

# The Use of Near-Infrared (NIR) Spectroscopy and Principal Component Analysis (PCA) To Discriminate Bark and Wood of the Most Common Species of the Pellet Sector

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**ABSTRACT:** The pellet energy market is expanding rapidly in Europe and also at the global level, in response to the continuously growing energy demand and because of the high degree of reliability, the easy handling, and the cheap and simple logistics, in comparison to other solid biomasses. The fast growth of this market has highlighted the problem of product quality, which has strong repercussions for technical, environmental, and economic aspects. The biomass quality is defined by several chemical–physical parameters that are directly measurable in the laboratory. In addition, there are quality attributes related to origin and source, difficult to investigate through traditional analyses, such as the type of wood (hardwood/softwood) and the presence of bark. The development of a rapid technique able to provide this information could be an advantageous tool for the energy sector proving indications on biofuel traceability and sustainability. More than 90 samples belonging to three of the most common European species for the energy pellet sector (fir, pine, and beech) have been collected and analyzed by means of Fourier transform near-infrared (FT-NIR) coupled with Principal Component Analysis (PCA). The results show that the main variation in the data is due to both differences between bark and wood, as well as differences between hardwood and softwood. The differences are mainly linked to changes in composition and amounts of cellulose, hemicellulose, lignin, and extractives. Moreover, 30 wood/bark blends (2%–20% (w/w)) were analyzed, indicating the ability of the system to recognize blends from pure material. This study has shown that spectroscopy coupled with multivariate data analysis is a useful tool verifying the compliance of producer declarations and assisting experts in evaluation of the biomass quality.

## 1. INTRODUCTION

During the last few decades, the European wood pellet market has continued to increase. In 2009, European pellet consumption was ~9.2 Tg,<sup>1</sup> and by 2020, the European Biomass Association expects a consumption of 50 Tg for the European countries.<sup>2,3</sup> Pellets are widely used because of the high degree of reliability, the easy handling, and the cheap and simple logistics, in comparison to other solid biomasses.<sup>4</sup>

The fast growth of the pellet market highlights the problem of product quality, which has strong repercussions for technical, environmental, and economic aspects.

In order to check the biomass quality both for industrial use and residential applications, CEN/TC 335 has established several standards (EN ISO 17225 series) related to different solid biofuel quality, including also woody pellet (EN ISO 17225-2<sup>5</sup>). Several chemical–physical parameters can be used to define the biomass class of quality on the basis of specific limits.

The standards also define quality attributes related to the origin and source of the woody material. These attributes are difficult to verify by traditional analyses, such as the type of wood (hardwood/softwood) and the presence of bark. This information can be obtained with complex laboratory analyses which require long procedures (e.g., microscopy techniques and chemical analysis) and skilled operators, which makes them slow, expensive, and potentially environmentally harmful. Such complex analysis does not match the real necessities of the market since the operators involved in the quality control need to have results as quickly as possible. Moreover, it is not feasible for

the entire industry to have such an experienced person working in the laboratory: it simply is too costly. Furthermore, there are no good standardized methods of bark analysis.<sup>6</sup>

Fourier transform near-infrared (FT-NIR) spectroscopy is a valid alternative to the time- and money-consuming standard methods. It is a relatively new technique that is widely used because of its potential to predict qualitative and quantitative attributes in a wide range of sectors (e.g., the food, pharmaceutical, and agricultural industries). The great potential of FT-NIR is that it is non-destructive, rapid, and cheap. Briefly, when broadband light is shined on a sample, chemical bonds of the molecule (such as C–H, O–H, or N–H) vibrate at different energy levels superior to the ground state of vibrational energy and depending on the molecular structure, chemical composition, or physical properties of the surface measured giving overtones and combination bands.

With this technique, biomass features such as quality sorting and determination of origin might be defined simultaneous with a single and fast measurement allowing biomass quality control.

Near-infrared (NIR) analysis has been found to be a good and rapid method for predicting wood compounds, since they are correlated with specific NIR bands and chemical composition.<sup>7–9</sup> In the literature, there are several works that use near- and mid-infrared spectroscopy for wood analysis with recognition

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purposes,<sup>9–12</sup> but only few studies investigate the discrimination between wood and bark.

