen in the bomb) to define products of combustion and of measuring the change in temperature caused by the total bomb process [23]. For this purpose, the sample pellet is placed inside the bomb and 1 ml of distilled water is also added inside. The bomb is then assembled and filled slowly with pure oxygen for about 30 seconds with a pressure of 30 bar [23]. After this, the bomb is ready to be mounted in the calorimeter can and once set up, the test begins. Fig. 10 describes the process:

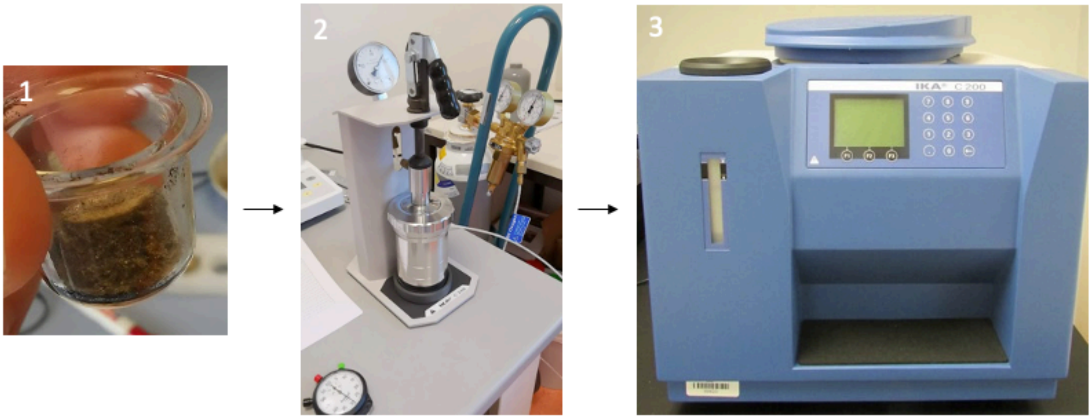

Fig. 10. Preparation for calorimeter test: (1) Pellet to be placed inside the bomb; (2) Bomb being filled with oxygen at 30 bar for 30 seconds; (3) Calorimeter IKA C200.

Once the tests have been completed, the calorimeter provides the GCV for each pellet sample tested. The formula provided in ISO 18125 was used to calculate the NCV [23]:

$$q_{V,net,m} = \left[q_{V,gr,d} - 206\, w(H)_d\right] * (1 - 0{,}01\, M) - 23{,}0\, M$$

where,

$q_{V,net,m}$ = Net calorific value at constat volume, in [J/g];

$q_{V,gr,d}$ = Gross calorific value at constant volume, in [J/g];

$w(H)_d$ = Hydrogen content of the moisture free (dry) biofuel, in [%];

M = Moisture content; on the air – dried basis, M = Mad, in [%].

For the samples studied, and according to the literature reviewed [20], [27], [28], a wheat straw hydrogen content value w(H)d of 5,5% on dry basis is used. Moisture content M is obtained as already explained in section 4.3.2.

4.3.6 Determination of ash melting behavior

The method of determination of ash melting behavior is followed according to CEN/TS 15370-1 [40]. The test method described in the standard provides information about fusion and melting behavior of the composite inorganic constituents of the solid biofuel ash at high temperatures. Furthermore, the guideline defines four characteristic temperatures [40]:

1. Shrinkage starting temperature (SST): temperature is defined as when the area of the test piece falls below 95 % of the original test piece area at 550 ºC due to shrinking of the test piece. Shrinkage may be due to liberation of carbon dioxide and volatile alkali compounds. It may also be due to sintering and may be a first sign of partial melting.
2. Deformation temperature (DT): temperature at which the first signs of melting occur. Deformation temperature can be seen as rounding of the edges, smoothing of surfaces, expansion of the cylinder or general changing of the cylinder shape.
3. Hemisphere temperature (HT): temperature at which the test piece forms approximately a hemisphere i.e., when the height is half of the base diameter.
4. Flow temperature (FT): temperature at which the ash is spread out over the supporting tile in a layer, the height of which is half of the height of the test piece at the hemisphere temperature.

Fig. 11 helps to illustrate every characteristic temperature [40]:

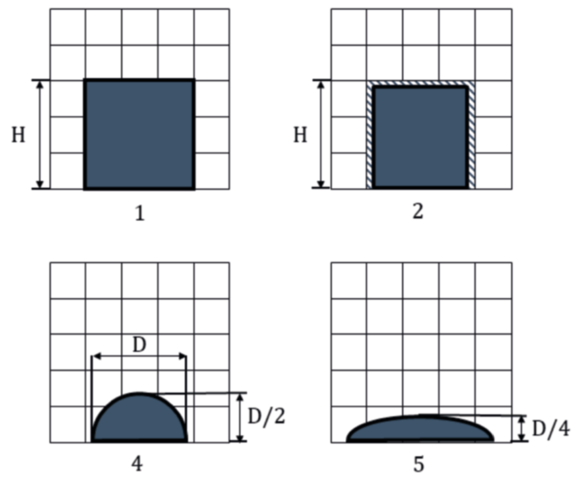

Fig. 11. Ash melting temperatures: (1) Original shape at reference (ashing) temperature; (2) SST, Shrinkage starting temperature; (3) DT, Deformation temperature; (4) HT, Hemisphere temperature; (5) FT, Flow temperature.

To get reproducible results, duplicates are carried out for each sample. The thermo-optical analysis is conducted using a Heating Microscope Hesse EM301. The outer shape changes of each specimen are recorded as the temperature increased from 550 to 1500 °C.

The ash used for the test is a homogeneous material, prepared from the fuel by ashing at 550 °C as explained in section 4.3.3 according to the guideline ISO 18122. Then, about 1 gram of ashes is ground in a mortar as fine as possible. Enough of the prepared ash with ethanol is mixed to make a paste which is pressed into a mold with a spring press. Thus, the test piece is allowed to dry and mount on its support as vertically as possible. A smooth cylindrical specimen made of ashes is obtained and introduced in the heating microscope.

Fig. 12 below shows the cylindrical specimen and the heating microscope during a test:

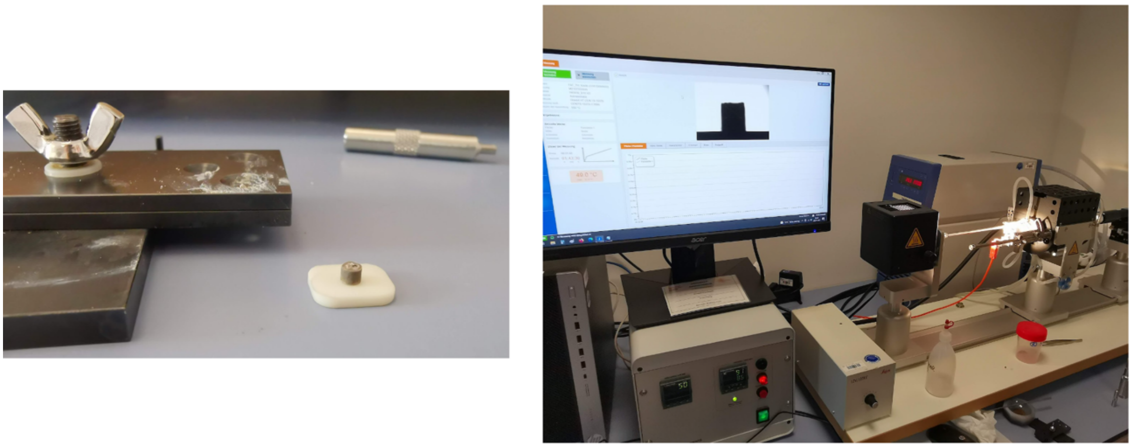

Fig. 12. Procedure to determine the characteristic temperatures. Left: cylindrical specimen made of ashes. Mold on the left side and spring press on back. Right: Heating microscope during a test.

4.4 Statistical analysis

4.4.1 ANOVA calculation

ANOVA was performed using Microsoft Excel. A two-factor analysis of variance was used considering the information obtained from the duplicates with a $p \leq 0{,}05$. If p-value $\leq 0{,}05$ is concluded that the effect being tested is statistically significant [35].

4.4.2 Two-sample t-Test calculation

A two-sample t-Test calculation was performed using Microsoft Excel. It was considered a null hypothesis $H_0: \mu_1 \leq \mu_2$. The alternative hypothesis is considered as a two-sided hypotheses test $H_1: \mu_1 > \mu_2$. Besides an $\alpha = 0{,}025$ is considered according to the literature [36]. The results are calculated using the information obtained from the duplicates.

5. Results and discussion

5.1 Ash content

5.1.1 Ash content for wheat straw based (SW) samples

The ash content results for the nine pretreated SW samples before and after the washing process and Straw, are presented in Table 9:

Table 9. Ash content of nine pretreated wheat straw-based (SW) samples before and after the washing process and untreated Straw. SW30, straw with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

Samples	Ash content (% d.b) [a]	
	Unwashed pretreated samples	Washed pretreated samples
SW30_a120B	5,9	0,5
SW30_I	6,1	1,6
SW30_B	5,5	2,4
SW30_a140B	5,3	2,5
SW30_Control	5,8	2,5
SW30_a140I	5,7	2,8
SW30_a120I	5,7	3,5
SW30_a120Control	6,1	3,9
SW30_a140Control	5,7	4,0
	Untreated	
Straw	6,2	

[a] Average results from duplicates.

As explained in section 4.3, the samples are already pretreated and the difference between one stage and the other is the washing phase. Fig. 13 below shows graphically the results obtained:

Fig. 13. Ash content variation of nine pretreated wheat straw-based (SW) samples and Straw before and after the washing process. SW30, straw with water, dry matter 30%; a: autoclaved at 120 °C or 140 °C; I: aerobically incubated for 15 days at 25 °C; B: anaerobically incubated for 15 days at 55 °C.

