

Article

Viability of Agricultural and Forestry Residues as Biomass Fuels in the Galicia-North Portugal Region: An Experimental Study

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Received: 9 September 2020; Accepted: 3 October 2020; Published: 5 October 2020



Abstract: In this study, an experimental approach was utilized to assess the viability of three biomass fuels in a small laboratory-scale combustor. Three feedstocks currently considered as residues were selected based on their widespread presence in the Euroregion Galicia-North Portugal, and some were modified to improve their behavior by removing fine particles or adding substances to increase the melting point of the ashes. The experimental facility was a highly modifiable, fixed-bed combustor with air-staging capabilities and a wide array of sensors intended to measure a large quantity of parameters. A series of tests was performed to cover the widest range of total air flows possible for the facility, with values of 0.223, 0.279 and 0.334 kg/m²s being used, while 30% of the total air flow enters from below the combustion bed and 70% over it. Results from the proximate and elemental analyses show high proportions of ash in every fuel compared to commercial wood pellets, and empirical deposition indexes suggest a high risk of fouling and slagging. Testing confirmed the analysis predictions, resulting in the kiwi- and vine-based fuels not being suitable for a facility without ash elimination systems. Some modifications of the gorse fuel showed improved behavior compared to unmodified gorse fuel, namely, the addition of a 2% mass fraction of CaCO₃ and the removal of fine particles. The former prevented ash sintering, and the latter greatly decreased the fouling of the heat exchanger tubes. These results suggest that some of the vegetal species studied might be suitable for their use in small-scale biomass burners, and besides the accuracy of one of the deposition indexes used is confirmed.

Keywords: biomass combustion; fixed-bed; low-grade fuels; forestry residues; additives; deposition indexes; slagging; fouling

1. Introduction

The rising awareness of climate change on a global scale is pushing governments towards the enforcement of ever-growing shares of renewable energies. In the EU, the target was set at 20% in 2020, although some nations have surpassed that baseline years ago and are aiming at higher percentages [1]. To achieve and maintain sustainable development, biomass is key among the renewable sources of energy [2]. The production of pelletized biomass allows for a more compact and more homogeneous fuel, addressing two of the main issues associated with biomass, while also allowing the use of more efficient transportation, handling and storage methods [3–5]. In addition, phasing out coal or diesel boilers in favor of biomass decreases the amount of CO₂ and SO₂ emissions [6]. Non-woody biomass fuels may play a major role by functioning as a means to effectively dispose of vegetal material that

is currently considered waste, thereby adding to the supply of raw material for the production of biomass fuels; however, the use of vegetal materials presents their own share of problems that need to be assessed [7–9].

These challenges are derived not only from the chemical composition of the raw material, which has remarkably high contents of chlorine, potassium, aluminum, silicon, phosphorous and other elements known to be responsible for corrosion [10] and slag formation due to their participation in low melting point mineral phases [11–14] but also from the high sulfur and nitrogen oxide emissions [15]. Other studies have found that slag and ash formation can be prevented by mixing additives such as kaolinite and calcite with the raw material prior to pelletization [16–19]. These additives increase the melting point of the oxides present in the ashes, thus inhibiting the formation of solid aggregates.

Given the variability of sources available worldwide, there is interest in testing the suitability of non-woody biomass fuels with different origins, such as blended wood-straw pellets [20], cork-vine pellets [21], pine residues [22], groundnut shells [23] or sugarcane bagasse [24]. Raw materials are often selected according to the available non-woody biomass in the area due to the long-distance transportation issues previously mentioned; however, in some cases, a representation of the widest possible range of biomass is intended and biomass species from a large area, or even a continent, are selected [25]. In this study, the fuels are chosen according to some of the most common non-woody forestry and agricultural residues present in Euroregion Galicia-North Portugal. This scope is selected in accordance to the objectives pursued by the Biomasa AP [26] project that this research stems from. The project intends to establish a knowledge hub bonding both sides of the Spanish-Portuguese border through the cooperation in research and the development of technologies and techniques that focus on the use of local resources, sustainability and energy efficiency [27].

The main objective of this paper is to determine the suitability of vine, kiwi and gorse prunings to be used as fuels in a fixed-bed, small-scale, underfed biomass combustor. Data from combustion tests were gathered, as well as data from proximate, ultimate and ash composition analyses. Results were compared to those obtained from analogous tests with a commercial wood pellet that was used for reference. In addition, combustion tests were also carried out with the same non-woody biomasses blended with additives such as kaolinite and calcite to study the effects of these additives on slag formation.

In the following Section 2 the selected fuels are described, and their main characteristics are stated. Similarly, the facility utilized to carry out the tests is described, and the methodology followed for each test is presented. In Section 3 predictions of fouling, slagging and nitrogen oxides emissions based on previous research are shown, as well as the results of the tests performed in the experimental facility. The results are accompanied by a brief discussion to provide some insight on the possible explanation for the phenomena observed. Section 4 summarizes the main conclusions extracted from the data gathered.

2. Materials and Methods

2.1. Fuel Characterization

Three species of non-woody biomass were tested in the experimental facility. The selection criteria for these species were focused on the availability of the resources in Euroregion Galicia-North Portugal. The three species selected were vine prunings (*vitis vinifera*), gorse (*ulex europaeus*), gorse without fine particles (labelled as the N1 batch) and kiwi prunings (*Actinidia deliciosa*). The first two were also blended with 2% kaolin (labelled as N2 batches) or 2% calcium carbonate (labelled as N3 batches). For reference, tests with commercial wood pellets were also performed as a means to determine the deviation of the experimental pellets from the optimal quality (ENplus A1) as described in the European standard EN 17225-2. Table 1 condenses the characteristics of every fuel tested, such as the heating values in kJ/kg (calculated as in [28]), mechanical durability in a percentage relative to a standard (according to ISO 17831), particle density in kg/m³ (ISO 18847), bulk density in kg/m³

(ISO 17828) and fusibility. Accordingly, the composition of the fuels was also determined via elemental analysis in a Fisons Carlo Erba EA1108 microanalyzer following the procedure established in ISO 16948 and ISO 16994, thereby obtaining the C, H, N and S percentages present in the fuels. In addition, a proximate analysis of the fuels was also performed, resulting in the weight percentage of the dry base as received, and including the moisture, char and volatile results from the thermogravimetric analysis in a Labsys TGA-DTA/DSC device. The ash content was determined according ISO 18122. The composition of these ashes was also studied, by means of X-Ray fluorescence. This technique is performed with a Siemens SRS3000 spectrometer, and the results can be seen in Table 2.

All of the new feedstocks utilized in this research presented acceptable behavior when transformed into pellets, with the notable exception of kiwi prunings. Pellets made from kiwi prunings showed a low durability and high moisture content compared to the other tested fuel feedstocks, resulting in brittle, uncompacted pellets that were unsuitable for feeding into the available facility. When these pellets reached the combustion chamber after being transported by an endless screw, only a very fine sawdust powder remained, making it impossible for the primary air flow to maintain the combustion reaction due to the low permeability of the medium. This result made clear the necessity of creating a second batch of kiwi fuel. Through a more prolonged drying process, a fuel with significantly less moisture and better durability was created, allowing it to be tested in the facility; however, the durability problem was still present to some extent. It is also worth noting that the fuels containing additives showed inferior durability compared to those without additives. This result could be explained by the fact that lignin, the natural binding substance present in pellets, is absent in additives, leading to a poor union between particles.

Regarding the bulk density, commercial wood pellets resulted in the highest value, while all the experimental fuels ranged from 500 to 600 kg/m³ except for the kiwi pellets, which were closer to the wood pellet density.

2.1.1. Nitrogen Oxides Prediction

In order to establish the relative risk of nitrogen oxides emission of the experimental fuels compared to one another and to the reference wood pellet, empirical relations have been used as a means to predict the NO yield of each fuel tested. Other authors that have focused their research on the prediction of NO_x emissions in biomass boilers have differentiated three main mechanisms of nitric and nitrogen oxide formation [29]. In the field of biomass, two of these processes are dismissed as irrelevant, namely, prompt NO_x and thermal NO_x, as they require fuel-rich, high-temperature environments, as well as a long residence time for the gases; these conditions are not met by most biomass boilers. Thus, the main contributor to NO_x emissions in biomass boilers is fuel NO_x. Nitrogen contained in the fuel is released during combustion and oxidizes in the presence of air (O₂) to form NO. Biomass is a solid fuel, and some authors have linked the processes of NO_x formation to those of coal and therefore concluded that, in cases of fuel with a very low mass fraction of nitrogen, 70% to 100% of fuel N is converted to NO [30]. Moreover, studies have shown that it is possible to correlate the fuel nitrogen to the NO conversion and the O/N and H/N ratios [31–33]. High oxygen and hydrogen to nitrogen ratios enhance the conversion of fuel nitrogen to certain intermediate compounds, such as NH₃ and HCN, which lead to the formation of NO.