Most of them have been focused on bark analysis for the pulp and paper industry,<sup>13,14</sup> since the incorporation of bark in the wood pulping could have an effect on pulp properties.<sup>15</sup> To our knowledge, no study has been carried out on bark determination in wood samples in the biomass sector, especially on ground materials.

Therefore, the main purpose of this study is aimed at verifying the usefulness of the FT-NIR technique in combination with Principal Component Analysis (PCA)<sup>16</sup> for extracting information about biomass origin and source from spectral data. PCA is a well-known statistical method for extracting information from noisy data by converting the original variables into a set of uncorrelated linear combinations of the original variables (i.e., principal components (PCs) containing most of the variability of the dataset).

In this study, more than 90 bark and wood samples belonging to three of the most common European species of the energy pellet sector (fir, pine, and beech) have been collected and analyzed by means of FT-NIR coupled with PCA. To test the performance of the PCA model, 30 blends of bark and wood at different concentration levels have been projected onto the PCA model from the pure wood and bark samples.

## 2. MATERIALS AND METHODS

**2.1. Sample Collection and Preparation.** Thirty two (32) bark and 60 wood samples of the most common European species in the energy pellet sector (i.e., fir, pine, and beech) have been selected and collected (see Table 1). Wood samples were obtained from whole pieces

**Table 1. Dataset of Wood and Bark Samples**

	number of wood samples	number of bark samples
beech ( <i>Fagus sylvatica</i> )	17	10
pine ( <i>Pinus spp.</i> )	22	10
fir ( <i>Abies spp.</i> )	21	12

of wood as tree log disks, wood slices, beams, or boards taken from different sawmills. First of all, the material was stabilized at 45 °C for 24 h, so that the same moisture content of 6%–7% was reached.

Subsequently, bark samples were obtained by manually debarking wood slices. All the samples were first chopped into smaller pieces, and subsequently ground to a particle size of <1 mm of by means of a cutting mill (Model SM 2000, Retsch).

A total of 30 blends were prepared at different bark concentration levels. The blending degrees were between 2% and 20% (w/w) of bark in 2% (w/w) increments. In order to increase the representativeness of the material, average samples for each species of bark and wood were prepared by collecting the same quantity of material of 10 samples of the same species. For each average bark sample, the correspondent average wood sample has been added and mixed in a plastic container. The blends were analyzed in the same way as the pure samples. All the blends are between the wood and the bark of the same species.

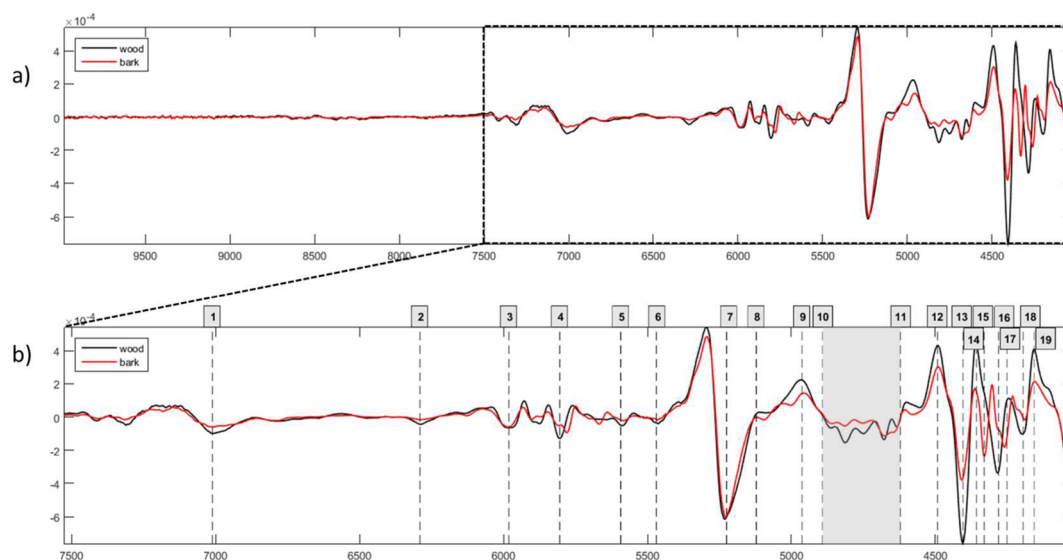
**2.2. Near-Infrared (NIR) Spectroscopy.** An Antaris II FT-NIR spectrophotometer (Thermo Fisher Scientific, Inc., USA) was used to collect near-infrared (NIR) spectra. The instrument is equipped with a halogen lamp as a source and an InGaAs detector. The samples were acquired in diffuse reflectance, using an integrating sphere and were kept in rotation during the acquisition by means of a sample cup spinner to increase the representativeness of the material.

