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Influence of Long-Term Outdoor Storage of Rockrose (*Cistus laurifolius* L.) Shrub Biomass on Biofuels Quality, Pre-Treatment and Combustion Processes

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Simple Summary: Rockrose (*Cistus laurifolius* L.) is a pyrophyte species with allelopathic effects that colonizes acid forest soils in the Mediterranean basin. Its continuous spread contributes to increasing the wildfire risk, even more so in the current context of forecasts of increasingly intense and prolonged heat waves and droughts. Its mechanized collection and transformation into biofuels contributes to climate change mitigation, the economic development of rural areas and wildfire risk reduction. Biomass storage is an essential requirement in the supply chain of biorefineries and biomass plants. This research aims to evaluate the influence of long-term outdoor storage (1 year) of baled rockrose shrub biomass on the quality of biofuels (30 mm milled material and pellets), on pre-treatment processes and on combustion emissions in an industrial boiler. After storage, no significant differences were observed in the biomass pre-treatment processes or in the emissions in an industrial combustion boiler. Biomass weight loss was 12% after storage. Some quality biofuels parameters improved, being the reduction of the ash content the most outstanding aspect, what allowed to classify 30 mm milled material as class I1, according to ISO 17225-9:2022 and rockrose pellets as class I3 class for industrial use, according to ISO 17225-2-2021 standard.

Abstract: Biomass storage is an essential requirement in the supply chain of bio-refineries and power plants. This research aims to evaluate the influence of long-term outdoor storage (1 year) of baled rockrose (*Cistus laurifolius* L.) shrub biomass on biofuel´s quality, pre-treatment processes and on combustion emissions in an industrial boiler. The raw material was obtained from different rockrose shrublands in North-center Spain. 233 t_{WM} (tones of wet matter) of biomass were used to produce biofuels (30 mm milled biomass and Ø 8 mm pellets) in the pre-treatment pilot plants at CEDER-CIEMAT. The combustion tests were conducted in an industrial moving grate boiler with a thermal power of 50 MWth, in a 17 MWe power plant. Outdoor storage improved some quality biofuels parameters, mainly the reduction in ash content, what allowed to classify 30 mm milled material as class I1 (ISO 17225-9:2022) and pellets as class I3 (ISO 17225-2-2021). No significant differences were observed in the total specific mass flow and energy consumptions in the pre-treatment processes. The combustion tests had similar results, being the emissions below the limits established in the Directive (EU) 2015/2193. The results obtained indicated that 1-year outdoor store of rockrose-baled biomass under Mediterranean conditions was feasible for its subsequent use as biofuel.

Keywords: scrub; milling; pelletisation; emissions; ash content

1. Introduction

Forest biomass from woody shrub species is an important alternative feedstock for bioenergy in European countries [1,2]. Biofuels from shrub species can contribute to climate change mitigation, economic development of rural areas and wildfire risk reduction, especially in Mediterranean countries, such as Spain, where 8.4 million hectares (17% of the country) are occupied by shrublands.

In this country, energy production from biomass accounts for 28.7% of total primary energy production (5.5% in the electrical sector and 23.2% in the thermal sector) [3]. Last year, the production of solid biofuels amounted to 8.1 million t_{DM}/year (tonnes of dry matter per year), of which 56% came from wood chips, 19% from firewood, 10% from olive pomace and 7% from pellets [4].

Many forest managers try to control wildfires by prevention measures based on maintaining cleaned and cleared forests, grazing lands and paths and promote the reduction of fuel by shrublands clearing [5]. The uncontrolled spread of shrub is often an environment conducive to the outbreak and proliferation of new fires in the European Mediterranean countries [6–9]. In Spain, the number of fires sized over 1.0 hectare were 3,760 per year (2010-2020 decade), affecting an annual total of 92,494 hectares, 54,249 ha out of them were covered by scrub [10].

Cistaceae bushes, one of the most abundant shrub formations in Spain, occupy more than 5.7 million ha, especially in non-calcareous soils, where they cover nearly 600,000 ha as dominant species [11]. Rockrose (*Cistus laurifolius* L.), associated with oak, pine and holm oak forests in acidic or limestone soils, occupies 51,377 ha in the Iberian Peninsula as dominant species and 680,856 ha as secondary species [11,12]. This species abounds in the Iberian Peninsula (East, Centre and South) and it is also distributed around the Aegean Sea, in Anatolia and the western Mediterranean (Tuscany, in Italy, Corsica, southern France and Morocco). Different mechanised harvesting trials on monospecific stands of rockrose (*Cistus laurifolius* L.) shrublands in central Spain [5,13] showed, in two years after clearing, an average of 83% reduction in fire spread speed, 63% reduction in heat per unit area, 83% reduction in fire line intensity and up to 77% reduction in flame length, which demonstrates the effectiveness of shrublands clearings [14].