Table 1. Fuel characteristics.

Fuel	Denomination	Wood	Vine	Gorse	Kiwi	Gorse N1	Gorse N2	Gorse N3	Vine N2	Vine N3
	ID	wp	vp	gp	kp	gN1	gN2	gN3	vN2	vN3
Elemental analysis ¹ [%wt.]	N	0.1	0.8	1.1	1	1.2	1.2	1.4	0.8	0.8
	C	47.2	47.8	49.5	47	49	48.1	48.5	47.4	47.6
	H	6.3	5.8	6.1	5.5	6.6	6.5	6.5	6	6.2
	O	46	45.5	43.3	46.5	43.2	44.2	43.7	45.8	45.4
Proximate analysis ² [%wt.]	Moisture	5.2	7.5	9.8	8.2	8.9	7.2	7.4	10.5	9.8
	Volatiles	71.6	72.6	72.2	70.8	73.1	73.1	72.7	68.3	69.1
	Fixed carbon	22.8	16.5	16.1	17.8	16.2	16.1	16	17.4	16.7
	Ash	0.4	3.5	1.8	3.2	1.9	3.7	3.9	3.8	4.4
Heating value	LHV [kJ/kg]	17,663.6	17,419	17,162.6	16,128.5	18,508.8	18,122	18,113.7	18,455	17,958.6
	HHV [kJ/kg]	19,190.6	18,741.5	18,485	17,451	19,831.3	19,444.5	19,436.1	19,777.5	19,281.3
Physical properties	Durability [%]	-	98.6	99.2	99	90.9	90.9	85.8	97.9	96.9
	Particle density [kg/m ³]	-	1	1	1	1	1	1	1	1
	Bulk density [kg/m ³]	-	595	505	645	554	568	529	547	542
Fusibility	(T < 1000 °C)		WS	WS	WS	WS	WS	WS	WS	WS
	(1000 °C < T < 1100 °C)		WS	WS	WS	HS	WS	WS	WS	WS
	(1100 °C < T < 1150 °C)		-	MELT	-	MELT	MELT	HS	WS	WS

Notes: ¹ dry basis, other elements below 0.03% are under the detection limit; ² as received; HS: hard sinter; MELT: melted sinter; WS: weak sinter.

Table 2. Ash analysis.

Fuel	Denomination	Wood	Vine	Gorse	Kiwi	Gorse N1	Gorse N2	Gorse N3	Vine N2	Vine N3
	ID	wp	vp	gp	kp	gN1	gN2	gN3	vN2	vN3
XRF ash analysis [mg/kg]	Na	21.5	325	1790	300	327	1205	1721	539	552
	Mg	482.2	1183	1100	1476	225	870	1088	3350	3366
	Al	681.5	897	671.9	1176	64	3377	636	310	155
	Si	354.9	2064	1795	2503	-	-	-	2979	7019
	P	32.4	1011	431.6	1055	34	219	261	868	779
	S	96.8	660	843.1	809	780	706	740	581	524
	Cl	34.1	312	559.6	300	1100	983	1099	310	155
	K	661.7	6753	4120	8237	653	3012	3510	6455	5421
	Ca	589	10250	2772	7433	248	1179	3481	10877	6489
	Ti	5.5	21	55.8	43.7	1	6	7	15	18
	Mn	59.4	86	342.4	32.6	37	215	258	91	105
	Fe	65.1	410	684.7	627	24	416	475	180	255
	Ni	2.1	-	4.3	2.9	1	3	4	2	5
	Cu	0	-	15.6	43.2	4	2	3	29	30
	Zn	5.2	91	40.8	49.7	4	21	26	56	61
	Rb	4.4	-	53.3	49.2	1	8	5	19	27
	Sr	7.2	-	21.5	36.1	2	12	31	39	40
Ba	0	-	56.2	51.8	4	5	5	67	67	

2.1.2. Deposition Indexes

To predict the fouling and slagging tendencies of the biomass experimental fuels, in order to study possible countermeasures to these phenomena [34–36], some research has developed a series of numerical correlations to assign a value to the proportion of certain components to others. These correlations are the so-called fouling indexes [37–40]. These indexes can estimate the extent of fouling and slagging in biomass combustion in several ways, such as through the K and Na oxide proportions and the lower heating value (LHV) in the alkali index (AI) that evaluates the fouling tendency of a fuel ($AI = (K_2O + Na_2O)/LHV$ [kg/GJ]). Another evaluation index, the base-to-acid ratio that is used with coal for estimating the slagging risk ($Rb_a = (Fe_2O_3 + CaO + MgO + K_2O + Na_2O)/(SiO_2 + TiO + Al_2O_3)$), is argued to not properly reflect the behavior of slagging in biomass, so Hu et al. [41] proposed a new index $(MgO + Al_2O_3 + Fe_2O_3)/(CaO + P_2O_5)$, also known as slagging evaluation index. Both the alkali index and the slagging evaluation index have been used to estimate the risks of utilizing each fuel.

2.2. Experimental Rig

The combustor used for testing the fuels is a small, underfired experimental biomass combustor that yields 5–12 kW (300–900 kW/m²). A diagram displaying the main parts and systems is provided in Figure 1. It is equipped with an air-staging system that allows the distribution of air flow between two inlets, one of them under the fixed-bed grate (primary air) and the other over the bed (secondary air), and both flows can be controlled independently. Air staging is a proven strategy for the decrease in solid particulate matter (PM) [42] and has been successfully used at this facility in previous studies [43]. The Omrom E5CK controller used to control the air flow has an error of ± 0.002 kg/m²s.

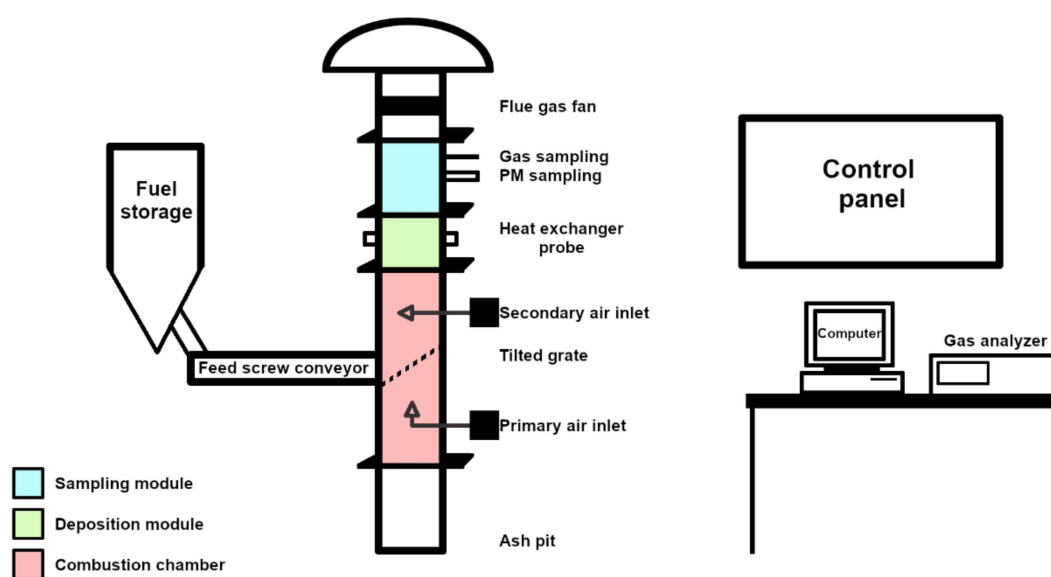


Figure 1. Facility diagram.

The fuel is transported to the tilted fixed bed via an endless screw that pushes the bed upwards. This screw is controlled by an on/off system, ensuring equilibrium between feeding and burning. The facility also incorporates a deposition module used to collect samples of solid aggregates driven by the air current, in which the aggregates adhere to the water-cooled probe inside the facility. This module is a scaled-down model for the real deposition that occurs in commercial biomass boiler heat exchangers, and the water circuit operates at 3 bar and keeps the temperature at 25–35 °C by means of a fan coil unit. A more thorough description of the facility can be found in previous works [11,43,44].

A PM sampling probe is attached to the facility on top of the deposition module. A fraction of the chimney gas is extracted and driven through a Dekati low-pressure impactor (DLPI) where the PM is deposited on removable aluminum foil substrates due to the aerodynamic diameter of the particles traversing the holes that are present in the impactor. Thus, the PM is retained and classified according to its size and results in not only the mass of PM per cubic meter of the measured gas but also a size distribution curve. This low-pressure impactor is operated at 120 °C to ensure the absence of liquid water in the current.

A Servomex Servopro 4900 continuous gas analyzer is employed to detect four gaseous species present in a sample of chimney gas (O₂, CO, CO₂ and NO_x) collected downstream from the heat exchanger module. This analyzer has an intrinsic error of ±0.1% when analyzing O₂ and 1% in the case of CO, NO_x and CO₂ samples. The gas sample is maintained at 120 °C to avoid condensates and then cooled to the dew point in a gas conditioning station. The gas must enter the analyzer without moisture or solid PM to avoid malfunction.