Untreated straw has the highest ash content average with 6,2%. This value is within the range of values found in the literature for wheat straw [22] as already explained in section 3.2.1. Besides, in all nine unwashed pretreated SW samples, it is possible to observe a decrease in the percentage of ash content after the pretreatments compared to untreated straw.

ANOVA was used to determine the significance of pretreatments for nine pretreated SW samples. In this analysis the wheat straw data is left out, since it does not have a composition of 30% dry matter, with the following results in Table 10:

Table 10. ANOVA output for nine pretreated wheat straw-based (SW) samples, unwashed.

Source	Sum of Squares	df	Mean Square	F - value	Prob > F	Remarks
Autoclave	0,294	2	0,147	7,419	0,0125	Significant
Incubation	0,396	2	0,198	9,992	0,0052	Significant
Interaction	0,401	4	0,100	5,065	0,0204	Significant
Error	0,178	9	0,020			
Total	1,269	17				

According to the results obtained from Table 10, the autoclave pretreatment at either 120 °C or 140 °C significantly affects the ash content, likewise, the incubation pretreatment, either aerobic at 25 °C or anaerobic at 55 °C significantly affects the ash content. It is possible to conclude this because both results have a p-value $< 0,05$.

On the other hand, the interaction of both pretreatments, i.e., (1) the interaction of autoclave pretreatment at 120 °C in conjunction with aerobic incubation at 25°C or anaerobic at 55 °C or (2) the interaction of autoclave pretreatment at 140 °C in conjunction with aerobic incubation at 25 °C or anaerobic at 55 °C, is shown to be significant, since a p-value $< 0{,}05$ was obtained. These trends can be seen in Fig. 14 below:

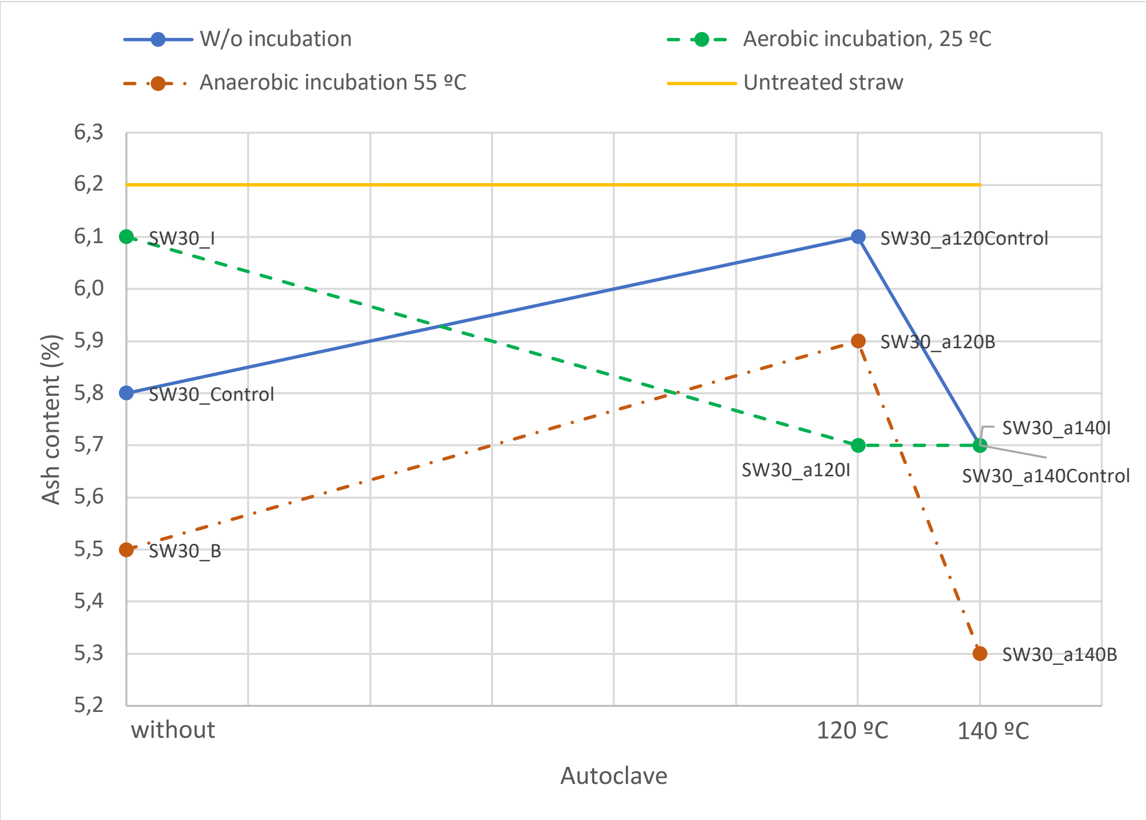

Fig. 14. Ash content variation of nine pretreated and unwashed SW samples and Straw without any pretreatment. SW30, straw with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

Since the lines representing the autoclave pretreatment in the plot are not parallel, this suggests an interaction effect between autoclave and the type of incubation (the lines would be approximately parallel if there were no interaction) reaffirming that the pretreatments of autoclaving, incubation and their respective interaction significantly affect the response, as described above.

In addition, if the average ash content of untreated wheat straw is considered as shown in Fig. 14, the use of the autoclave, the various types of incubation and the interaction between them have an ash content reduction effect.

On the other hand, among the washed pretreated SW samples in Fig. 13, it is possible to observe the positive impact of the washing process together with the pretreatments in the decrease of the ash content when compared to SW samples only pretreated. This reduction is due, as expected because the removal of different minerals that favor the formation of ash, such as K, Cl or Na [8]–[10] during the washing as described in section 3.4. To test this hypothesis, it was decided to perform a two-sample t-Test analysis. It was considered as hypothesis null and alternative hypothesis as follow:

$$H_0: \mu_{\text{unwashed samples}} \leq \mu_{\text{washed samples}}$$
$$H_1: \mu_{\text{unwashed samples}} > \mu_{\text{washed samples}}$$

Where μ, is the mean ash content of unwashed or washed samples. As for the ANOVA analysis, the wheat straw data is left out since it does not have a composition of 30% dry matter. The results are shown in Table 11:

Table 11. t-Test: Two-Sample assuming unequal variances. Results for nine unwashed pretreated SW samples and 9 washed pretreated SW samples based on the ash content.

	Unwashed pretreated SW samples	Washed pretreated SW
Mean (%)	5,764	2,620
Variance	0,068	1,230
Observations	9	9
Pearson Correlation	0,649	
Hypothesized Mean Difference	0	
df	16	
t Stat	8,279	
P(T<=t) one-tail	1,772E-07	
t Critical one tail	2,120	

Within Table 11 it is possible to observe a t-Stat (8,279) > t Critical (2,120), thus the null hypothesis can be immediately rejected. This is also in line with the p-value result since the value 1,772E-07 < 0,025, therefore the null hypothesis H_0 is rejected and it is possible to accept the alternative hypothesis H_1. Thus, it is concluded that there is sufficient evidence to indicate that the ash content before the washing process is significantly greater than after the washing process.

Therefore, it is possible to conclude based on the data obtained, that for the SW pretreated samples, all the pretreatments applied separately, i.e., the use of autoclave (at 120 ºC and 140 ºC), as well as incubation (either aerobic at 25 ºC or anaerobic at 55 ºC) significantly affect the ash content response. This response is also observed when the treatments were performed together. Furthermore, when the response is contrasted with the initial ash content of untreated wheat straw, a reduction in ash content is observed in all samples.

On the other hand, before the washing process, there is a significantly higher ash content than after for the samples studied. Therefore, based on the analyses described above, it is possible to conclude that washing has a positive effect on decreasing ash content. If both results are quantified with respect to the ash content of untreated straw, an average reduction of 5,8% was achieved after pretreatments and 55,8% after pretreatments and washing.
Lastly, all the results obtained show an ash content of less than 10%, satisfying the ISO 17225-6 for residential, small commercial and public building applications.

5.1.2 Ash content for compost-wheat straw (SKW) samples

The ash content results for nine pretreated SKW samples and Compost, before and after the washing process are presented in Table 12:

Table 12. Ash content of nine pretreated compost-wheat straw (SKW) samples before and after the washing process and untreated Compost; SKW30 straw-compost and water, dry matter 30%; a: autoclaved at 120ºC or 140ºC; I: aerobically incubated for 15 days; B: anaerobically incubated for 15 days.

Samples	Ash content (% d.b) [a]	
	Unwashed pretreated samples	Washed pretreated samples
SKW30_a140I	33,6	12,9
SKW30_Control	43,7	22,2
SKW30_a140B	27,5	22,3
SKW30_I	38,1	22,5
SKW30_a140Control	34,0	22,8
SKW30_a120I	48,5	23,9
SKW30_a120Control	39,9	24,3
SKW30_a120B	43,3	24,9
SKW30_B	43,3	25,4
	Untreated	
Compost	69,0	

[a] Average results from duplicates.

It is possible to observe that the Compost sample has the highest ash content with 69%, these values are within the values found in the literature [30], [31], as clarified in section 3.3.