Biomass is one of the few renewable energy sources that can be stored and can generate energy on-demand [15]. Since the supply of forest material is not well aligned with consumption needs, storage is a necessary requirement in the supply chain, especially for bio refineries and power plants [16]. In the case of shrublands, clearing is often hampered by factors related to weather, fauna and soil conditions, among others [5], so it is necessary to take maximum advantage of the periods when shrublands can be harvested, what generates a stock of raw material that needs to be stored.

During biomass storage, moisture content is considered the most important quality parameter, since it affects other factors such as the calorific value, storage properties and transport costs, and it is taken into account in the pricing of the fuel [17–21]. However, the concentration of several inorganic elements, such as Chlorine or Sulphur, which are also biomass quality parameters that determine the classification of biomass according to ISO 17225-9:2022 and ISO 17225-2:2022 and can contribute to the corrosion of boilers and to emissions, can be modified during storage. Natural drying is a cheap and easy method to reach adequate moisture content in forest biomass [16,22]. Although there is a cost associated with immobilized capital, the developed heating markets consider differentiated prices of wood fuel, according to their moisture content [20], which can offset the opportunity cost associated with fixed capital. Natural drying can be carried out after harvesting and before milling to reduce the moisture content of biomass to less than 30 % (wet basis), which makes it suitable for the supply of cogeneration or combined heat and power plants (> 5 MW) and also for the supply of district heating systems and central heating systems (< 5MW) [21,23].

Some shrubs can be an appropriate biomass to produce biofuels, such as pellets or milled material [9]. However, the composition of this kind of biomass could lead to fouling, slagging and high emissions of NOx or particulate matter, especially in domestic combustion devices, where systems for mechanical cleaning or abatement of particles and NOx do not exist or are very simple [9,24].

This research seeks to evaluate the influence of 1-year outdoor storage of baled rockrose (*Cistus laurifolius* L.) shrub biomass on solid biofuels quality, on pre-treatment processes and on combustion emissions in an industrial boiler (50 MWth). The investigation was conducted in the framework of the Life+ Enerbioscrub project (Project LIFE13 ENV/ES/000660) which aimed to reduce the risk of forest fires by obtaining sustainable solid biofuels from shrublands of high flammability risk.

2. Materials and Methods

2.1. Raw Material

Rockrose (*Cistus laurifolius* L.) baled biomass from forest clearings in three shrublands located in Navalcaballo, Lubia and Torretartajo (Soria) was used as raw material. A harvester-baler system (Biobaler WB55) was used to produce round bales (ϕ=1.2 m, width=1.2 m, density=340 kg m^{-3}) with an average productivity of 1.6 Mg_{DM} PMH^{-1} (Mg of dry matter per productive machine hour) and an average yield of 0.7 ha PMH^{-1} [13] (Figure S1).

Baled biomass (233.27 Mg_{WM} [156.68 Mg_{DM}]) was taken to CEDER-CIEMAT (Centre for the Development of Renewable Energy Sources) in Lubia (Soria) for biomass storage study, pre-treatment tests and biofuel characterisation. Afterwards, 30 mm milled biomass was used in combustion tests in an industrial power plant boiler in Garray (Soria), 30 km far from the cleared areas. The pre-treatment and combustion tests were repeated with just-harvested biomass and with 1-year outdoor storage biomass, following the same procedures.

2.2. Biomass Storage

Collected biomass was stacked outdoors at CEDER-CIEMAT in three-bale-height piles on a concrete deck with a perimeter fence. The baled biomass was stored for one year from 3/2/2016 to 31/1/2017. The storage area has a continental Mediterranean climate [26,27], with an average annual temperature of 10.7 ºC and an average annual rainfall of 472 mm over the last ten years (2009-2017). Meteorological data were obtained from Lubia Weather Station, placed 50 m far from the storage area.

Rockrose baled biomass was stored for 1 year to evaluate the influence of outdoor storage on biomass weight dry matter losses and biofuels physicochemical properties.

Biomass dry matter variation, expressed as a percentage, was calculated as the difference between dry biomass weight before and after the storage period, divided by the mass before the storage. For it, 45 rockrose bales, stored outdoors in a three-bale pile (Figure S2) were weighted individually before and after storage using a weighing hook (500 kg ± 200 g) attached to the bucket arm of a tractor.