2.3. Design of Experiments

The experimental tests performed in the facility covered most of the air staging configurations and total air flows adequate for the operation of the facility to check the suitability of the fuels for their use in different environments, data from 64 unique tests were gathered. Three configurations of total air flow were employed. Considered to be at the lowest, intermediate and highest points of normal operation in a facility, these air flows were 0.223, 0.279 and 0.334 kg/m²s, respectively. The notation for the split of air flow between the inlets is XX_YY, where XX is the percentage of total air flow entering through the primary inlet and YY is the percentage of total air flow entering by the secondary inlet. The distributions used were 20_80, 25_75, 30_70 and 40_60. To adapt the tests to the availability of fuel, tests with an air staging configuration of 30_70 were deemed the standard and carried out with every experimental fuel except pure kiwi and vine with additives. In the case of pure kiwi, no 30_70 test lasted long enough to obtain samples, while with the vine with additives, some shorter tests could be run. Other configurations were tested to explore the limitations of each fuel considering their behavior in the 30_70 tests. Thus, wood pellets were not tested in 40_60 conditions, as the high quantity of primary air causes high combustion chamber temperatures that endanger the facility and its measurement instruments; however, the same air staging (40_60) was used in the vine, gorse and kiwi tests. A detailed recapitulation of all the tests performed is provided in Table 3.

Table 3. Tests performed.

Air-Staging Ratio	Total Air Flow [kg/m ² s]	Wood	Vine	Gorse	Kiwi	Gorse N1	Gorse N2	Gorse N3	Vine N2	Vine N3
		wp	vp	gp	kp	gN1	gN2	gN3	vN2	vN3
20_80	0.223	X	X				X			
	0.279	X	X				X			
	0.334	X	X				X			
25_75	0.223	X				X	X			
	0.279	X				X	X			
	0.334	X				X	X			
30_70	0.223	X	X	X	X		X	X	X	X
	0.279	X	X				X	X	X	X
	0.334	X	X				X	X	X	X
40_60	0.223		X			X	X			
	0.279		X			X	X			
	0.334		X			X	X			

X = successful test lasted the required 4 hours.

2.4. Test Methodology

Standard combustion tests are four hours long, of which the first 45 min belong to a transient unstable phase characteristic of the facility. In the following three hours, the combustion is maintained in a steady state; hence, the acquisition of significant data is possible. The last 15 min belong to a

switch-off period, in which the feeding of fuel is decreased to zero and the combustion reaction stops after consuming the fuel present in the combustion chamber.

PM samples are collected twice during each test, at 30 and 120 min in the stable-state phase. This is done to test the evolution of the combustion reaction and the effect of ash and slag accumulation in the combustion bed. Past studies in this facility have shown that this accumulation produces an increase in emitted PM in the second sample by up to four times the amount collected in the first sample [43]. PM mass measurements were made with a Gram series VXI weighing scale, with an error of 0.01 mg, while ash mass measurements were performed with a Radwag PS 1000.R1, with an error of 1 mg.

In order to summarize the methodology and present it in a comprehensive manner, Figure 2 was elaborated. In this way, the relationship between the different phases and methodologies employed is shown, as well as the geographical location of the area this study focuses on.

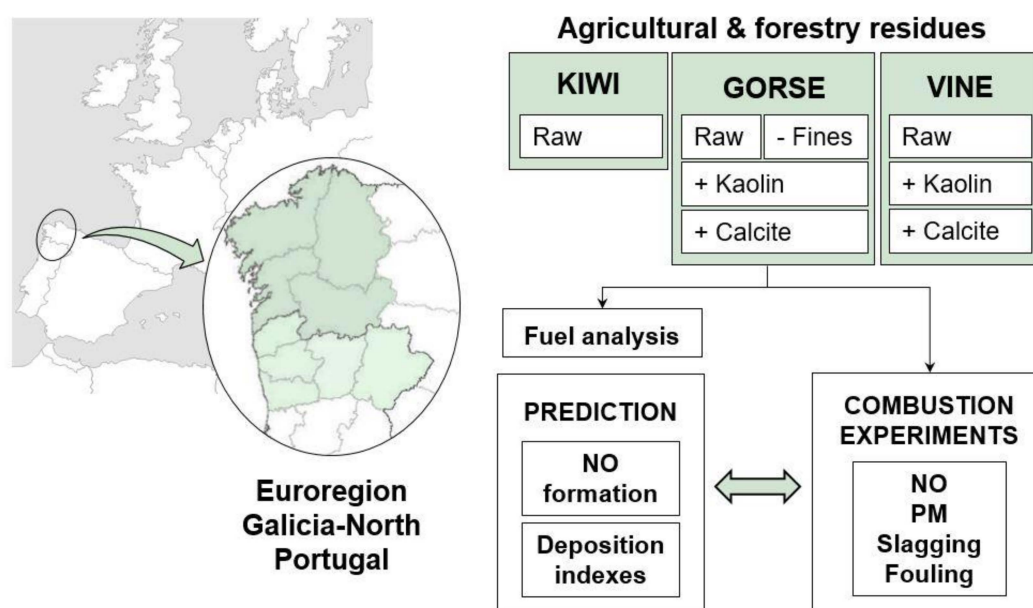


Figure 2. Methodology followed in this study.

3. Results and Discussion

The results are divided into sections according to the sample analyzed. In addition, in each section where data from the experimental tests is studied, a global comparison is established between all fuels, followed by a detailed analysis of the gorse pellet results, as this fuel has the most extensive data set of all the experimental fuels tested.

3.1. Ash Analysis

The proximate analysis of the fuels reveals a significantly high ash content in the experimental fuels compared to the content in commercial wood pellets, as shown in Table 1. This result suggests the possibility of ash-related problems when the fuels are tested in the experimental facility. These problems can be narrowed down to two main issues: (1) the obstruction of the air flow due to an accumulation of ash in the combustion chamber and (2) slag formation. The former becomes especially critical in fixed-grate burners with no system for ash removal, which can lead to shorter periods of continued utilization and increase the amount of emitted PM, as finer ash particles can be driven by the air flow. On the other hand, some species formed during combustion and the remaining ash in the combustion chamber present low melting points. Thus, these compounds can melt, and form coalesced solid entities, severely hindering the air flow and thus limiting the effectiveness of the process. The compounds usually related to these slag issues are those that form low melting point oxides, such as K, Na, Si, P,

or Cl, as suggested in other research [10,34,42,43]. The addition of certain elements known to form high melting point oxides, such as Ca or Al, has been proposed as an effective strategy to counter slag formation [16,19]. Other strategies, such as increasing the amount of excess air to keep fly ash from sticking to the heat transfer surfaces and forming slag, have also been proven successful but are expensive [10]. Therefore, a detailed study of the composition of the ash is required in order to make a complete assessment of the properties of the biomass fuels studied.

The contents of the ash were thus analyzed (Table 2) to assess the risk of slag formation and study the differences with that of commercial wood pellets. The approach proposed by [44], with four chemical biomass ash types that are further divided into seven subtypes, was chosen, as it is an appropriate method to study the slag tendencies of fuels while comparing the results to the extensive data set gathered in the abovementioned research. In Figure 3, all experimental fuels utilized in the current research are characterized accordingly, and the woody biomass present in [44] is also shown as a reference. From this figure, it is clear that all three non-modified experimental fuel ashes have a similar composition (classified as C-type) and are in close proximity to that of wp. As expected, the addition of kaolinite drives the ash composition upwards towards Si- and Al-rich ashes, while calcium carbonate moves them downwards towards Ca-rich ashes. It is worth mentioning that the elimination of fine particles performed in the gN1 sample greatly reduces the proportion of Si, Al, Fe, Na and Ti oxides, suggesting that these components are concentrated in the fine particles.