On the other hand, when comparing the ash content between Compost and unwashed pretreated SKW samples, the latter shows a lower ash content. This is because the SKW samples are a homogeneous mixture of wheat straw – compost; therefore, there is less amount of compost material in them. Fig. 15 below shows graphically the ash content of Compost, unwashed pretreated SKW samples, and washed pretreated SKW samples:

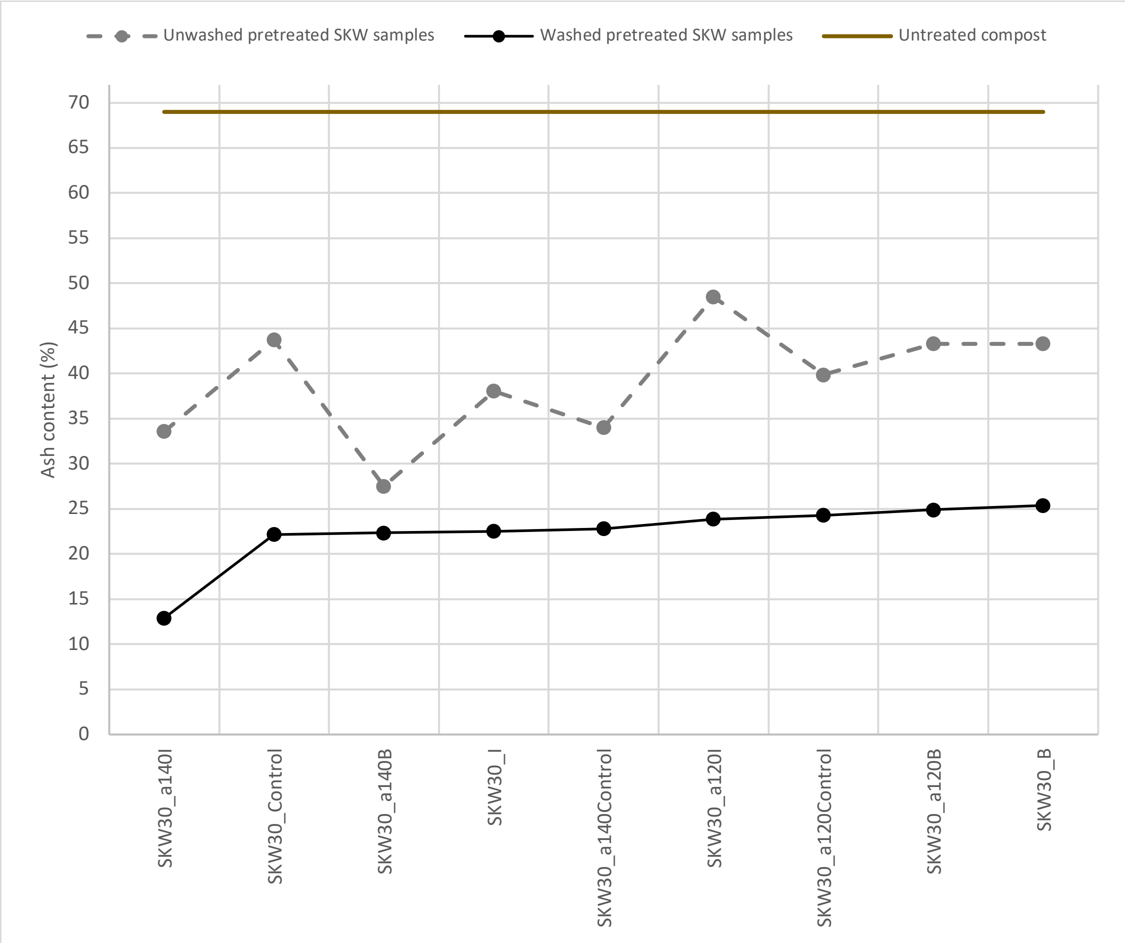

Fig. 15. Ash content variation of nine pretreated compost-wheat straw (SKW) samples before and after the washing process and untreated compost. SKW30 straw-compost and water, dry matter 30%; a: autoclaved at 120ºC or 140ºC; I: aerobically incubated for 15 days; B: anaerobically incubated for 15 days.

Within the unwashed pretreated SKW samples great variability is observed. For example, SKW30_a120I has the highest ash content with 48,5% while another similarly pretreated sample SKW30_a140I has 33,6%. A similar phenomenon is observed with sample SKW30_a120B with 43,3% ash content, while SKW30_a140B has 27,5% ash content. To be able to correctly interpret the impact of pretreatments ANOVA was used to determine its significance. In this analysis compost data is left out, since it is not a sample mixed with wheat straw, with the following results in Table 13:

Table 13. ANOVA output for nine pretreated compost-wheat straw (SKW) samples, unwashed.

Source	Sum of Squares	df	Mean Square	F - value	Prob > F	Remarks
Autoclave	506,257	2	253,129	11,916	0,003	Significant
Incubation	12,075	2	6,038	0,284	0,759	Not Significant
Interaction	155,220	4	38,805	1,827	0,208	Not Significant
Error	191,187	9	21,243			
Total	864,740	17				

According to the results obtained from Table 13, and in contrast to the data obtained for the SW samples analyzed in section 5.1.1, only the autoclave pretreatment at either 120 ºC or 140 ºC significantly affects the ash content, since its p-value 0,003 < 0,05.

On the other hand, the incubation pretreatment either aerobic incubation at 25ºC or anaerobic at 55 ºC as well as the interaction between autoclave and incubation shows that they are not varying the ash content response.

To verify these results, the ash content behavior of each sample as a function of the pretreatments applied is shown in Figure 16:

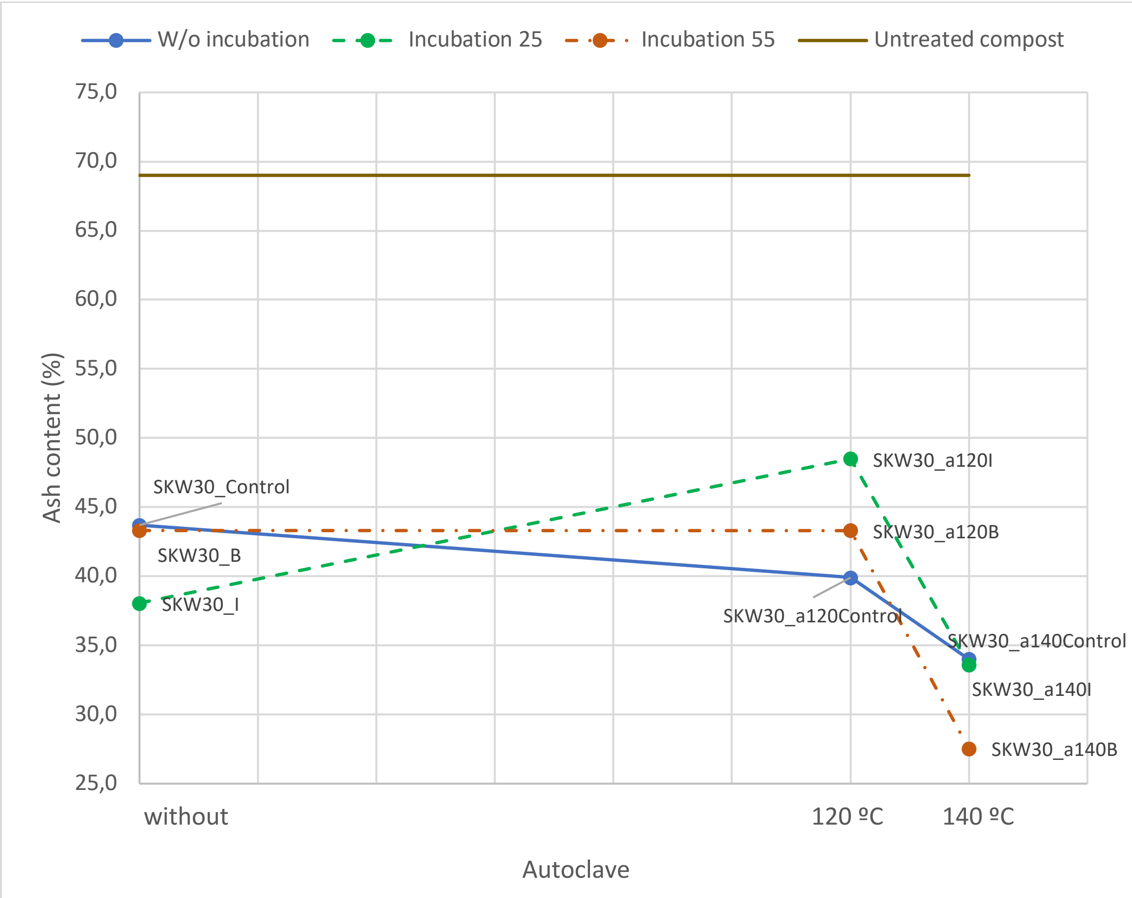

Fig. 16. Ash content variation of nine pretreated and unwashed SKW samples and Untreated compost. SKW30, straw-compost with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

Since the lines representing the autoclave pretreatment in the plot are not parallel, this suggests an interaction effect between autoclave and the type of incubation (the lines would be approximately parallel if there were no interaction). This is in contradiction with the result presented in Table 13. For this reason, it is recommended in the literature [35] that these graphs should not be utilized as the sole technique of data analysis because their interpretation is subjective and their appearance is often misleading.

To confirm the conclusions presented above, i.e., that only the autoclave variable is significantly affecting the ash content response, it was decided to run a new ANOVA, but this time leaving aside the interaction variable. The results are presented in Table 14:

Table 14. ANOVA output for nine pretreated compost-wheat straw (SKW) samples, unwashed. Interaction is not considered.

Source	Sum of Squares	df	Mean Square	F - value	Prob > F	Remarks
Autoclave	593,407	5	118,681	4,577	0,019	Significant
Incubation	12,075	2	6,038	0,233	0,796	Not Significant
Error	259,258	10	25,926			
Total	864,740	17				

Again, the autoclave variable significantly affects ash content (p-value 0,019 < 0,05) while the incubation period is not significant (p-value 0,796 > 0,05). Therefore, it is concluded that for SKW samples the only variable that significantly affects the ash content is the use of autoclave.