Solid biofuels (30 mm milled biomass and Ø 8 mm pellets) were produced with just harvested biomass and with 1-year stored biomass following the same pre-treatment processes. Biofuel samples for subsequent analytical characterization were obtained according to the following procedure:

a) 30 mm milled biomass: Three bales of just-harvested biomass were randomly selected for subsequent shredding at 30 mm. A combined sample of milled material, consisting of 6 sub-samples of 2 kg each, was prepared for laboratory analysis. After the storage period, three bales, stacked at different heights, were randomly selected to be shredded and sampled for analysis. In addition, to evaluate the bale moisture content variation throughout the storage period, one bale was shredded at 30 mm every 2 months, from those placed in the central height of the piles, and a biomass sample was taken following the protocol described above.

b) Ø 8 pellets: Three pelletisation tests were carried out with just harvested biomass and another three tests with 1-year stored biomass. In each test, 6 subsamples of 2 kg each were taken from moving material at the outlet of the bagging bin of the pelletisation pilot plant described in section 2.3 Afterwards, sub-samples were mixed, and a combined sample was taken for analytical characterisation. The same sampling protocol was used to sample stored biomass pellets.

2.3. Biofuels Production

As mentioned in the previous section, two different biofuels were produced from rockrose bales: 30 mm milled biomass to feed an industrial boiler and Ø 8 mm pellets to evaluate their quality and possible application in the domestic or industrial sector. The pre-treatment tests were performed with just-harvested biomass and with 1-year outdoor storage biomass, following the same procedures.

For the production of biofuels, the following biomass pretreatment plants were used. It should be noted that, since the initial bales moisture content was 38.5%, a previous drying process in a rotary dryer was needed before just-harvested biomass shredding.

a) Communition equipments. A 90 kW pre-shredder was used to reduce in size rockrose bales in order to ensure a proper boiler feed and optimum efficiency of the combustion system. In this equipment, the material was pressed against a monorotor by a hydraulic feeder with a pusher stroke of 1100 mm. This rotor (ϕ 450 mm, 1400 mm length) was provided with 102 embedded blades (40×40 mm) that milled the biomass by passing it through a 30 mm mesh. The biofuels produced were used to power an industrial combustion boiler without previous sieving and drying processes (Figure S3-left).

Subsequently, part of the shredded biomass was milled for further pelletisation. A 75 kW hammer mill with a 4 mm mesh was used to mill shredded bales for pellet production (Figure S3-center).

b) Pelletisation plant

Pelletisation tests were carried out in a pilot plant with a 30 kW flat die press, Ø 500 mm die diameter and 4.4 compression ratio flat die (ratio of the effective working length of the die holes [35 mm] to the die hole diameter [8 mm]) (Figure S3-right).

The following amount of biomass was used before storage and the same quantity was also processed after storage:

- Pre-shredder tests: Three batches of 80 bales (35 t_{WM} per lot) were crushed to 30 mm for the industrial boiler. Part of the obtained material (4.3%) was post-grinded for pelletisation tests.
- Post-grinder tests: Three batches of 30 mm shredded biomass (1500 kg_{WM} per batch) were processed in the hammer mill to 4 mm for pelletisation tests.
- Pelletisation tests: Three batches of 4 mm biomass (1500 kg_{WM} per batch) were pelletised to obtain Ø 8 mm pellets.

During the biomass pre-treatment tests (shredding, milling and pelletisation), the specific mass flow and the specific energy consumed in the different processes were recorded when the equipments reached steady state conditions. The specific mass flow (MF, kg_{DM} h^{-1} kW^{-1}) was obtained by dividing the mass of the processed material (kg_{DM}) by the time used to shred, mill or pelletise it (h) and by the power of the corresponding equipment (kW). To obtain the specific energy (E, kWh Mg_{DM}^{-1}), the active electric energy (kWh) required by the shredder, mill and pelletisation press was divided by the mass of the processed material (Mg_{DM}) in each case.

2.4. Biomass Combustion

The combustion tests were conducted in an industrial moving grate boiler with a thermal power of 50 MW_{th}, in a 17 MWe power plant. The boiler allows a steam production of 58.5 Mg h^{-1} overheated at 93 bar and 487 °C, which generates an electricity production of 108,333 MWh per year. Designed to be fueled by forest biomass, mainly wood logs, pruning waste bales and milled wood, it was fed for the trial with milled rockrose. The combustion gases were filtered through a multicyclone and bag filter to treat a gas flow of 74,000 Nm^3 h^{-1} before being emitted to the atmosphere.

Combustion tests were performed with 30 mm milled material during a steady state period of 4 hours, following the same procedure for just-harvested biomass and after 1-year outdoor storage biomass, in order to compare emissions (NO_x, SO_2 and particles). During the combustion tests, different settings were modified with the aim of adjusting the installation operational parameters to the rockrose fuel, and emissions were measured under steady state conditions. Previously, the combustion of a forest fuel commonly used in the power plant was also monitored during the same time and steady conditions. Continuous measurement of the gaseous composition of exhaust gases was carried out with a portable Fourier Transform Infrared (FTIR) Spectroscopy analyser. Furthermore, three discontinuous measurements of total solid particles (TSP) were performed applying EN 13284-1:2017, through isokinetic samplings.