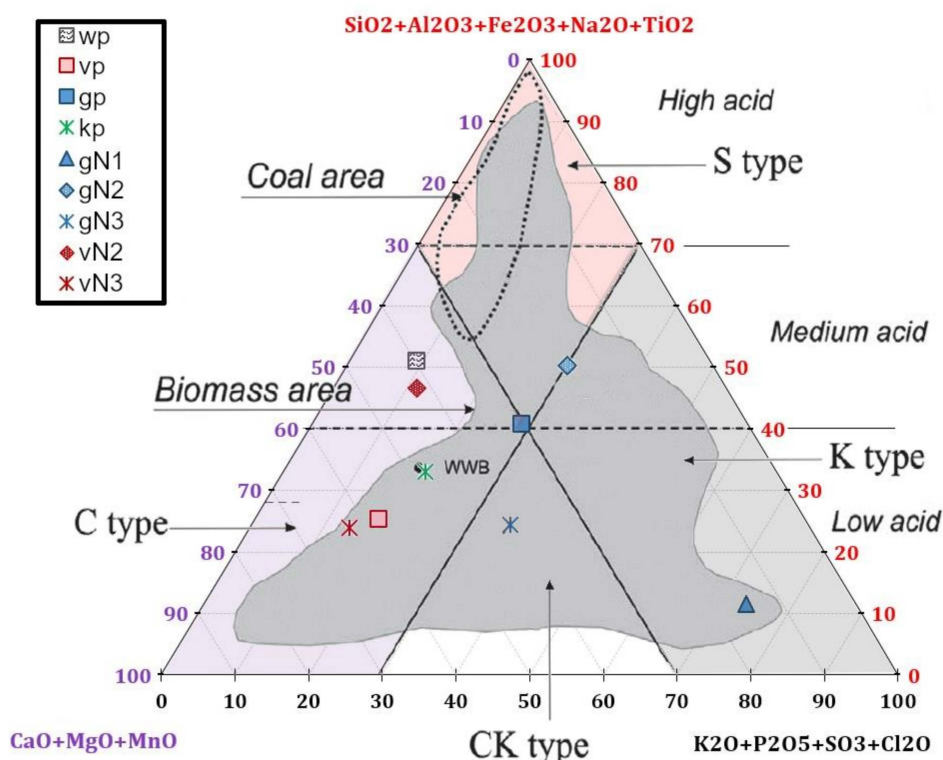


Figure 3. Classification of the experimental fuels as in [44].

3.2. PM Emissions

As seen in Figure 4, the PM emissions for the experimental fuels are higher than those of wp at a 30_70 air-staging ratio, ranging from a minimum increase of two times the emitted PM in the case of gN2 at a low total air flow to a maximum of more than seventeen times the emitted PM for gN3 at a high total air flow. Among the experimental fuels, vp emits less PM at low total air flows, while gp exhibits a low tendency to emit PM at high total air flows. Regarding the used additives and pretreatments for the fuels, both gN1 and gN2 show better PM emission results at low and intermediate total air flows, with the PM emissions being cut in half from that of the original gp fuel. The gN2

sample (2% kaolin) seems to show a particularly effective decrease in the amount of PM emitted in these cases. However, for high total air flows, the unchanged gp shows the best behavior among the experimental fuels. On the other hand, gN3 shows a similar behavior to gp at low total air flows but exceeds every other PM value at intermediate and high total air flows.

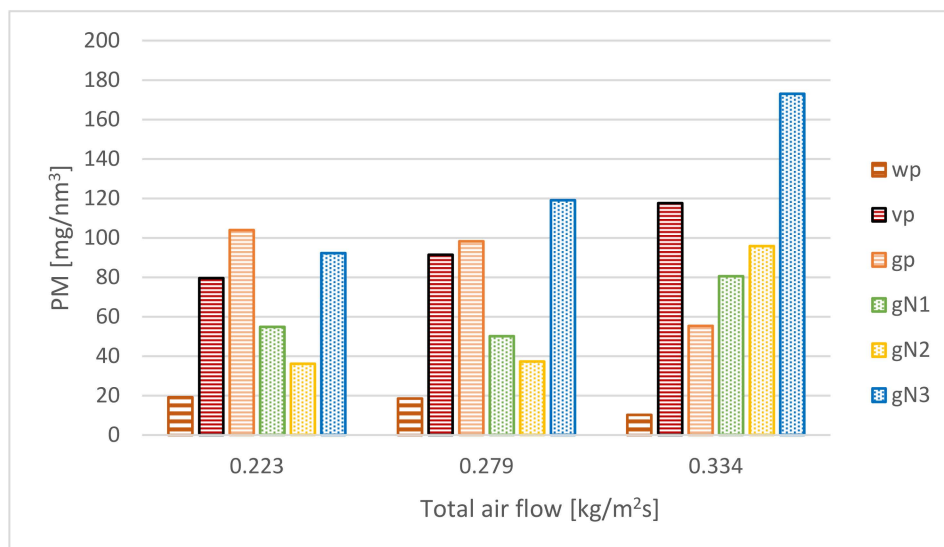


Figure 4. PM emissions at a 30_70 air-staging ratio for the three total air flows considered.

There is a noticeable difference in the trend followed by PM emissions when the total air flow is increased. For gp, the emissions tend to decrease, while for pellets with additives or pretreatments, opposite behavior is detected. These results can be explained by the fact that pellets with additives have a high ash content; thus, the higher the total flow is, the more ash driven by the air current. As vp has a similar proportion of ash content, the same behavior is observed.

Regarding the evolution of combustion represented in Figure 5 for gp, the PM emission seems to decrease as time goes by, and this effect is less noticeable at high total air flows. First sample is collected 30 min into the stable combustion phase, and second sample is collected 120 min into said phase. Regarding the pellets with additives and pretreated pellets, the inverse trend is noticed. At low to intermediate total air flows, the PM emissions seem to remain at similar values or even experimentally increase, while at high total air flows, the PM emissions decrease. A value cannot be obtained for gN1 at a high total air flow because the high accumulation of ash in the combustion grate made the reaction unstable and unsustainable. This observation can explain the decrease in the PM emissions of gN2 and gN3, given that the combustion is poorer due to the high ash accumulation; thus, there is less biomass reacting with oxygen, which decreases the PM emissions.

The size distribution of the PM in the experimental fuels and wp, as shown in Figure 6, follows a unimodal distribution with the peak being under $0.1 \mu\text{m}$. The data in Figure 6 are obtained by calculating the mean value of the percentage of total mass gathered in each of the 13 scales of the impactor for every test made with each fuel. These data correlate with that of wp, following the same unimodal pattern and approximate sizes. Two notable exceptions are the two fuels containing additives, gN2 and gN3, which show some minor accumulations of large particles. This size distribution also coincides with that of previous research [11,45–47].

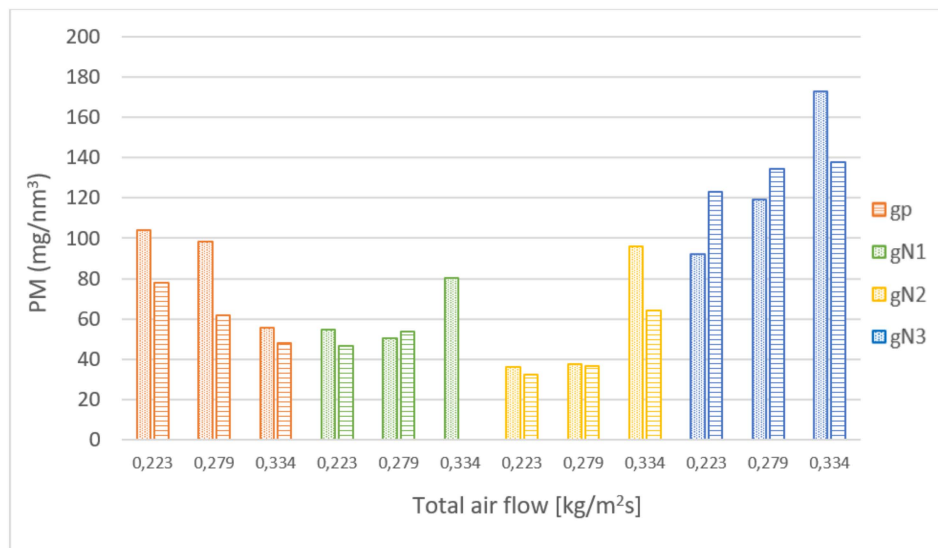


Figure 5. Effect of pretreatment and additives for the 30_70 gorse tests, according to the three total air flows considered. First samples are the dotted bars and second samples are the striped bars.

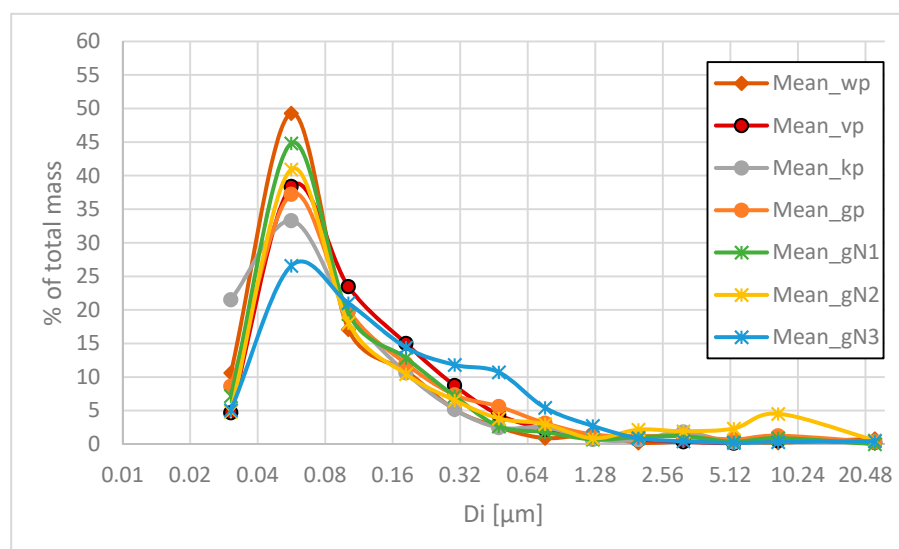


Figure 6. Distribution of the PM size for the experimental fuels and wp.