In this aspect, it is observed in Table 12 and Fig. 15 that unwashed pretreated SKW samples that were subjected to autoclave treatment at 140 ºC: SKW30_a140B, SKW30_a140I and SKW30_a140Control show the lowest ash content of the nine samples. Compared to the pretreated sample without heat treatment SKW30_Control, ash reduction values of 37%, 23% and 22%, respectively, are observed. That is an average reduction of 27,3%.

If the same comparison is made for the case of autoclaving at 120ºC, SKW30_a120Control and SKW30_a120B show a reduction in ash content of 8,8% and 0,9%, respectively. But SKW30_a120I shows an increase in ash content of 10,9%. That is an average increase of just 0,4%.

Therefore, better results are observed when pretreatment in autoclave at 140ºC is used. Autoclaving at 120ºC shows a smaller decrease in the average ash content and, in addition, the reduction of this variable was not always achieved.

On the other hand, among the washed pretreated SKW samples in Fig. 15, it is possible to observe the positive impact of the washing process together with the pretreatments in the decrease of the ash content when compared to unwashed pretreated SKW samples. Furthermore, after the washing process, the ash content of the samples seems to have stabilized around 22-25%, except for the SKW30_a140I material, which shows an ash content of about 13%. Washing is likely affecting the ash content due to its ability to remove minerals that favor ash formation [8]–[10] as described in section 3.4.

To test this hypothesis, it was decided to perform a two-sample t-Test analysis. It was considered as hypothesis null and alternative hypothesis as follow:

$$H_0: \mu_{\text{unwashed samples}} \leq \mu_{\text{washed samples}}$$
$$H_1: \mu_{\text{unwashed samples}} > \mu_{\text{washed samples}}$$

Where μ, is the mean ash content of unwashed or washed samples. Compost data is left out since it is not a sample mixed with wheat straw. The results are shown in Table 15:

Table 15. t-Test: Two-Sample assuming unequal variances. Results for nine unwashed pretreated SKW samples and nine washed pretreated SKW samples based on the ash content.

	Unwashed pretreated SKW samples	Washed pretreated SKW
Mean (%)	39,095	22,360
Variance	42,103	13,926
Observations	9	9
Pearson Correlation	28,015	
Hypothesized Mean Difference	0	
df	16	
t Stat	6,707	
P(T<=t) one-tail	2,516E-06	
t Critical one tail	2,120	

Within Table 15 it is possible to observe a t Stat (6,707) > t Critical (2,120), thus the null hypothesis can be immediately rejected. This is also in line with the p-value result since the value 2,516E-06 < 0,025, therefore the null hypothesis H_0 is rejected and it is possible to accept the alternative hypothesis H_1. It is concluded that there is sufficient evidence to indicate that the ash content before the washing process is significantly greater than after the washing process.

Washed pretreated SKW samples showed a strong decrease in the ash content with an average of 22,4% ± 3,7%. The results from the washing process are summarized in Table 16:

Table 16. Average ash content for nine SW samples and nine SKW samples.

	Ash content (% d.b), average	
	SW samples	SKW samples
Unwashed and pretreated	5,8 ± 0,3	39,1 ± 6,5
Washed and pretreated	2,6 ± 1,1	22,4 ± 3,7

After the washing process, an average ash reduction of 43% was achieved for SKW samples, while an average ash reduction of 55% was achieved for SW samples.

It is possible to conclude that washing has a positive effect on decreasing ash content in SKW samples.

Lastly, SKW samples show an ash content greater than 10%, not satisfying the ISO 17225-6 for residential, small commercial and public building applications since a homogeneous mixture of compost and straw was made. To obtain values within the standard, it is required to adjust the percentage of compost mixed with wheat straw.

5.2 Calorific values and moisture content

5.2.1 Calorific values and moisture content for wheat straw based (SW) samples

The calorific results of pellets obtained from SW samples pretreated and washed, untreated Straw and its and moisture content, are presented in Table 17:

Table 17. Gross calorific value and Net calorific value of SW pellets pretreated, after washing. SW30, straw with water, dry matter 30%; a: autoclaved at 120ºC or 140ºC; I: aerobically incubated for 15 days; B: anaerobically incubated for 15 days.

Samples	GCV ($kJ.kg^{-1}$) [a]	Moisture content (% d.b) [a]	NCV ($kJ.kg^{-1}$) [a]
SW30_a140B	18175	5,2	16032
SW30_I	18093	5,3	15931
SW30_Control	17913	3,0	16207
SW30_a120Control	17765	4,0	15880
Straw (untreated)	17698	2,9	16022
SW30_B	17547	6,1	15279
SW30_a120B	17521	5,3	15396
SW30_a140Kont	17508	3,7	15684
SW30_a120I	17154	4,9	15121
SW30_a140I	16907	4,9	14887

[a] Average results from duplicates

As expected, there are no significant differences in the moisture content of SW samples, because all samples are dried at 105 ºC in air atmosphere for 24 hours until a constant mass is reached. The GCV and NCV trends are presented in Figure 17:

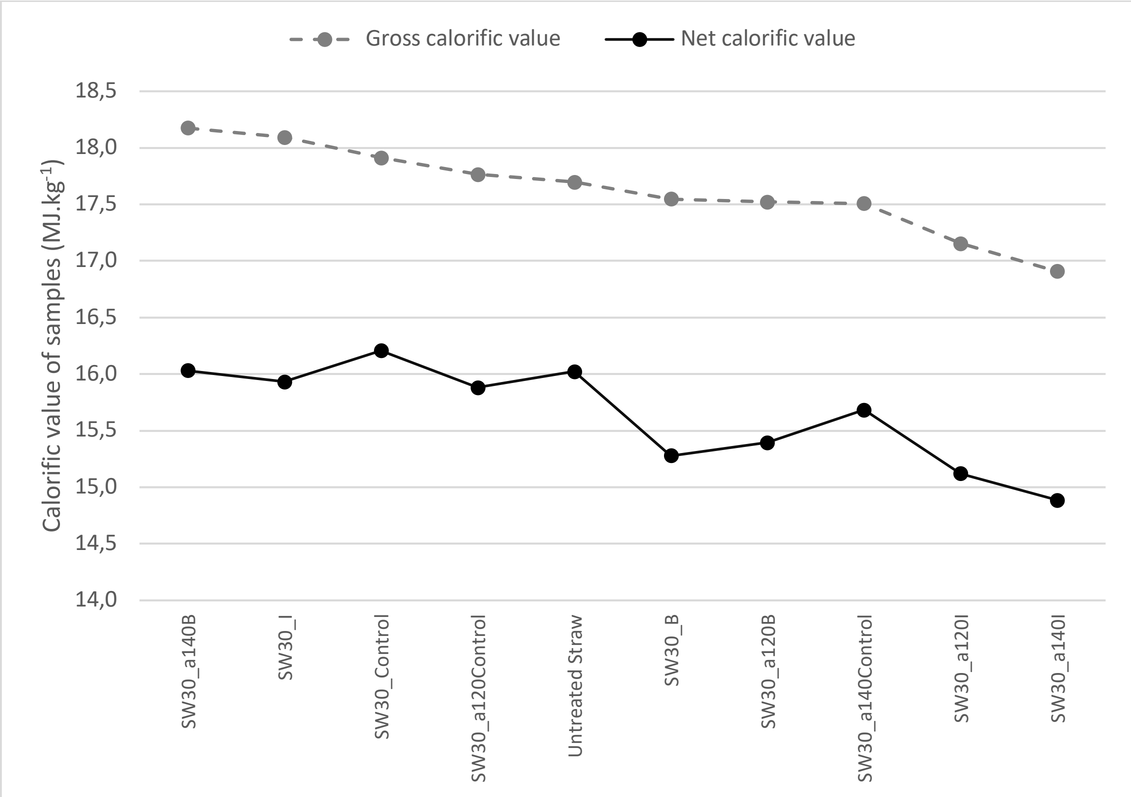

Fig. 17. Variation of GCV and NCV for SW pellets with different pretreatments. SW30, straw with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

Although the NCV is the most important characteristic of the fuel, it depends on the moisture content. Therefore, the GCV results will be analyzed mainly as these are directly delivered by the calorimeter. The average GCV of Untreated Straw pellets was 17,7 MJ/kg, this value is within the normal range for this type of material [22] as explained in section 3.2.2. Nine pretreated SW pellets also fall within the normal GCV ranges for wheat straw [22] with a range between 16,9 (SW30_a140I) – 18,2 MJ/kg (SW30_a140B) and an average of 17,6 ± 0,4 MJ/kg. Furthermore, the disparity of GCVs in pretreated SW sample pellets, as shown in Fig. 17, suggests that the pretreatments are not significantly influencing the calorific value. To evaluate this hypothesis, an ANOVA analysis is performed with the results in Table 18. In this analysis the untreated straw data is left out since it does not have a composition of 30% dry matter:

Table 18. ANOVA output for nine pretreated wheat straw (SW) pellets, washed.

Source	Sum of Squares	df	Mean Square	F - value	Prob > F	Remarks
Autoclave	485342,111	2	242671,056	0,481	0,633	Not Significant
Incubation	500460,778	2	250230,389	0,496	0,624	Not Significant
Interaction	1795581,556	4	448895,389	0,891	0,507	Not Significant
Error	4536066,500	9	504007,389			
Total	7317450,944	17				

It is observed that the main effects of autoclave (p-value 0,633), incubation (p-value 0,624) and their interaction (p-value 0,507) are not significantly influencing the response, i.e., the calorific value, because all p-values are greater than 0,05.