2.5. Analytical Procedures

Biofuels were analysed in the Laboratory of Biomass Characterisation at CEDER-CIEMAT. Analytical samples were prepared according to ISO 14780:2017 standard, by means of homogenisation, division, grinding and drying. In order to evaluate changes in physical and chemical properties, the following parameters were analysed: moisture content, calorific value, ultimate analysis (C, H, N, S and Cl), major and minor elements, ash content and ash composition, all by following the standards and analytical methods shown in Table 1.

Table 1. Standards and analytical methods used at CEDER-CIEMAT Biomass Characterisation Laboratory.

Property	Technique of analysis	Standard
Sampling	Solid biofuels sampling	ISO 21945
Analytical sample preparation	Homogenisation, division, drying and grinding	ISO 14780
Bulk density	Mass of a known volume	ISO 17828
Particle size distribution	Separation into defined size fractions (sieves)	ISO 17827-1 ISO 17827-2
Moisture	Drying at 105 ºC	ISO 18134-2
Ash	Calcination at 550 ºC	ISO 18122
Volatile matter	Heating at 900 ºC	ISO 18123
Ultimate analysis C, H, N S and Cl	Elemental analysis (TruSpec, Leco) Ion chromatography (883 Basic IC Plus, ISO 16994 Methrom) after sample combustion (C5003, Ika Verke) and lixiviation	ISO 16948 ISO 16994
Calorific value	Automatic calorimeter (C5003, Ika Verke)	ISO 18125
Major elements	Microwave digestion (Ethos Pro, Milestone) and ICP-AES (Jarrell ash, Thermo Scientific)	ISO 16967
Minor elements	Microwave digestion (Ethos Pro, Milestone) and ICP-MS (iCAP Q, Thermo Scientific) Thermal decomposition/gold amalgamation/absorption spectrophotometry (DMA-80, Milestone) for Hg	ISO 16968

3. Results

3.1. Biomass Storage

After 1-year outdoor storage with climate conditions shown in Table 2, rockrose bale piles remained stable, bales kept most of the leaves but their density decreased from 340 kg m^3 to 222 kg m^3 and most of the baling ropes were loose and some of them broken (Figure S4). Biomass moisture content decreased from 38.5% to 22.5% after the first 4 months of storage (February-May 2016) and from 22.5% to 17.8% after the next 8 months (June 2016-January 2017) (Table 3). Biomass dry matter variation after 1-year outdoor storage was 12.3% (Table 3).

Table 2. Atmospheric mean values during the storage period, year 2016 and 2009-2017 period.

Parameter	**Unit**	**Storage period**	**2016**	**2009-2017**
Mean temperature	ºC	11.0	10.7	10.7
Absolute maximum temperature	ºC	35.6	35.6	34.7
Absolute minimum temperature	ºC	-11.7	-7.5	-10.2
Mean maximum temperature	ºC	17.2	17.3	17.5
Mean minimum temperature	ºC	4.6	4.8	4.3
Precipitation	mm	431.7	540.2	471.8
Direct solar radiation	MWh m^{-2}	1.42	1.40	1.4
Relative humidity	%	68.4	69.5	66.8
Wind speed	m s^{-1}	1.9	2.0	n.a.
Wind direction	Degrees	261.4	258.9	n.a.

n.a.: not available.

Table 3. Moisture content and dry matter variation during 1-year outdoor storage period (3/2/2016 to 31/1/2017).

Description	**Value**
Initial moisture content (%)	38.5
2-month moisture content (%)	30.3
4-month moisture content (%)	22.5
6-month moisture content (%)	21.4
8-month moisture content (%)	19.1
10-month moisture content (%)	20.6
Final moisture content (%)	17.8
Initial stored wet biomass (kg_{WM})	20,748
Initial stored dry biomass (kg_{DM})	12,760
Initial wet weight per bale (kg_{WM} per bale)	461.1
Initial dry weight per bale (kg_{DM} per bale)	283.5
Final stored wet biomass (kg_{WM})	13,611
Final stored dry biomass (kg_{DM})	11,188
Final wet weight per bale (kg_{WM} per bale)	302.5
Final dry weight per bale (kg_{DM} per bale)	248.6
Dry matter variation (kg_{DM})	1,572
Dry matter variation (%)	12.3

3.2. Biofuels Production

The values of specific mass flow (MF) and specific energy (E) of the pre-treatment tests (shredding, milling and pelletisation processes) for just-harvested biomass and after 1-year outdoor storage biomass are shown in Table 4.

Table 4. Results of rockrose communition and pelletisation tests with just-harvested biomass and after 1-year outdoor storage period.