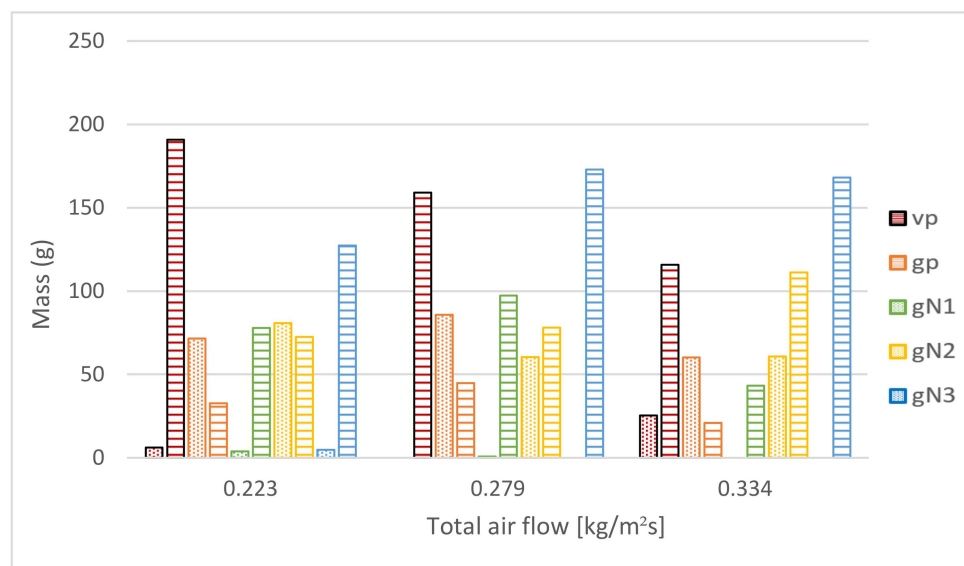
3.3. Ash and Slagging

As mentioned in Section 2.1.2, the slagging evaluation index was used to establish a first approach to the slagging risk of each fuel tested. The results of the calculations are shown in Table 4.

Table 4. Slagging evaluation index for the fuels tested.

Slagging Evaluation Index					
$SEI = \frac{\%MgO + \%Al_2O_3 + \%Fe_2O_3}{\%CaO + \%P_2O_5}$					
SEI < 0.7		High slagging risk			
0.7 < SEI < 1.7		Medium slagging risk			
SEI > 1.7		Low slagging risk			
Fuels	Index	Fuels	Index	Fuels	Index
wp	2.4	Low slagging risk	gp	0.8	Medium slagging risk
kp	0.4	High slagging risk	gN1	1.2	Medium slagging risk
vp	0.2	High slagging risk	gN2	3.9	Low slagging risk
vN2	0.4	High slagging risk	gN3	0.7	High slagging risk
vN3	0.6	High slagging risk			

After the tests were performed, a comparison between the 30_70 air staging tests is carried out for the different fuels, as shown in Figure 7. As it stands out from the graph, vp is characterized by a high ash yield and a comparatively low slagging output when compared to those of pure gp. When pretreatments and additives are included, it is clear that both gN1 and gN3 result in an almost total disappearance of slagging, while showing a tendency to form higher amounts of ash. Regarding gN2, the slagging tendency is similar to that of gp, while the ash yields are comparatively higher. The vp with additives is not included in this graph because no test lasted the required time; thus, no ash or slagging sample could be gathered. This result could be related to the high amount of ash detected in the vp test. With additives, the amount of ash increases, as shown in the gp with additives, thereby making combustion unsustainable for long periods.

**Figure 7.** Slagging (dotted) and ash (striped) yields at the 30_70 air-staging ratio.

The batch of gp is tested with several different air staging configurations to study the influence of this parameter on the ash and slagging yields; the results are displayed in Figure 8. At a low primary air content (20_80 air staging ratio), the amount of ash residues decrease as the total air flow increases, while at high proportions of primary air (40_60 air staging ratio), the inverse trend is detected. The intermediate configuration (30_70 air staging ratio) results in mixed behavior, characterized by the highest slagging amount among the three air-staging ratios. This result makes this last configuration the most interesting to work with, as the intended decrease in slagging caused by pretreatments and

additives should become clearer. Thus, this is one of the main reasons why the 30_70 air-staging ratio is selected as the working configuration for the modified fuels.

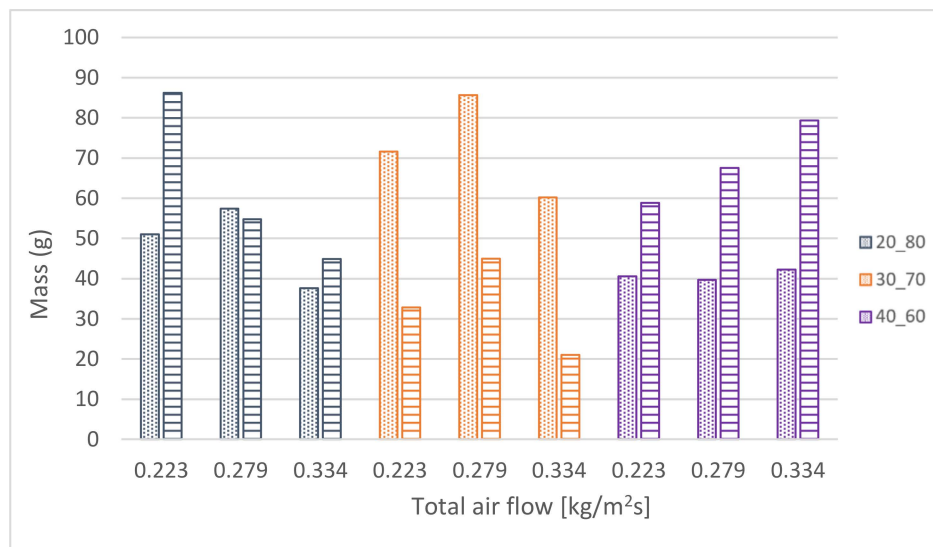


Figure 8. Slagging (dotted) and ash (striped) yields for the gorse pellet tests, according to the air staging.

Regarding the accuracy of the prediction of slagging yield obtained in Table 4, it is clear that the slagging evaluation index has failed to approximate the behavior of the tested fuels. It predicted a high slagging amount with gN3 and a low slagging amount with gN2; however, the opposite results are obtained.

3.4. Fouling

As mentioned in Section 2.1.2, the alkali index gives an estimation of the amount of fouling a certain fuel is expected to yield. In Table 5 this index is calculated for every fuel tested.

Table 5. Alkali index for the fuels tested.

Alkali Index					
$\frac{1}{LHV \left[\frac{GJ}{kg} \right]} \cdot \%ash_{dry\ fuel} \cdot (\%K_2O_{ash} + \%Na_2O_{ash})$					
0 < AI < 0.17			No fouling		
0.17 < AI < 0.34			Probable fouling		
AI > 0.34			Certain fouling		
Fuels	Index		Fuels	Index	
wp	0.03	No fouling	gp	0.31	Fouling is probable
kp	0.52	Fouling is certain	gN1	0.25	Fouling is probable
vp	0.44	Fouling is certain	gN2	0.57	Fouling is certain
vN2	0.45	Fouling is certain	gN3	0.75	Fouling is certain
vN3	0.45	Fouling is certain			

On the experimental side, the deposited and adhered mass on the water-cooled probe was gathered for every test performed. The deposited mass refers to the particles that can be separated from the probe merely by rotating it, while the adhered mass must be removed with the help of tools. The results are displayed in Figure 9.

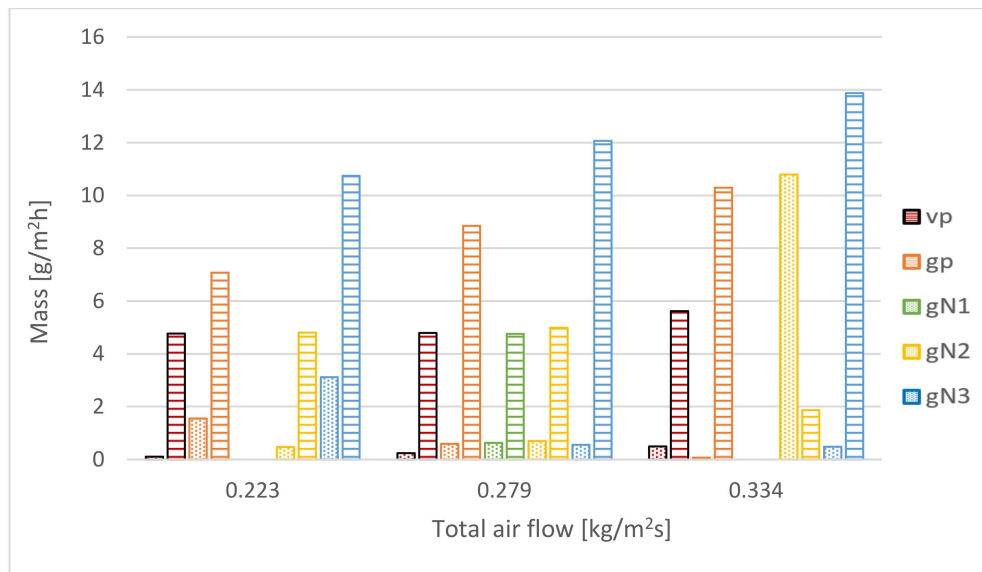


Figure 9. Deposited (dotted) and adhered (striped) masses at the 30_70 air-staging ratio.