Therefore, it is possible to conclude that pretreatments did not show any impact on the GCV, which according to literature is purely dependent on the material used, i.e. the chemical composition of the raw material and can therefore not be influenced [16].
Furthermore, the pellets studied in this section were washed but showed no significant difference in GCV compared to untreated wheat straw, suggesting that washing has a minor impact. This corroborates the literature studied in section 3.4 where it was found that the washing process with water has a minimal impact on the GCV [10].
Lastly, the calorific results allow all the SW pellets to satisfy industrial standards according to ISO 17225-6 since its value NCV is always greater than 14,5 MJ/kg [19].

5.2.2 Calorific values and moisture content for compost-wheat straw (SKW) samples

The results of the calorific value for pellets based on SKW samples after washing and their respective moisture content are presented in Table 19:

Table 19. Gross calorific value and Net calorific value of SKW pellets after different pretreatments, after washing. SKW30, straw-compost with water, dry matter 30%; a: autoclaved at 120ºC or 140ºC; I: aerobically incubated for 15 days; B: anaerobically incubated for 15 days.

Samples	GCV ($kJ.kg^{-1}$) [a]	Moisture content (% d.b) [a]	NCV ($kJ.kg^{-1}$) [a]
SKW30_a140Control	16762	2,0	13955
SKW30_a120B	16743	3,5	13691
SKW30_a140I	16708	4,8	13447
SKW30_a120I	15997	3,6	12953
SKW30_a140B	15544	4,5	12383
SKW30_Control	15280	3,3	12303
SKW30_B	14306	4,2	11236
SKW30_a120Control	13985	3,8	10995
SKW30_I	12623	4,7	9571
Compost	4716	2,3	2138

[a] Average results from duplicates

From Table 19, there are no significant differences in the moisture content of SKW samples because are dried at 105 ºC in air atmosphere for 24 hours until a constant mass is reached. Fig. 18 graphs the results:

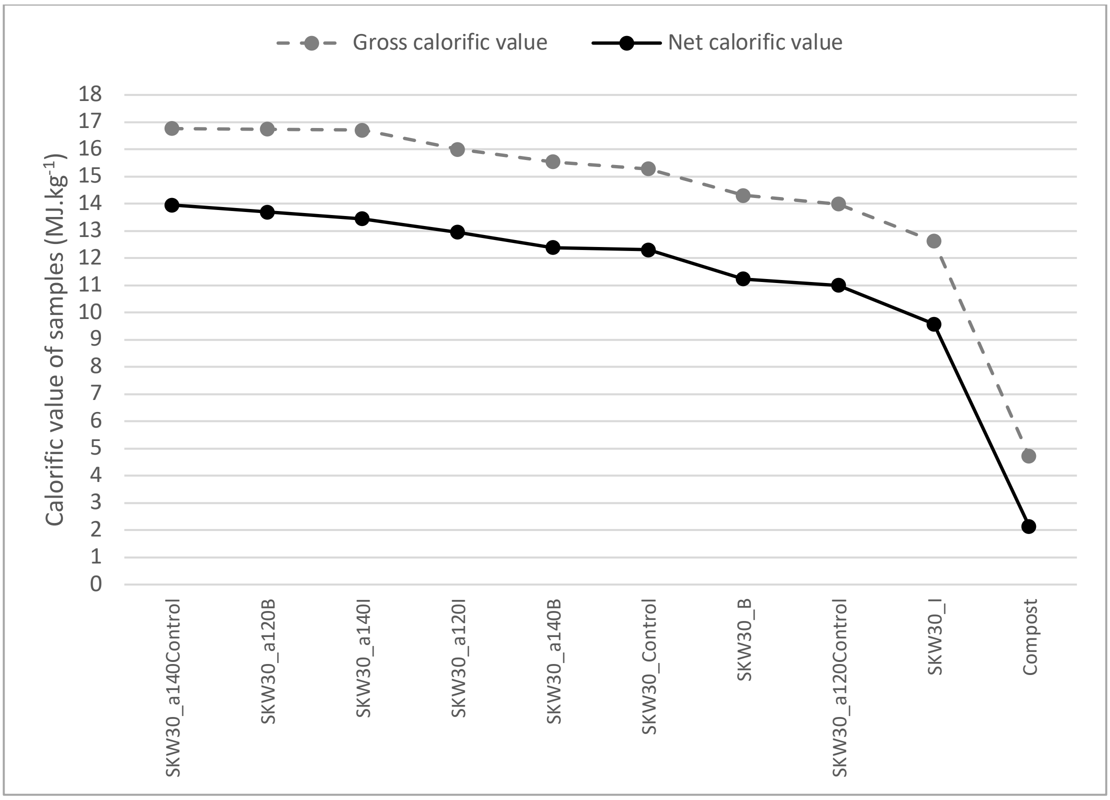

Fig. 18. Variation of GCV and NCV for SKW pellets with different pretreatments. SKW30, straw-compost with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

As in section 5.2.1, the analysis of results will be carried out for GCV, since it is a value delivered directly by the calorimeter and does not consider the moisture content.
It is possible to observe that the Compost pellet presented the lowest GCV with 4,7 MJ/kg. In general, the nine SKW pellets recorded an average GCV of 15,3 ± 1,4 MJ/kg.
Furthermore, it is observed that four pellet samples (SKW30_a120B, SKW30_a140I, SKW30_a120I and SKW30_a140B) that were subjected to incubation pretreatment together with autoclaving have a higher GCV than pellets that were subjected only to incubation (SKW30_B, SKW30_I). In addition, when observing the autoclave pretreatments alone, a better result was obtained with the autoclave at 140 °C than at 120°C.
To evaluate the impact of pretreatments on the response variable GCV, an ANOVA analysis was performed. In this analysis, Compost pellets are not considered because they are not mixed with wheat straw. The results are shown in Table 20:

Table 20. ANOVA output for nine pretreated compost-wheat straw (SKW) pellets, washed.

Source	Sum of Squares	df	Mean Square	F - value	Prob > F	Remarks
Autoclave	15987067,111	2	7993533,556	34,103	6,305E-05	Significant
Incubation	534996,778	2	267498,389	1,141	0,36164	Not Significant
Interaction	16727524,889	4	4181881,222	17,841	0,00026	Significant
Error	2109573,500	9	234397,056			
Total	35359162,278	17				

It is observed that the main effects of autoclave (p-value 6,305E-05) and interaction (p-value 0,00026) are significantly influencing the response because p-values are lower than 0,05. While incubation alone is not significant. Therefore, when working with SKW pellets, both the use of autoclave and the incubation-autoclave interaction affect the calorific value.
The results obtained from ANOVA suggest that:

- When autoclaving (regardless of temperature) is used in conjunction with incubation (regardless of type), relatively similar results are obtained, generating an increase in GCV. On average these four types of pellets (SKW30_a120B, SKW30_a140I, SKW30_a120I and SKW30_a140B) had a GCV of 16,2 MJ/kg, which is equivalent to a 6% improvement over the SKW30_Control pellets that were not subjected to pretreatment.
- In addition, it is observed that the use of autoclave alone at 140 °C obtains better results than autoclave at 120 °C. Autoclave at 140 °C shows an improvement of about 10% over the SKW30_control pellets that were not subjected to thermal pretreatment.
- Finally, the use of autoclave alone at 120°C seems to be negatively affecting the GCV result with respect to the SKW30_Control pellets, since there is a reduction of around 8% in GCV.

In addition, according to the influence of lignin described in section 3.3.1, it was found in the literature that the higher the lignin content, the higher the GCV [11]. Similarly, Beuel et al., reported lignin degradation for wheat straw-wheat compost mixtures under aerobic conditions comparable to those discussed here [6].

Therefore, a similar effect was expected in this investigation: due to the degradation of lignin and its lower content, a lower calorific value was also expected. Indeed, the pellets subjected to aerobic incubation SKW30_I recorded the lowest GCV with an average value of 12,6 MJ/kg. However, the pellets that were subjected to aerobic incubation in conjunction with autoclaving at 120 ºC and 140 ºC such as SKW30_a120I and SKW30_a140I recorded GCVs of 15,9 and 16,7 MJ/kg respectively. These values are among the best performers among the SKW pellets.

Lignin degradation may play a role in decreasing the calorific value, as evidenced in the SKW30_I sample; however, it is not possible to conclude categorically, since the SKW30_a120I and SKW30_a140I materials were subjected to similar treatments and the ANOVA table indicates that the incubation variable is not affecting the calorific value.

To understand the cause of this difference, the results obtained from the duplicates were re-evaluated and are shown below:

Table 21. GCV results of the two calorimeter tests for SKW30_I, SKW30_a120I and SKW30_a140I.

	GCV (kJ.kg^{-1})		
Samples	First run	Second run	Standard deviation
SKW30_I	12743	12503	170
SKW30_a120I	15574	16419	598
SKW30_a140I	16576	16840	187

It is observed in Table 21 that the differences between the first and second runs are relatively low. The highest error corresponds to 5% for the sample SKW30_a120I; therefore, human error in the experiments can be discarded.

It is hypothesized, thus, that this difference in the GCV for aerobic treatment may have another cause. Lignin is characterized by its high carbon content, so its content is likely to vary with degradation, ultimately affecting the GCV. Therefore, it is recommended to perform an elemental analysis for these three samples to evaluate the carbon content and to elucidate the real effect of lignin degradation.