Pre-treatment process	**Test 1**	**Test 2**	**Test 3**	**A**	**SD**	**%RSD**	**α**
Shredder (30 mm)							
Just-harvested biomass							
MF (kg h^{-1} kW^{-1}) (d.b.)	17.8	19.3	12.8	16.6	3.4	20.5	
E (kWh Mg^{-1}) (d.b.)	11.7	10.6	12.9	11.7	1.2	9.8	
M (wt.%) (w.b.)	25.0	30.0	23.0	26.0	3.6	13.9	
After 1-year biomass storage							
MF (kg h^{-1} kW^{-1}) (d.b.)	19.3	17.4	15.0	17.2	2.2	12.5	

E (kWh Mg^{-1}) (d.b.)	11.7	11.7	13.4	12.3	1.0	8.0	
M (wt.%) (w.b.)	17.5	18.8	18.3	18.2	0.7	3.6	
P-value of the F-test (95% prob.)							
MF (kg h^{-1} kW^{-1}) (d.b.)							0.809
E (kWh Mg^{-1}) (d.b.)							0.574
Post-grinder (4 mm)							
Just-harvested biomass							
MF (kg h^{-1} kW^{-1}) (d.b.)	10.6	9.7	12.3	10.9	1.3	12.2	10.6
E (kWh Mg^{-1}) (d.b.)	58.1	57.3	53.8	56.4	2.3	4.1	58.1
M (wt.%) (w.b.)	22.1	13.8	13.5	16.5	4.9	29.6	22.1
After 1-year biomass storage							
MF (kg h^{-1} kW^{-1}) (d.b.)	9.1	9.0	8.9	9.0	0.1	1.0	9.1
E (kWh Mg^{-1}) (d.b.)	58.5	53.5	52.0	54.7	3.4	6.2	58.5
M (wt.%) (w.b.)	19.2	14.3	16.6	17.9	1.8	10.3	19.2
P-value of the F-test (95% prob.)							0.071
MF (kg h^{-1} kW^{-1}) (d.b.)							0.505
E (kWh Mg^{-1}) (d.b.)							
Pelletisation (Ø 8 mm)							
Just-harvested biomass							
MF (kg h^{-1} kW^{-1}) (d.b.)	6.0	5.8	7.3	6.4	0.8	12.8	6.0
E (kWh Mg^{-1}) (d.b.)	128.0	137.2	117.1	127.4	10.1	7.9	128.0
M (wt.%) (w.b.)	10.0	9.1	11.0	10.0	1.0	9.5	10.0
After 1-year biomass storage							
MF (kg h^{-1} kW^{-1}) (d.b.)	6.2	7.3	5.5	6.3	0.9	14.3	6.2
E (kWh Mg^{-1}) (d.b.)	131.0	117.0	157.7	135.2	20.7	15.3	131.0
M (wt.%) (w.b.)	11.5	11.0	10.2	10.9	0.7	6.0	11.5
P-value of the F-test (95% prob.)							
MF (kg h^{-1} kW^{-1}) (d.b.)							0.965
E (kWh Mg^{-1}) (d.b.)							0.588

A: Average value; MF: specific mass flow; E: specific energy; M: moisture content (wt.%: weight %; d.b.: dry basis; w.b.: wet basis; SD: standard deviation; RSD: relative standard deviation (%); P-value: significance level (α) of the F-tests pre-treatment processes (95% of probability).

3.2.1. Communition Tests

Shredding results at 30 mm indicated that there were not significant differences before and after the storage period. Relative increases of 3.6% in specific mass flow (MF), from 16.6 to 17.2 kg h^{-1} kW^{-1} (d.b.) and of 5.1% in specific energy (E), from 11.7 to 12.3 kWh Mg^{-1} (d.b.), were observed when using stored biomass.

Milling results at 4 mm were also similar in terms of specific mass flow (10.9 vs. 9.0 kg h^{-1} kW^{-1}) and specific energy demand before and after storage (56.4 vs. 54.7 kWh Mg^{-1} [d.b.]), with similar values of biomass moisture content. An analysis of variance (ANOVA) of MF and E in shredding and milling processes was carried out, taking into account the storage duration factor. Significance levels (α) of the F-tests are shown in Table 5. A significance level less than 0.05 indicates that a factor has a statistically significant effect on the measured property at the 95.0% of probability. No differences in shredding and milling were found between just-harvested biomass and after 1-year outdoor storage at the 95% probability (α=0.05), although 4 mm milling MF would show differences after 1-year outdoor storage if the statistical contrast was carried out at the 90% probability (α =0.10).

Table 5. Physical and chemical characterisation of 30 mm milled rockrose and Ø 8 mm rockrose pellets, before and after storage.