In Figure 10, the relationship between the samples of mass and an increasing amount of primary air flow is shown for tests performed with gp.

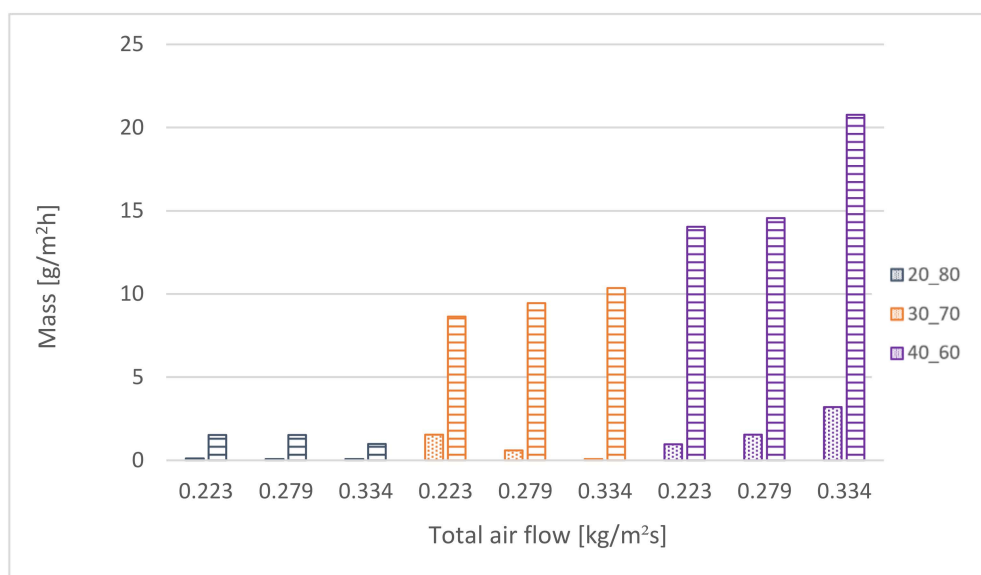


Figure 10. Deposited (dotted) and adhered (striped) masses for the gp tests, according to the air staging.

The empirical prediction given by the alkali index suggests that gN3 will produce the heaviest deposition over the heat exchanger, while gN1 will produce the lightest, but every experimental fuel is expected to produce intermediate to high amounts of fouling.

As for the data gathered from the tests performed, the vp samples seem not to be affected by the increase in total air flow, staying at approximately $5 \text{ g/m}^2\text{h}$, the gN1 sample is practically nonexistent in two of the tests performed, while the gN3 sample is exceedingly high, suggesting that the addition of CaCO_3 results in an increase of the solid matter emissions. The gN2 sample shows intermediate behavior that is between that of gp and gN3, but it is noticeable that, under higher total air flows, this kaolinite-rich fuel yields high masses of adhered material, unlike any other fuel, suggesting a higher proportion of tar and chlorine compounds.

When comparing the prediction with the 30_70 air-staging tests, the accuracy of the index is revealed to be remarkable, having correctly predicted most of the behaviors detected in the experimental tests.

When studying the effect of primary air on the total amount of mass adhered to the water cooled probe, a correlation between the mass gathered and primary air is clear: the higher the air flow entering the combustion chamber via the primary air inlet is, the higher the mass found in the sample. While the tests are long enough for a significant sample of adhered mass to form, this is not the case for the deposited mass, which requires longer combustion times, and thus little to no sample is acquired.

3.5. NO Emissions

From the elemental and proximate analysis, it is clear that the amount of fixed carbon is significantly lower, while the amount of moisture increases in the experimental fuels when compared to wood pellet. These results are expected based on similar research on alternative biomass fuels [11,16]. A higher nitrogen content than that in wood pellets is also detected.

According to the findings mentioned in Section 2.1.1, Figure 11 was elaborated to show the O/N and H/N proportion for the experimental fuels tested in this study, as well as their linear approximations. The linear regression line formula is calculated as in [31].

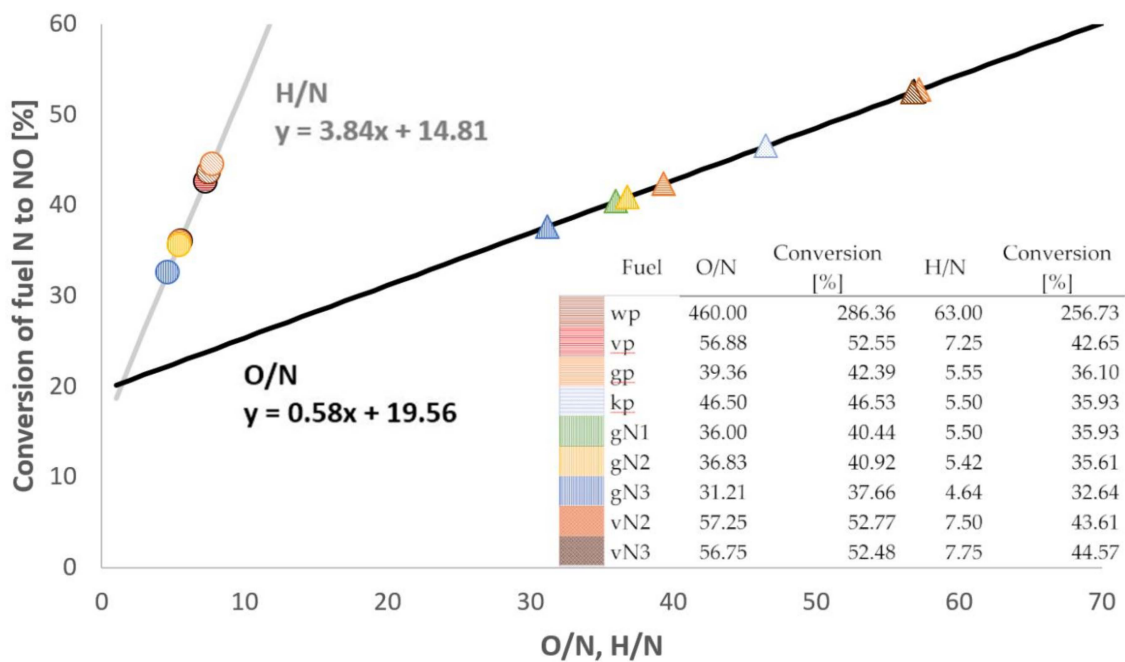


Figure 11. Linear approximation of the nitrogen conversion in biomass fuels as in [31].

On the experimental side, nitrogen oxide emissions are also recorded and analyzed after each test. The results are shown in Figure 12.

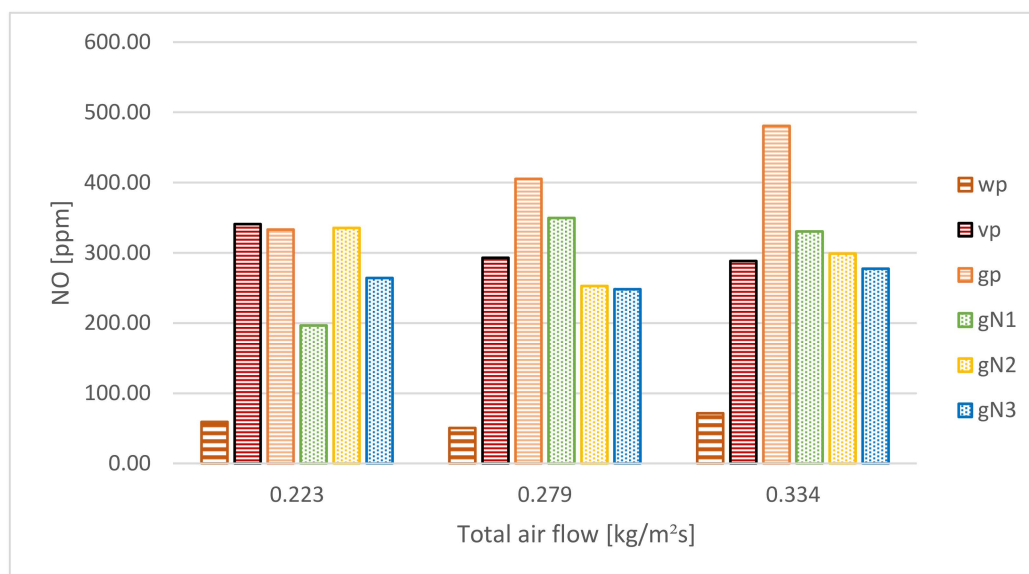


Figure 12. NO emissions of the experimental fuels.