It is also possible that the washing process is positively affecting GCV, causing an increase in the latter. This is because one of the effects of the reduction in ash content observed in section 5.1.2 (Table 16) is the increase in calorific value [20], and according to the literature studied in section 3.4, the washing process with water has an impact on the GCV, although minimal [10]. The SKW samples achieved an average reduction of about 43% of the ash

content; therefore, to quantify this effect is recommended to perform calorimetric tests for samples before and after washing.
On the other hand, when comparing the average GCV obtained for SW pellets (17,6 MJ/kg) and SKW pellets (15,3 MJ/kg), around 13% less GCV is obtained for the latter. This is expected since the ash content for the SKW samples is higher, and the calorific value of the Compost is low.

Lastly, the calorific results for the nine studied SKW pellets do not satisfy industrial standards according to ISO 17225-6 since its value NCV is always lower than 14,5 MJ/kg [19]. The calorific value of SKW pellets is affected by the high ash content and low calorific value of the compost since these samples were homogeneously mixed. It is therefore recommended to adjust the percentage of compost mixed with straw.

5.3 Ash melting behavior

5.3.1 Ash melting behavior for wheat straw (SW) based samples

The characteristic ash temperatures for mixtures based on SW samples, after washing and untreated straw are summarized in Table 22:

Table 22. Characteristic temperatures for ashes based on nine pretreated and washed SW samples and Straw without any pretreatment. SW30, straw with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

	Ash temperatures (ºC) [a]			
Samples	SST	DT	HT	FT
Straw (untreated)	710	1153	1391	1434
SW30_a140I	719	1437	1455	>1500
SW30_I	724	1342	1386	1422
SW30_120I	746	1268	1456	>1500
SW30_Control	748	>1500	>1500	>1500
SW30_140Control	768	>1500	>1500	>1500
SW30_120Control	770	>1500	>1500	>1500
SW30_B	778	>1500	>1500	>1500
SW30_a120B	783	>1500	>1500	>1500
SW30_a140B	783	>1500	>1500	>1500

[a] Average results from duplicates

Although this work provides data on the four melting temperatures, it was decided to focalize the interest on the shrinkage starting temperature (SST), which according to the guideline DIN CEN/TS 15370-1, is when the first signs of partial melting may be observed [40].
Besides, the heating microscope measured all the SST, but some ash specimens reached DT, HT, and FT above the maximum measurement temperature of 1500 ºC.
Lastly, the use of straw-based fuels, especially in small scale boilers up to 100 kW_{th} is troublesome due to the low softening and melting temperature of the ash [20].

The results of Table 22 are plotted in Fig. 19 below:

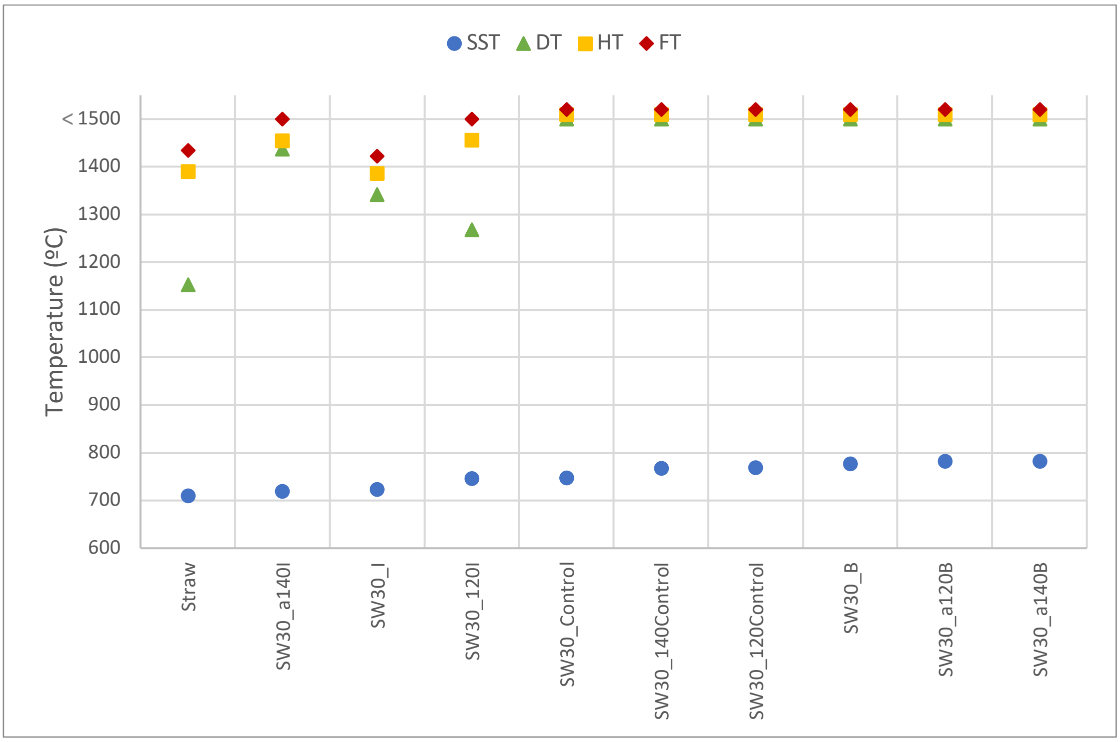

Fig. 19. Characteristic temperatures for ashes based on nine pretreated and washed SW samples and Straw without any pretreatment. SW30, straw with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

Ash of untreated Straw had the lowest average values of the characteristic temperatures. Its SST was determined as 710 °C which can cause serious problems when using this type of fuel in small boilers [20]. Then there is a gradual increase in the SST of the nine samples tested, showing an average of 757 ± 24 °C, equivalent to an improvement of 6,6% over wheat straw without pretreatment. The best results are obtained in the samples that underwent anaerobic treatment (SW30_B) and had autoclave treatment at either 120 °C (SW30_a120B) or 140 °C (SW30_a140B). With respect to Straw, these three materials show an improvement of around 10% respectively.

To understand the main and interaction effects and evaluate if they are statistically significant, two-way ANOVA was performed with respect to the dependent measurement, i.e., SST. Straw data is not considered since it does not have a composition of 30% dry matter. The results are shown in Table 23:

Table 23. ANOVA output for nine pretreated and washed wheat straw (SW) ash pellets.

Source	Sum of Squares	df	Mean Square	F - value	Prob > F	Remarks
Autoclave	807,444	2	403,722	2,803	0,113194	Not Significant
Incubation	8121,444	2	4060,722	28,189	0,000133	Significant
Interaction	630,889	4	157,722	1,095	0,415274	Not Significant
Error	1296,500	9	144,056			
Total	10856,278	17				

It is observed that only the main effects of incubation (p-value 0,000133) are statistically significant because its p-value is below 0,05 generating a response in the SST. On the other hand, autoclave (p-value 0,113194) and contrary to what is shown in Fig. 19 interaction (p-value 0,415274) are not associated with SST.

If the main effect of incubation on SST is analyzed, it is observed that there are dissimilar results. For example, when ashes that underwent anaerobic treatment, i.e., SW30_B, SW30_a120B and SW30_a140B, are compared to ashes that did not receive thermal treatment, SW30_Control, SST improvements of 3,9%, 4,6% and 4,7%, respectively, are obtained; this is an equivalent average improvement of 4,4%. These three materials coincide with those with the greatest increase.

On the other hand, when the same comparison is made for ashes that were subjected to aerobic treatment, i.e., SW30_120I, SW30_I and SW30_a140I, they obtained a decrease in SST of 0,3%, 3,3% and 3,9%, respectively; this is an equivalent average decrease of 2,5%. These three materials had the lowest values after untreated wheat straw.

Therefore, these results suggest that the anaerobic incubation pretreatment has a positive effect on the SW materials since it generates an increase in SST. On the other hand, the aerobic incubation pretreatment decreases SST.

Furthermore, it is feasible that the improvement in nine pretreated samples observed compared to untreated wheat straw is also due to the washing process. As explained in section 3.2.3 and section 3.4, washing removes minerals such as K, Na, Cl or S that decrease the melting temperatures of wheat straw [8]. Consequently, the melting temperatures increase. In addition, similar results to those presented here have been found in the literature for wheat chaff, i.e., SST around 800 °C, and values for DT, HT and FT above 1500 °C, which can be explained precisely by the low K and high SI content [41]. However, this could not be quantified. Future research is recommended to evaluate the ash temperature for pretreated materials prior to washing and after the washing process.

To evaluate the improvement observed concerning wheat straw ashes, a comparison is made between untreated Straw and ashes from SW30_a140B that achieved the best performance with respect to its temperatures. Figures below show the results of the thermo-optical analysis:

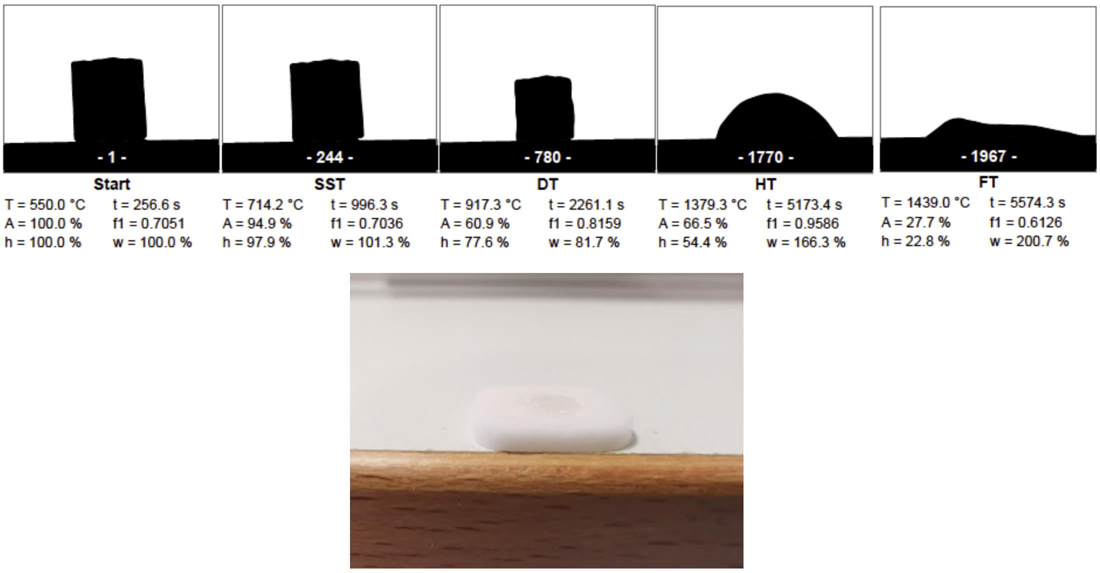

Fig. 20. Characteristic temperatures for untreated wheat straw ashes and photo of the ash pellet once the process is completed.