Parameter	**Unit**	**Milled rockrose**		**Rockrose pellets**	
		BS	**AS**	**BS**	**AS**
Diameter	mm	-	-	8	8
Moisture content	wt.% (w.b.)	16.5	10.9	7.2	9.4
Bulk density	kg m^{-3} (w.b.)	280	250	700	670
Mechanical durability	%	-	-	97.3	99.2
Fines	%	10.5	5.5	0.2	0.3
Calorific values:					
GCV	MJ kg^{-1} (d.b.)	19.61	19.85	19.9	19.9
GCV	MJ kg^{-1} (w.b.)	16.38	17.69	18.5	18.0
NCV	MJ kg^{-1} (d.b.)	18.33	18.55	18.9	18.6
NCV	MJ kg^{-1} (w.b.)	14.9	16.26	17.4	16.6
Inmediate analysis:					
Ash	wt.% (d.b.)	4.7	2.8	4.2	3.0
Volatile matter	wt.% (d.b.)	78.8	80.4	78.6	79.9
Ultimate analysis:					
Carbon	wt.% (d.b.)	49.3	49.6	50.2	50.4
Hydrogen	wt.% (d.b.)	5.9	6.0	5.8	5.9
Nitrogen	wt.% (d.b.)	0.45	0.42	0.40	0.40
Sulphur	wt.% (d.b.)	0.04	0.03	0.04	0.02
Chlorine	wt.% (d.b.)	0.01	0.01	0.01	0.01
Ash composition:					
Al_2O_3	wt.% (d.b.)	2.2	1.5	2.9	1.7
BaO	wt.% (d.b.)	0.13	0.19	0.16	0.15
CaO	wt.% (d.b.)	18	42	23	28
Fe_2O_3	wt.% (d.b.)	2.0	0.62	16.0	1.0
K_2O	wt.% (d.b.)	4.4	6.0	6.7	6.0
MgO	wt.% (d.b.)	1.8	3.4	2.7	2.8
Mn_2O_3	wt.% (d.b.)	0.52	0.77	0.64	0.61
Na_2O	wt.% (d.b.)	0.14	0.20	0.21	0.15
P_2O_5	wt.% (d.b.)	2.1	1.8	2.8	2.4
SO_3	wt.% (d.b.)	1.8	1.6	1.5	1.4
SiO_2	wt.% (d.b.)	51	19	35	31
SrO	wt.% (d.b.)	0.031	0.059	0.039	0.047
TiO_2	wt.% (d.b.)	0.18	0.088	0.23	0.12
ZnO	wt.% (d.b.)	0.12	0.11	0.072	0.074
Sum	wt.% (d.b.)	84.0	80.3	76.8	76.2
Trace elements on biomass					
As	mg kg^{-1} (d.b.)	0.21	<0.10	0.19	<0.10
Cd	mg kg^{-1} (d.b.)	0.27	0.28	0.29	0.25
Cr	mg kg^{-1} (d.b.)	8.1	1.6	3.9	1.8
Cu	mg kg^{-1} (d.b.)	5.6	3.1	5.0	2.5
Pb	mg kg^{-1} (d.b.)	1.6	1.7	1.7	1.7
Hg	mg kg^{-1} (d.b.)	0.005	0.004	0.005	0.004
Ni	mg kg-1 (d.b.)	18.0	5.0	11.0	2.9
Zn	mg kg-1 (d.b.)	26	22	22	17

BS: before storage; AF: after storage; GCV: gross calorific value; NCV: net calorific value; wt.%: weight %; w.b.: wet basis; d.b.: dry basis.

3.2.2. Pelletisation Tests

Similar results of specific mass flow were obtained when pelletising just-harvested biomass and after 1-year outdoor storage biomass (6.4 vs. 6.3 kg h^{-1} kW^{-1} [d.b.]) (Table 5). The specific energy was slightly higher (6.1% in relative percentage) with stored biomass (127.4 vs. 135.2 kWh Mg^{-1} [d.b.]), although no significant differences were found at the 95% probability (α=0.05).

The total specific mass flow and energy consumptions in the shredding, milling and pelletisation processes were similar before and after storage (33.9 vs. 32.6 kg h^{-1} kW^{-1} [d.b.] and 195.5 vs. 202.2 kWh Mg^{-1} [d.b.]), taking into account that an initial drying in a rotary dryer was needed before just-harvested biomass shredding, with an energy consumption of 21 kWh Mg^{-1} (d.b.).

3.3. Biofuels Characterisation

The physical and chemical characterisation of the rockrose biofuels (30 mm milled material and Ø 8 mm pellets) with just-harvested biomass and after 1-year outdoor storage can be seen in Table 5.

The cumulative particle size distribution of the 30 mm milled rockrose before and after storage was similar (Figure 1). The most notable difference was observed in the fraction of fines (<3.5 mm) of milled rockrose before and after storage (10.5% vs. 5.5%). Calorific values in dry basis remained almost constant after storage in both biofuels. Ash content decreased from 4.7 to 2.8% in the case of 30 mm milled rockrose and from 4.2 to 3.0% in the case of pellets. Ash chemical composition indicated that the content of Si, Al, Fe, P and Ti, elements typically present in the soil, were reduced after storage, which could explain that the decrease in ash content was due to the action of the wind and biomass washing process by rainfall, together with the handling during de-stacking. The content of C and H was also reduced after storage (12% and 11% respectively), what suggested a biological degradation of the stored biomass. Cl content was not modified during storage and S content decreased. Trace elements also decreased after storage in both biofuels.