Following the predictions of nitrogen oxides emissions developed by other authors, the linear approximations show that the conversion rates of the fuel nitrogen to NO_x are expected to be approximately 40% for all fuels tested, significantly below the values for wood pellets that are assumed to be 100%. After gathering the data from the tests, it is clear that all the experimental fuels yield a higher quantity of NO than wood pellet. No clear trend is detected, but gorse fuels with additives yield lower quantities of nitrogen oxides than pure gp. These results for NO emissions are in stark contrast with the predictions made, as the fuel expected to convert 100% of its nitrogen into NO_x yields less of these compounds than any other experimental fuel. This could be explained by the fact that experimental fuels had a higher proportion of nitrogen in their composition compared to wood pellet, so even with poorer transformation ratios, the quantity of nitrogen oxides emitted is higher.

4. Conclusions

In view of the results, some experimental fuels showed an acceptable behavior when tested in a small-scale facility. The utilization of gorse and vine pruning pellets, even without additives, results in a stable combustion and could be implemented in commercial facilities provided that they implement an automated ash elimination system. On the other side, kiwi pellet was unsuitable for use in the small-scale boiler employed in this research. A second batch of kiwi pellet with higher durability and lower moisture content was tested but also yielded poor results. The few tests that were carried out successfully showed very inconsistent results and subpar behavior. Similarly, the addition of additives to vine pruning pellet proved to be counterproductive, as the accumulation of ash even over short times stopped the facility from functioning. Nevertheless, the additives and pretreatment added to gorse pellet proved successful in removing the dangers posed by slagging, at the cost of higher ash yields. The research centered in this feedstock with calcium carbonate as an additive seems to be the most promising.

PM emissions and fouling were similarly higher for all the experimental fuels when compared to wood pellet. This result could be due to the high ash proportion in these fuels that might cause two main effects: on the one hand, part of this ash was driven by the air current towards the exterior; on the other hand, this increased amount of ash could diminish the efficiency of the oxygen to fuel mixture, causing an increased amount of unburned particles to be emitted.

The experimental deposition indexes proved to have mixed success in the foreshadowing of the slagging and fouling tendencies of the fuels tested. On the one hand, the slagging evaluation index was incapable of correctly predicting the behavior of the fuels, even offering predictions that later on

were proven to be the opposite of experimental results. On the other hand, the alkali index resulted in very accurate predictions.

Overall, this research shows the potential of several of the most common agricultural and forestry residues of the Galicia-North Portugal region. It opens the path to further research in the field of the utilization of locally available residues as biomass feedstocks, as well as contributing to the cross-border knowledge hub of the Euroregion. The use of these feedstocks could have a positive impact on the sustainability of biomass facilities in the area, as the fuels being produced locally eliminates most transport and storage necessities. This scope also reveals the main limitation of the study, as the wide variety of crops and forestry residues present around the world implies that a direct extrapolation of the data presented here to other residues may not be accurate, although it can be utilized as a reference for comparison.

Author Contributions: Conceptualization, J.J.R.; Methodology, J.J.R.; Validation J.J.R., R.P.-O., N.C. and A.L.; Formal Analysis, N.C. and A.L.; Investigation, J.J.R.; Data Curation, J.J.R., N.C. and A.L.; Writing—Original Draft Preparation, J.J.R., R.P.-O. and N.C.; Writing—Review & Editing, J.J.R. and R.P.-O.; Visualization, J.J.R. and R.P.-O.; Supervision, J.L.M.T.; Project Administration, J.L.M.T.; Funding Acquisition, J.L.M.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Biomasa-AP project, which was approved by the INTERREG V-A España-Portugal 2014-2020 programme (POCTEP) and co-financed by the European Regional Development Fund (FEDER). The work of Raquel Pérez-Orozco has been supported by the grant FPU-15/02430 of the Ministry of Education, Culture and Sports (Spain). The work of Natalia Cid was supported by the Predoctoral Program Xunta de Galicia [ED481A-2019/225].

Acknowledgments: The authors would like to acknowledge the financial support from the Biomasa-AP project, which was approved by the INTERREG V-A España-Portugal 2014-2020 programme (POCTEP) and co-financed by the European Regional Development Fund (FEDER). The work of Raquel Pérez-Orozco has been supported by the grant FPU-15/02430 of the Ministry of Education, Culture and Sports (Spain). The work of Natalia Cid was supported by the Predoctoral Program Xunta de Galicia [ED481A-2019/225].

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this article

AI	Alkali index [kg/GJ]
DLPI	Dekati low-pressure impactor
gN1	Gorse pellet without fines
gN2	Gorse pellet with 2% kaolin
gN3	Gorse pellet with 2% calcium carbonate
gp	Gorse pellet
HHV	Higher heating value [kJ/kg]
HS	Hard sinter
kp	Kiwi pruning pellet
LHV	Lower heating value [kJ/kg]
MELT	Melted sinter
PM	Particulate matter
SEI	Slagging evaluation index (-)
vN2	Vine pellet with 2% kaolin
vN3	Vine pellet with 2% calcite
vp	Vine pruning pellet
wp	Commercial wood pellet
WS	Weak sinter
XRF	X-Ray fluorescence

References

1. European Union. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the Promotion of the Use of Energy from Renewable Sources and Amending and Subsequently Repealing Directives 2001/77/EC and 2003/30/EC. *Off. J. Eur. Communities* **2015**, *269*, 1–15.
2. Akhtar, A.; Krepl, V.; Ivanova, T. A Combined Overview of Combustion, Pyrolysis, and Gasification of Biomass. *Energy Fuels* **2018**, *32*, 7294–7318. [[CrossRef](#)]
3. Holm, J.K.; Stelte, W.; Posselt, D.; Ahrenfeldt, J.; Henriksen, U.B. Optimization of a multiparameter model for biomass pelletization to investigate temperature dependence and to facilitate fast testing of pelletization behavior. *Energy Fuels* **2011**, *25*, 3706–3711. [[CrossRef](#)]
4. Kargbo, H.; Harris, J.S.; Phan, A.N. Drop-in fuel production from biomass: Critical review on techno-economic feasibility and sustainability. *Renew. Sustain. Energy Rev.* **2021**, *135*, 110168. [[CrossRef](#)]
5. Obernberger, I. *The Pellet Handbook—The Production and Thermal Utilisation of Biomass Pellets*; Earthscan: Perth, Australia, 2010.
6. Madlener, R.; Koller, M. Economic and CO₂ mitigation impacts of promoting biomass heating systems: An input-output study for Vorarlberg, Austria. *Energy Policy* **2007**, *35*, 6021–6035. [[CrossRef](#)]
7. Patel, M.; Zhang, X.; Kumar, A. Techno-economic and life cycle assessment on lignocellulosic biomass thermochemical conversion technologies: A review. *Renew. Sustain. Energy Rev.* **2016**, *53*, 1486–1499. [[CrossRef](#)]
8. Gilbe, C.; Lindström, E.; Backman, R.; Samuelsson, R.; Burvall, J.; Öhman, M. Predicting slagging tendencies for biomass pellets fired in residential appliances: A comparison of different prediction methods. *Energy Fuels* **2008**, *22*, 3680–3686. [[CrossRef](#)]
9. Chandrasekaran, S.R.; Hopke, P.K.; Newtown, M.; Hurlbut, A. Residential-scale biomass boiler emissions and efficiency characterization for several fuels. *Energy Fuels* **2013**, *27*, 4840–4849. [[CrossRef](#)]
10. Niu, Y.; Tan, H.; Hui, S. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. *Prog. Energy Combust. Sci.* **2016**, *52*, 1–61. [[CrossRef](#)]
11. Regueiro, A.; Jezerská, L.; Pérez-Orozco, R.; Patiño, D.; Zegzulka, J.; Nečas, J. Viability evaluation of three grass biofuels: Experimental study in a small-scale combustor. *Energies* **2019**, *12*, 1352. [[CrossRef](#)]
12. Regueiro, A.; Jezerská, L.; Patiño, D.; Pérez-Orozco, R.; Nečas, J.; Židek, M. Experimental study of the viability of low-grade biofuels in small-scale appliances. *Sustainability* **2017**, *9*, 1823. [[CrossRef](#)]
13. Vassilev, S.V.; Vassileva, C.G.; Song, Y.C.; Li, W.Y.; Feng, J. Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion. *Fuel* **2017**, *208*, 377–409. [[CrossRef](#)]
14. Yao, X.; Xu, K.; Yan, F.; Liang, Y. The influence of ashing temperature on ash fouling and slagging characteristics during combustion of biomass fuels. *BioResources* **2017**, *12*, 1593–1610. [[CrossRef](#)]
15. Nussbaumer, T. *Aerosols from biomass combustion. Technical report on behalf of the IEA Bioenergy Task 32; 3-908705-33-9*; Verenum Research: Zurich, Switzerland; Lucerne University of Applied Sciences and Arts: Horw, Switzerland, 2017; p. 32.
16. Boström, D.; Grimm, A.; Boman, C.; Björnbom, E.; Öhman, M. Influence of Kaolin and Calcite Additives on Ash Transformations in Small-Scale Combustion of Oat. *Energy Fuels* **2009**, *23*, 5184–5190. [[CrossRef](#)]
17. Mack, R.; Kuptz, D.; Schön, C.; Hartmann, H. Combustion behavior and slagging tendencies of kaolin additivated agricultural pellets and of wood-straw pellet blends in a small-scale boiler. *Biomass Bioenergy* **2019**, *125*, 50–62. [[CrossRef](#)]
18. Bäfver, L.S.; Rönnbäck, M.; Leckner, B.; Claesson, F.; Tullin, C. Particle emission from combustion of oat grain and its potential reduction by addition of limestone or kaolin. *Fuel Process. Technol.* **2009**, *90*, 353–359. [[CrossRef](#)]
19. Wang, L.; Hustad, J.E.; Skreiberg, Ø.; Skjevrak, G.; Grønli, M. A critical review on additives to reduce ash related operation problems in biomass combustion applications. *Energy Procedia* **2012**, *20*, 20–29. [[CrossRef](#)]
20. Zeng, T.; Weller, N.; Pollex, A.; Lenz, V. Blended biomass pellets as fuel for small scale combustion appliances: Influence on gaseous and total particulate matter emissions and applicability of fuel indices. *Fuel* **2016**, *184*, 689–700. [[CrossRef](#)]
21. Mediavilla, I.; Fernández, M.J.; Esteban, L.S. Optimization of pelletisation and combustion in a boiler of 17.5 kW_{th} for vine shoots and industrial cork residue. *Fuel Process. Technol.* **2009**, *90*, 621–628. [[CrossRef](#)]