Fig. 20 correspond to typical values for wheat straw, according to the literature reviewed and explained in section 3.2.3. Within the process, it is possible to observe the four characteristic temperatures and finally the result of the completely melted ashes after the tests were completed. Straw presents the lowest temperatures of all the ashes tested, and as mentioned is problematic for the combustive processes.

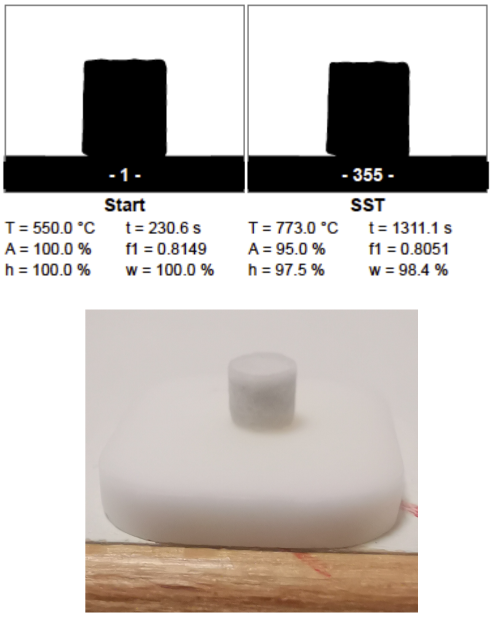

Fig. 21. Characteristic temperatures for SW30_a140B ashes and photo of the ash pellet once the process is completed.

On the other hand, Fig. 21 shows the results for SW30_a140B ashes. It presents the highest temperatures among the materials evaluated in this section. It was only possible to record the SST since DT, HT and FT values are above 1500 °C. In particular, HT and FT values are comparable to the melting temperature of wood and can significantly reduce the technical effort for combustion applications [41]. However, due to the low sintering temperature and the ash content (2,5%, Table 9), it is expected that the application of a moving grate is necessary for pellet combustion [41].

5.3.2 Ash melting behavior for compost-wheat straw (SKW) samples

The characteristic ash temperatures for mixtures based on SKW samples, after washing and untreated Compost, are summarized in Table 24:

Table 24. Characteristic temperatures for ashes based on nine pretreated and washed SKW samples and Compost without any pretreatment. SKW30, straw-compost with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

	Ash temperatures (ºC) [a]			
Samples	SST	DT	HT	FT
SKW30_a140Control	1163	>1500	>1500	>1500
SKW30_a140I	1164	1411	1445	>1500
SKW30_I	1168	1455	>1500	>1500
SKW30_a120Control	1184	>1500	>1500	>1500
SKW30_Control	1185	1455	>1500	>1500
Compost	1189	1441	>1500	>1500
SKW30_a120I	1192	>1500	>1500	>1500
SKW30_B	1215	>1500	>1500	>1500
SKW30_a140B	1268	>1500	>1500	>1500
SKW30_a120B	1368	>1500	>1500	>1500

[a] Average results from duplicates.

Under the same criteria used in section 5.3.1, it was decided to focus this study on SST. From the information obtained from Table 24, it is observed that pure Compost has an SST of 1189 ºC. It is also observed that when a homogeneous mixture of compost-wheat straw is made, as in the case of the nine SKW samples, the SST values remain above 1163 ºC, preserving this property.

The results of Table 24 are graphed in Fig. 22 below:

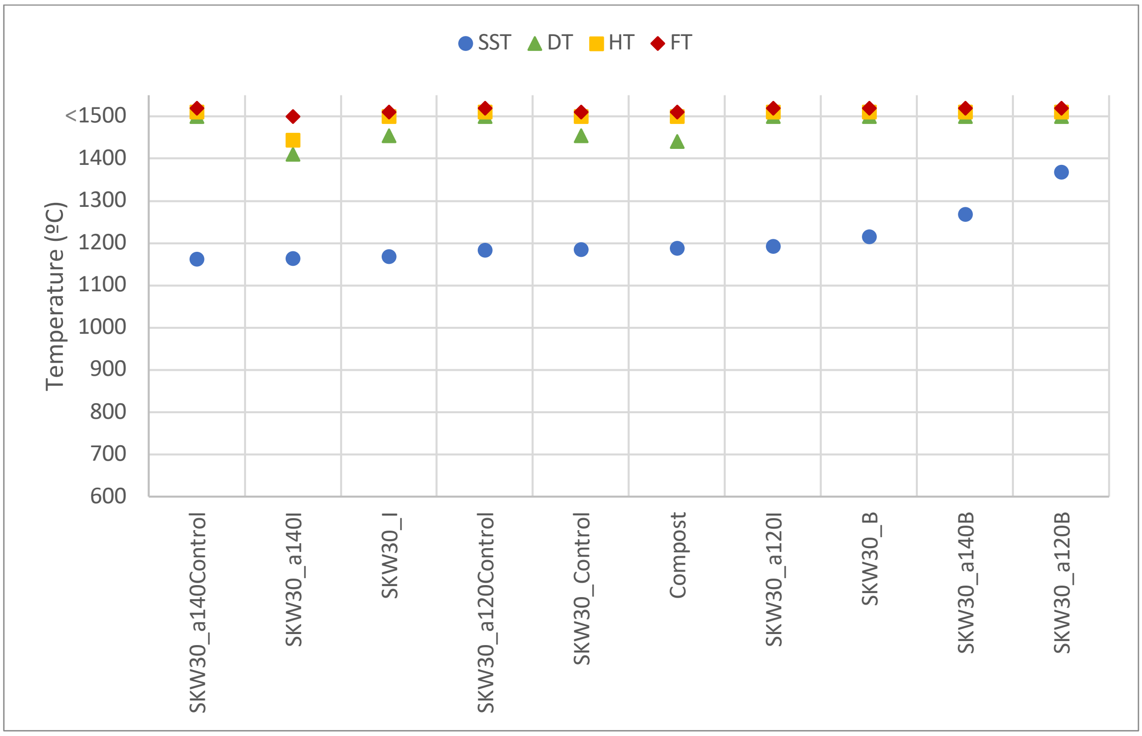

Fig. 22. Characteristic temperatures for ashes based on nine pretreated and washed SKW samples and Compost without any pretreatment. SKW30, straw-compost with water, dry matter 30%; a: autoclaved at 120 ºC or 140 ºC; I: aerobically incubated for 15 days at 25 ºC; B: anaerobically incubated for 15 days at 55 ºC.

Significantly higher SST are observed than for the SW based samples. Within the nine SKW samples analyzed, an average SST of 1212 ± 67 ºC was obtained, which is a 60% increase to the average compared to pretreated SW samples. As in the case of SW-based ashes, particularly good results were obtained for the materials that underwent anaerobic incubation pretreatment SKW30_B and the combination with autoclave treatment SKW30_a140B and SKW30_a120B.

To evaluate the interaction of pretreatments on the response of the SST, ANOVA was performed for nine SKW samples without considering Compost since it is not mixed with wheat straw. The results are presented in Table 25 below:

Table 25. ANOVA output for nine pretreated and washed compost-wheat straw (SKW) ash pellets.

Source	Sum of Squares	df	Mean Square	F - value	Prob > F	Remarks
Autoclave	11965,923	2	5982,962	2,016	0,189	Not Significant
Incubation	46357,503	2	23178,752	7,809	0,011	Significant
Interaction	13575,353	4	3393,838	1,143	0,396	Not Significant
Error	26713,160	9	2968,129			
Total	98611,940	17				

The results show that both the main effects of autoclave (p-value 0,189) and the main effects of interaction autoclave-incubation (p-value 0,396) are statistically non-significant, as both p-values are greater than 0,05. Only the incubation effect is significant, as p-value 0,011 < 0,05;

therefore, it is affecting the SST response. This result is like that of section 5.3.1 for SW ash samples.

When the main effect of incubation on SST is analyzed, the results depend on the type of incubation performed. If ashes that underwent anaerobic treatment such as SKW30_B, SKW30_a140B or SKW30_a120B are compared to the ashes that did not receive thermal treatment, SKW30_Control, SST improvements of 2,6%, 7,0% and 15,4%, respectively are obtained, an equivalent average improvement of 8,3%. These three materials coincide with those with the higher SST.
On the other hand, when the same comparison is made for ashes subjected to aerobic treatment like SKW30_a140I or SKW30_I is obtained a decrease in SST of 1,8% and 1,4% respectively. However, SST of SKW30_a120I is slightly above SKW30_Control with an improvement of 0,6%. The improvement is not considered as significant as in the case of anaerobic incubation. An equivalent average decrease of 0,9% is registered.
Like for SW ashes, the results suggest that anaerobic incubation pretreatment has a positive effect on SKW samples since it generates an increase in SST. On the other hand, the aerobic incubation pretreatment causes a decrease in SST.