The instrument was set to acquire the spectra at a wavelength range from 10 000 to 4000  $\text{cm}^{-1}$ , 32 scans per sample, and a spectral resolution of 8  $\text{cm}^{-1}$ .

A blank spectrum was acquired every hour to remove any random effects associated with the instrument or environment (e.g., room temperature, humidity, carbon dioxide concentration). Spectra were recorded at room temperature (18–20 °C) and in duplicate for each sample.

**2.3. Data Processing and Principal Component Analysis (PCA).** NIR spectra contain bands that are often overlapped and are relatively weak in intensity. The use of chemometric techniques is ideal for extracting information from this type of data.<sup>10,17</sup>

Since NIR spectra of solid samples are prone to scattering effects, such as offset, slope, and non-linear effects, it is important to pretreat the samples.<sup>18</sup> In the current investigation, it was determined that using the second derivative and smoothing was sufficient in order to remove the scattering. Pretreating the spectra with second-order derivatives enhances spectral differences and removes both additive and slope effects in the spectra.<sup>18</sup> The second derivative is easier to interpret, in comparison with the first derivative. In fact, peaks in the raw spectra appear as valleys in the loadings while the first derivative deforms the influence of the peak value as the peaks will have values near zero and enhance the influence of the inflection. The derivative spectra were smoothed according to the Savitzky–Golay<sup>19</sup> algorithm with 13



**Figure 1.** Bark and wood spectra pretreated with second derivatives (red line represents data for bark samples; black line represents data for wood samples). Dotted lines marked with numbers refer to the main spectral differences also reported in Table 2.

**Table 2. Infrared Absorption Band Assignment Associated with the Main Spectral Differences between Wood and Bark (the First Column Refers to Numbers Associated with Spectral Differences Highlighted in Figure 1)**

No.	measured wavenumber (cm <sup>-1</sup> )	bibliography wavenumber (cm <sup>-1</sup> )	assignment <sup>a</sup>	compound <sup>b</sup>
1	7012	7000	first OT of O–H str. (water and amorphous region in cellulose) <sup>10</sup>	C
2	6291	6286	first OT O–H str. <sup>20</sup>	C
3	5982	5980	first OT of the aromatic skeletal vibration <sup>10,20</sup>	L
		5981	first OT C–H str. (L) <sup>36</sup>	L
4	5805	5800	first OT C–H str. <sup>10,20</sup>	H
			first OT C–H str. (aromatic associated C–H) <sup>36</sup>	L
5	5593	5587	first OT C–H str. <sup>10,20</sup>	C
6	5469	5464	O–H str. + 2nd OT C–O str. (C) <sup>10,20,36</sup>	C
7	5219	5219	O–H str. and O–H deformation vibration of water <sup>10</sup>	water
8	5122	5220–5150	O–H asymmetric str. + O–H deformation of H <sub>2</sub> O <sup>20</sup>	water
9	4964		holocellulose <sup>37</sup>	C, H
10–11	from 4890 to 4620	from 4890 to 4620	O–H str. + C–H deformation <sup>10</sup>	C
12	4493		holocellulose <sup>37</sup>	C, H
13	4405	4404	C–H <sub>2</sub> str. + C–H <sub>2</sub> deformation <sup>10</sup>	C
		4405	O–H str. + C–O str. <sup>20</sup>	C
14	4358	4365	C–O str. + O–H str. or C–H <sub>2</sub> bend. + C–H <sub>2</sub> str. <sup>20</sup>	C
15	4331		holocellulose <sup>37</sup>	C, H
16	4281	4280	C–H str. + C–H deformation <sup>10</sup>	C
			C–H str. + C–H <sub>2</sub> deformation <sup>20</sup>	L
		4282	C–H str. + C–H <sub>2</sub> deformation combination band (and second OT of C–H <sub>2</sub> str.) <sup>36</sup>	C
17	4252	4252	C–H str. + C–H deformation <sup>20,36</sup>	C
			second OT C–H <sub>2</sub> bend <sup>20</sup>	C
18	4196	4198	second OT of C–H deformation in holocellulose <sup>10</sup>	C, H
19	4158		cellulose <sup>37</sup>	C