22. Nurek, T.; Gendek, A.; Roman, K. Forest residues as a renewable source of energy: Elemental composition and physical properties. *BioResources* **2019**, *14*, 6–20.
23. Lubwama, M.; Yiga, V.A. Development of groundnut shells and bagasse briquettes as sustainable fuel sources for domestic cooking applications in Uganda. *Renew. Energy* **2017**, *111*, 532–542. [[CrossRef](#)]
24. Cardozo, E.; Erlich, C.; Alejo, L.; Fransson, T.H. Combustion of agricultural residues: An experimental study for small-scale applications. *Fuel* **2014**, *115*, 778–787. [[CrossRef](#)]
25. Verma, V.K.; Bram, S.; Gauthier, G.; de Ruyck, J. Evaluation of the performance of a multi-fuel domestic boiler with respect to the existing European standard and quality labels: Part-1. *Biomass Bioenergy* **2011**, *35*, 80–89. [[CrossRef](#)]
26. Biomasa-AP Project. Available online: <http://biomasa-ap.com/> (accessed on 2 October 2020).
27. Piñeiro, G.; Pérez, L.; Montero, A. Biomasa-AP: Proyecto para la valorización de subproductos vitícolas mediante la optimización de la explotación y el uso de la biomasa procedente de restos de poda. *Wetwine* **2019**. Available online: https://www.infowine.com/es/articulos_tecnicos/valorizacin_de_subproductos_vitvincolas_de_residuo_a_recurso_energetico_sostenible_y_de_alto_potencial_sc_18881.htm (accessed on 2 October 2020).
28. Channiwala, S.A.; Parikh, P.P. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* **2002**, *81*, 1051–1063. [[CrossRef](#)]
29. Sartor, K.; Restivo, Y.; Ngendakumana, P.; Dewallef, P. Prediction of SO_x and NO_x Emissions from a Medium Size. *Biomass Bioenergy* **2014**, *65*, 91–100. [[CrossRef](#)]
30. Miettinen, H.; Paulsson, M.; Strömberg, D. Laboratory Study of N₂O Formation from Burning Char Particles at FBC Conditions. *Energy Fuels* **1995**, *9*, 10–19. [[CrossRef](#)]
31. Vermeulen, I.; Block, C.; Vandecasteele, C. Estimation of fuel-nitrogen oxide emissions from the element composition of the solid or waste fuel. *Fuel* **2012**, *94*, 75–80. [[CrossRef](#)]
32. Aho, M.J.; Hämäläinen, J.P.; Tummavuori, J.L. Importance of solid fuel properties to nitrogen oxide formation through HCN and NH₃ in small particle combustion. *Combust. Flame* **1993**, *95*, 22–30. [[CrossRef](#)]
33. Hämäläinen, J.P.; Aho, M.J.; Tummavuori, J.L. Formation of nitrogen oxides from fuel-N through HCN and NH₃: a model-compound study. *Fuel* **1994**, *73*, 1894–1898. [[CrossRef](#)]
34. Davidsson, K.O.; Åmand, L.E.; Steenari, B.M.; Elled, A.L.; Eskilsson, D.; Leckner, B. Countermeasures against alkali-related problems during combustion of biomass in a circulating fluidized bed boiler. *Chem. Eng. Sci.* **2008**, *63*, 5314–5329. [[CrossRef](#)]
35. Oleschko, H.; Müller, M. Influence of coal composition and operating conditions on the release of alkali species during combustion of hard coal. *Energy Fuels* **2007**, *21*, 3240–3248. [[CrossRef](#)]
36. Niu, Y.; Zhu, Y.; Tan, H.; Hui, S.; Jing, Z.; Xu, W. Investigations on biomass slagging in utility boiler: Criterion numbers and slagging growth mechanisms. *Fuel Process. Technol.* **2014**, *128*, 499–508. [[CrossRef](#)]
37. Sommersacher, P.; Brunner, T.; Obernberger, I. Fuel indexes: A novel method for the evaluation of relevant combustion properties of new biomass fuels. *Energy Fuels* **2012**, *26*, 380–390. [[CrossRef](#)]
38. Hu, Y.; Cheng, S.; Sun, P.; Xie, J.; Zhang, H. Research on fusion behavior of ash from mixedly burning biomass with coal. *Therm. Power Gen.* **2011**, *40*, 8–12.
39. Rogaume, T.; Auzanneau, M.; Jabouille, F.; Goudeau, J.C.; Torero, J.L. The effects of different airflows on the formation of pollutants during waste incineration. *Fuel* **2002**, *81*, 2277–2288. [[CrossRef](#)]
40. Regueiro, A.; Patiño, D.; Porteiro, J.; Granada, E.; Míguez, J.L. Effect of air staging ratios on the burning rate and emissions in an underfeed fixed-bed biomass combustor. *Energies* **2016**, *9*, 940. [[CrossRef](#)]
41. Febrero, L.; Granada, E.; Patiño, D.; Eguía, P.; Regueiro, A. A comparative study of fouling and bottom ash from woody biomass combustion in a fixed-bed small-scale boiler and evaluation of the analytical techniques used. *Sustainability* **2015**, *7*, 5819–5837. [[CrossRef](#)]
42. Nunes, L.J.R.; Matias, J.C.O.; Catalão, J.P.S. Biomass combustion systems: A review on the physical and chemical properties of the ashes. *Renew. Sustain. Energy Rev.* **2016**, *53*, 235–242. [[CrossRef](#)]
43. Gilbe, J.; Ohman, C.; Lindström, M.; Boström, E.; Backman, D.; Samuelsson, R.; Burvall, R. Slagging characteristics during residential combustion of biomass pellets. *Energy Fuels* **2008**, *22*, 3536–3543. [[CrossRef](#)]
44. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the chemical composition of biomass. *Fuel* **2010**, *89*, 913–933. [[CrossRef](#)]
45. Pérez-Orozco, R.; Patiño, D.; Porteiro, J.; Míguez, J.L. Bed cooling effects in solid particulate matter emissions during biomass combustion. A morphological insight. *Energy* **2020**, *205*, 118088.

46. Båfver, L.S.; Leckner, B.; Tullin, C.; Berntsen, M. Particle emissions from pellets stoves and modern and old-type wood stoves. *Biomass Bioenergy* **2011**, *35*, 3648–3655. [[CrossRef](#)]
47. Kinsey, J.S.; Kariher, P.H.; Dong, Y. Evaluation of methods for the physical characterization of the fine particle emissions from two residential wood combustion appliances. *Atmos. Environ.* **2009**, *43*, 4959–4967. [[CrossRef](#)]



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