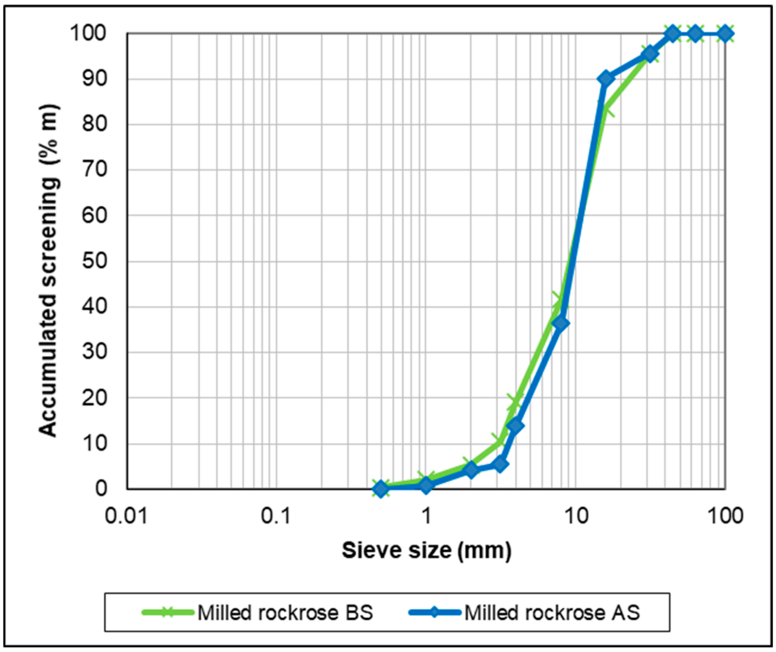

Figure 1. Cumulative particle size distribution of 30 mm milled rockrose before storage (BS) and after 1-year outdoor storage (AS).

3.4. Biomass Combustion

The industrial boiler (50 MW_{th}) fed with 30 mm milled rockrose was operated without mechanical problems, allowing a homogeneous boiler feeding and stable combustion conditions. Gaseous and particle emissions during the steady state period of the combustion tests, referred to dry basis and reference O_2 of 6 v.%, are shown in Table 6.

Table 6. Emissions during the steady state of the combustion tests in an industrial boiler (50 MW_{th}) referred to dry gas basis and reference O_2 of 6%v.

Biofuel	**NO_x (mg/Nm^3)**		**SO_2 (mg/Nm^3)**		**TSP (mg/Nm^3)**	
	A	**SD**	**A**	**SD**	**A**	**SD**
Commonly used fuel	367	23	11	1.7	13	4.2
Milled rockrose (BS)	367	23	13	2.1	17	5.5
Milled rockrose (AS)	338	22	11	2.0	16	5.8
Directive (EU) 2015/2193 and RD 1042/2017 limits	650		200		30	

%v.: % volume; BS: before storage; AS: after storage; A: average value; SD: standard deviation; NO_x: NO + NO_2, shown as NO_2; TSP: total solid particles.

4. Discussion

4.1. Biomass Storage

Prolonging outdoor storage more than one year might not be recommended, since picking-up loose bales with broken strings could be a risk during de-stacking work.

The decrease in moisture content was greater in the first 4 months, with a cumulative rainfall of 259.6 mm, than in the remaining 8 months, with 172.1 mm rainfall, mainly concentrated in November (Figure S5). As can be seen in Table 2, weather in 2016 was similar to the average one during the period 2009-2017, with 14.5% more precipitation (540 mm) and the same annual mean temperature (10.7 ºC). This proves that outdoor-baled rockrose storage, under Mediterranean climate, is an effective solution to dry biomass that requires little capital investment. In contrast, in the North of the Iberian Peninsula, with Atlantic climate, 1-year pine woodchips storage is not a good solution to dry biomass, since the moisture content of the pile increases with storage time [28].

Regarding biomass dry matter variation after 1-year outdoor storage (12.3%), similar or greater losses were referred in previous studies of Mediterranean shrub open storage trials along 1-year period (14% with baled broom or 14-30% with mulched gorse) [5].

Based on the mass balance carried out on rockrose before and after storage (Table 4), ash content was reduced by 47.8%. Ash chemical composition indicated that the content of Si, Al, Fe, P and Ti, elements typically present in the soil, were reduced after storage by 80%, 66%, 84%, 27% and 75% respectively, which could explain that the decrease in ash content was due to the action of the wind and biomass washing process by rainfall, together with the handling during de-stacking. The content of C and H was also reduced after storage (12% and 11% respectively), what suggested a biological degradation of the stored biomass.