Furthermore, it is feasible that the improvement observed in the nine pretreated SKW ashes is also due to the washing process. As explained in section 3.2.3 and section 3.4, washing removes minerals such as K, Na, Cl or S that decrease the melting temperatures of wheat straw [8]. Besides, as shown in Table 16, SKW samples went from having an average ash content of 39,1% to 22,4% after washing, which means a 43% reduction. Consequently, the melting temperatures increase. However, it was not possible to quantify the impact of this process on ash temperatures. Therefore, it would be advisable for future research to study the behavior of fusion temperatures before and after the washing process for the same material.

The results are considered satisfactory since a substantial increase in ash temperatures was achieved after mixing the straw with compost. Similar literature, in which wheat straw mixed with paper sludge was used, obtained results higher than 1080ºC [20]. However, the values obtained in this research are still higher and would not cause any ash sintering and slagging. Besides, there is a possibility of improving the process: although it is true that obtaining these values of ash temperature is beneficial for combustion, it also generates counter effects due to compost mixing as already described, i.e., it increases the ash content and decreases the GCV; therefore, it is proposed for future research to control the percentage of compost added to the wheat straw, to find the optimum point between these three variables.

Finally, a detailed comparison between the ashes that showed the lowest and highest characteristic temperature values., i.e., SKW30_a140Control with the lowest SST and

SKW30_a120B with the highest SST. The figures below show the results of the thermo-optical analysis:

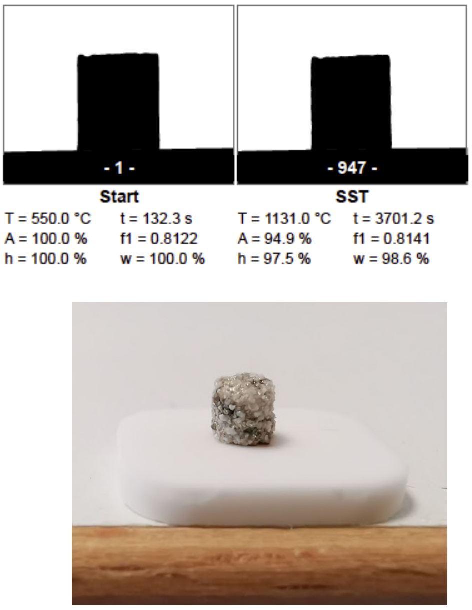

Fig. 23. Characteristic temperatures for SKW30_a140Control ashes and photo of the ash pellet once the process is completed.

SKW30_a140Control achieved the lowest results of the pretreated SKW samples with an average SST of 1161 °C. Fig 23. shows one of the tests performed with an SST of 1131 °C and DT, HT, FT above 1500 °C. The ash pellet is also presented after the end of the experiment. As can be seen, the deformation is minor and practically maintained its original shape. This type of material would not cause sintering or slagging.

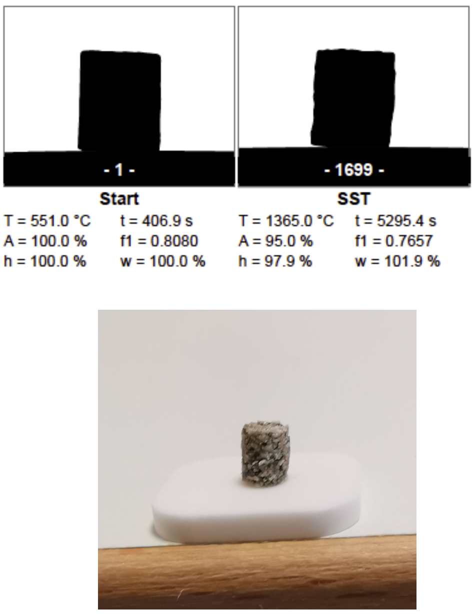

Fig. 24. Characteristic temperatures for SKW30_a120B ashes and photo of the ash pellet once the process is completed.

SKW30_a120B achieved the best result of the ashes evaluated with an average SST value of 1368 ºC. Fig. 24 shows one of the tests performed with an SST of 1365 ºC. As in the case described above, it was not possible to measure DT, HT, or FT because they were above 1500 ºC. As is shown in Fig. 24, cylindrical specimens from ash did not change their shape by increasing the temperature up to the test maximum of 1500 °C. This type of material would not cause sintering or slagging.

6. Conclusions

Wheat straw presents challenges due to its inferior combustion properties like high ash content, low gross calorific value (GCV), and low ash melting temperature. To address this, thermobiological pretreatments were carried out on both wheat straw and a mixture of compost-wheat straw and three combustive properties were studied: ash content, calorific value and ash melting behavior.

As for SW samples subjected to pretreatments:

- the ash content responded to the pretreatments of autoclaving, incubation, and the interaction between them. Compared to untreated straw, an average decrease in ash content of 5,8% is achieved. In addition, a drastic decrease in ash content was observed after the washing process, reaching an average of around 55% when comparing the same materials before and after washing. All the results obtained show an ash content of less than 10%, which satisfies the ISO 17225-6.
- pellets did not show statistically significant responses in calorific value due to pretreatment or washing. In comparison with unwashed wheat straw, no significant changes in GCV were detected after the washing process. The pellets met the criteria of the standard ISO 17225-6.
- ashes from nine pretreated SW samples showed an improvement of 6,6% in SST when compared to wheat straw without pretreatment. SST responded only to the incubation pretreatment, showing an increase for anaerobic incubation of 4,4% and a decrease in 2,5% for aerobic incubation when compared to pretreated material without heat treatment. In addition, there was evidence of an increase in melting temperatures due to the washing process in SST, DT, HT, and FT for all nine pretreated samples, but more research is needed to quantify this effect. Materials without aerobic treatment can significantly reduce the effort during combustion; however, a moving grate system for pellet combustion is necessary.

Although promising results are observed in terms of reduced ash content and increased melting temperatures, additional components would still be needed to achieve the use of this material as a pellet for combustion processes in small boilers, such as a moving grate system due to the low SST. However, it would be possible to use these pellets in medium or large-scale boilers. Improvements in ash content due to pretreatments and ash fusion temperatures due to anaerobic incubation were also observed, but the major effects came from the washing process. Lastly, the ISO 17225-6 standard for pellets is met.

As for SKW samples subjected to pretreatments:

- SKW samples have a higher ash content than SW samples because compost contributes with a high percentage of ash. The ash content changed when autoclave pretreatment was used in unwashed samples: pretreatment at 140 °C showed an average reduction of

27% with respect to the samples without heat treatment, but the impact of the response at 120ºC was lower and did not always reduce the ash content, on average an increase around 0,4% was recorded. A noticeable average decrease of 43% in ash content was achieved when the same materials before and after washing were compared. However, it was not possible to meet ISO 17225-6, since the ash content values before and after washing were on average 39% and 22%, respectively, exceeding the 10% required by the standard.

- average GCV for SKW samples is lower by 13% than for SW samples, due to the high ash content and low calorific value of the compost. Besides, the autoclave pretreatments and the autoclave-incubation interaction showed a response in GCV for SKW samples. An average improvement in GCV of 10% was observed when autoclaving at 140°C and an average improvement of 6% when autoclaving-incubation interaction was used. The use of autoclaving at 120 ºC was shown to be negatively affecting the calorific value since there was a reduction of around 8% GCV.
  In addition, a possible effect of lignin degradation was observed in the sample subjected to aerobic incubation SKW30_I since it presented the lowest GCV, which was expected. However, the same results were not obtained in other samples also subjected to aerobic treatments together with incubation. Therefore, it was recommended to perform an elemental analysis to elucidate the real impact effect of the lignin degradation.
  It is also possible that the washing process is positively affecting GCV because of the reduction of ashes, however, this effect could not be quantified. It is recommended to perform calorimetric tests for samples before and after washing. Lastly, the calorific results for the nine studied SKW pellets do not satisfy industrial standards according to ISO 17225-6 since its value NCV is always lower than 14,5 MJ/kg.
- during the ash melting test, an average 60% increase in SST was recorded for the pretreated SKW ashes due to the high melting temperature that the compost provides to the homogeneous mixture with wheat straw. Similar to SW samples, starting shrinkage temperatures of SKW samples responded only to the incubation pretreatment, where an average SST increase of 8,3% for anaerobic pretreatment and a decrease of 0,9% for aerobic pretreatment was recorded, when compared to pretreated SKW ashes without heat treatment. In addition, there was evidence of an increase in melting temperatures due to the washing process in SST, DT, HT, and FT with respect to the unwashed wheat straw, but more research is needed to quantify this effect. The results are considered satisfactory and would not cause any ash sintering and slagging.

Diverse responses were observed due to the addition of compost. Although the melting temperatures were indeed raised substantially to avoid the combustion problems described above, in keeping with the objective of this work, counter-effects were generated due to the homogeneous compost-wheat straw mixture: the ash content increased and GCV- NCV decreased. These negative effects were mostly reduced with the pretreatments of autoclaving at 140 ºC in conjunction with the washing process; however, the ISO 17225-6 standard for pellets is not met.

There is margin for process improvement and more studies are required to create a solid fuel based on the compost-wheat straw mixture; however, the potential of compost is promising. We recommend future research to mix controlled compost percentages to reduce these counter-effects.

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Declaration in lieu of oath

By

Felipe Antonio Torres Rivera

This is to confirm my Master's Thesis was independently composed/authored by myself, using solely the referred sources and support.

I additionally assert that this Thesis has not been part of another examination process.

Cologne, 28.12.2021

Place, Date

Signature