<sup>a</sup>Legend: str., stretching; bend, bending; and OT, overtone. <sup>b</sup>Legend: L, lignin; H, hemicellulose; C, cellulose; and E, extractives.

smoothing points and a second-order polynomial. However, since the Savitzky–Golay preprocessing inherently will lose six points at each end of each interval, the preprocessing was only performed once over the entire spectral range and not repeated at each variable selection step. Each sample replicate was investigated and no replicate outliers were found. Therefore, each sample was averaged across the replicates.

PCA was performed in order to explore the information about biomass origin and source from spectral data. PCA computation was performed on the pretreated data matrix of samples and on mean centered data. A confidence ellipse was calculated at a specific level of significance (99% confidence level) both for bark, hardwood, and softwood groups. The loading plot of the two first PCs was investigated to identify the compounds associated with the discrimination between bark and wood and between hardwood and softwood samples.

Finally, to check the performance of the PCA model, spectra of the blends between wood and bark were projected onto this model using the

loadings from the model on the pure wood and bark samples:

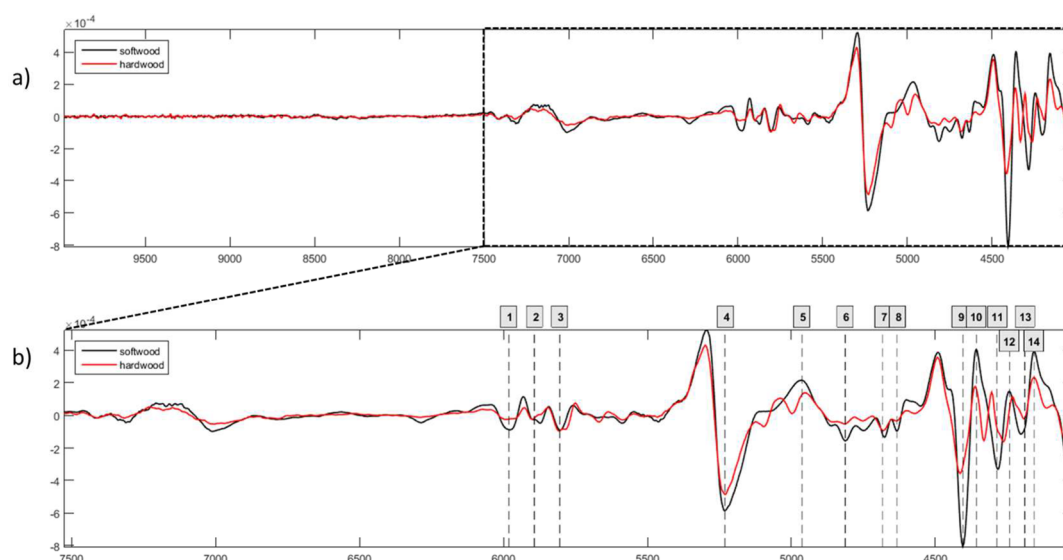
$$\mathbf{X} = \mathbf{T}\mathbf{P}^T + \mathbf{E} \quad (1)$$

$$\mathbf{X}_{\text{new}} = \mathbf{T}_{\text{new}}\mathbf{P}^T + \mathbf{E} \quad (2)$$