According to baled rockrose biomass total net costs, including harvesting and baling with Biobaler, bale gathering, loading and transport at destination (76.76 € Mg_{DM}^{-1}) [13], the biomass dry matter variation (12.3%) involved an increment of 13.4% in the cost of a dry biomass tone at destination.

Other outdoor storage systems that minimise biomass losses should be tested in the future. It would be interesting to assess biomass losses by placing round bales in rows of one height, with the flat side of one bale next to the next. The rows should face south-southwest to allow maximum exposure to the sun. The distance between the rows should be at least one meter to allow the wind to pass through.

On the other hand, it would also be interesting to estimate biomass losses by placing a waterproof and breathable tarpaulin over the prismatic bale stacks.

4.2. Biofuels Production

After analysing the specific mass flow and specific energy results of the biomass pre-treatment processes performed in triplicate before and after storage, no significant differences were observed in any of the shredding, milling and pelletisation tests.

Figures of specific mass flow and specific energy of shredding, milling and pelletisation processes, before and after the storage, were of the same order as the reported values to obtain 30 mm shredded material and Ø 8 mm pellets from broom bales in the same equipments [5,9]. As in previous works with other shrub biomass, small variations in communition results could be related to the differences in the milled biomass moisture content and with the lack of homogeneity of the baled material [9].

4.3. Biofuels Characterisation

Biomass storage contributed to improve some quality biofuels parameters, being the reduction in the ash content and trace elements the most outstanding aspects. In the case of 30 mm milled material, the ash content reduction after storage (≤ 3%) together with the decrease in Ni content (from 18.0 to 5.0 mg kg^{-1} d.b., below I1 class limit ≤ 10 mg kg^{-1}d.b.), allowed to classify this biofuel as class I1, according to ISO 17225-9:2022, dedicated to specification of graded hog fuel and wood chips for industrial use. The rest of the parameters were widely fulfilled. It should be noted that the stored biomass was shredded with new blades in the pre-shredder rotor, which were less alloyed in Cr and Ni than the previous ones. Therefore, the higher content of these elements in the just-harvested biomass could be due to the contamination caused by the blade´s wear. On the other hand, the fraction of fines of milled rockrose (graded hog fuel) was particularly high (10.5% <3.5 mm) (Table 6 and Figure 1) and a prior screening process before its use would be advisable to reduce fines.

According to ISO 17225-2-2021 standard, the pellets obtained after storage were suitable for industrial use (I3 class) due to the high ash content. Since this property is the only limiting factor for the rockrose pellets to be used in the domestic sector, with an appropriate pre-treatment, e.g. fines separation, which involves the reduction of the ash content of the pellets [29–31], they could be classified in category B class (≤2% ash content) of the aforementioned standard, for use in commercial and residential applications, that demand high-quality products with minimum ash content. Without prior screening, the use of rockrose biofuels seems to be more suitable in industrial boilers, where cleaning systems for abatement, such as multicyclones and fabric filters are usually present.

4.4. Biomass Combustion

Rockrose combustion in the industrial boiler fulfilled the limits established in the standard Directive (EU) 2015/2193 of the European Parliament and of the Council of 25 November 2015, on the limitation of emissions of certain pollutants into the air from medium combustion plants (Table 7). In addition, no differences in combustion emissions were observed between biofuels from just-harvested rockrose and 1-year outdoor storage rockrose, with emissions being similar to those of one of forest fuels commonly used in the biomass plant. With the use of bag filter, the TSP (total suspended particles) emitted through the stack were similar between milled rockrose before and after storage, despite having a higher ash content the milled rockrose from just-harvested biomass.

5. Conclusions

The results obtained in this study indicates that a long-term outdoor store (1 year) of rockrose-baled biomass in North-central Spain, under Mediterranean continental climate, is feasible for its subsequent use as biofuel.

Outdoor storage on a concrete deck proved to be an effective solution for biomass drying, assuming 12% biomass weight loss. It improved some quality biofuels parameters, being the reduction of the ash content the most outstanding aspect. This allowed to classify 30 mm milled material as class I1, according to ISO 17225-9:2022, dedicated to specification of graded hog fuel and wood chips for industrial use, and rockrose pellets obtained as class I3 class for industrial use, according to ISO 17225-2-2021 standard.

No significant differences were observed in the total specific mass flow and energy consumptions in the rockrose shredding, milling and pelletisation processes before and after storage. The combustion of the rockrose biomass before and after storage, had similar results, and did not produce higher emissions than one of the fuels commonly used in the industrial boiler, being therefore, below the limits established in the Directive (EU) 2015/2193.

In forthcoming research, inert element separation systems during pre-treatment processes will be tested to reduce the ash content of the resulting pellets and shredded material, in order to bring them closer to the commercial quality of non-industrial pellets.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org.

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