$$\mathbf{T}_{\text{new}} = \mathbf{X}_{\text{new}}\mathbf{P}^T \quad (3)$$

where  $\mathbf{X}$  is the original data matrix,  $\mathbf{T}$  and  $\mathbf{P}$  are the scores and loadings matrices, respectively, and  $\mathbf{E}$  represents the residuals matrix.  $\mathbf{X}_{\text{new}}$  and  $\mathbf{T}_{\text{new}}$  are the data and the score matrices of the blends samples to be projected onto the PCA model. It is important to note that the  $\mathbf{X}_{\text{new}}$  has been pretreated in the same way as  $\mathbf{X}$ , and that the average of  $\mathbf{X}$  has been used in the mean centering step of  $\mathbf{X}_{\text{new}}$ .

Matlab (ver. 7.10.0, The MathWorks) was used both for signal processing and for multivariate data analysis computation.



**Figure 2.** Hardwood and softwood spectra pretreated with second derivatives (red line represents data for hardwood samples; black line represents data for softwood samples). Dotted lines marked with numbers refer to the main spectral differences also reported in Table 3.

### 3. RESULTS AND DISCUSSION

**3.1. Spectra Analysis.** Figure 1 shows the second derivative with 13 smoothing points of the averaged FT-NIR spectra of all bark and wood samples in the spectral band from 10 000  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ . As can be seen, the most significant information is contained between 7500  $\text{cm}^{-1}$  and 4000  $\text{cm}^{-1}$ ; therefore, only this part of the spectra was considered for exploratory purposes. For interpretation purposes, it is important to take into account that a negative peak in the second derivative equals a peak in the regular spectra. Even if, at first glance, the two lines seem to have similar shape, some useful spectral differences are noticeable. The most important differences in the curves related to dissimilarities in chemical composition between bark and wood are marked with dotted lines in Figure 1. In particular, the concentration of lignin is higher in bark than in wood;<sup>6</sup> a similar relationship is observed for the concentration of inorganic material.<sup>6,15</sup> Extractives in bark are both much more abundant and more variable than they are in wood, with many types of extractives being present only in the bark.<sup>6,15</sup> Moreover, bark has substantially less polysaccharides than wood.<sup>6</sup>

In Table 2, the most relevant wavelengths for the discrimination of bark and wood samples are reported. The peak at 7012  $\text{cm}^{-1}$  related to the amorphous region in cellulose shows some small differences between bark and wood.<sup>10</sup> Minimal differences are reported in the range between 6291  $\text{cm}^{-1}$  and 5469  $\text{cm}^{-1}$ . No differences are noticed in the region of cellulose between 6800  $\text{cm}^{-1}$  and 6350  $\text{cm}^{-1}$ , demonstrating that this area is minimally affected by the variations between bark and wood. Minute differences are observed in the peak at 5219  $\text{cm}^{-1}$ . This band is characteristic for the combination band of O–H stretching and O–H deformation vibration of water,<sup>10</sup> indicating that the moisture content between the bark and wood samples is similar. Differences are also evident in the range from 4890  $\text{cm}^{-1}$  to 4620  $\text{cm}^{-1}$ . These bands are normally assigned to O–H stretching + C–H deformation in cellulose.<sup>10</sup>

Finally, evident differences are noticed in the peaks at 4405 and 4281  $\text{cm}^{-1}$ . These bands are assigned to semicrystalline and/or crystalline regions in cellulose, in particular to C–H stretching + C–H deformation and C–H<sub>2</sub> stretching + C–H<sub>2</sub> deformation, respectively.<sup>10,20</sup> Peaks related to cellulose

(4358, 4252, and 4158  $\text{cm}^{-1}$ ) and hemicellulose (4964, 4493, and 4196  $\text{cm}^{-1}$ ) confirm the differences between bark and wood and indicate that the amount of polysaccharides is higher in wood than bark.

Figure 2 shows the second derivative with 13 smoothing points of the averaged FT-NIR spectrum of all hardwood and softwood samples in the spectral band from 10 000  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ . In any case, it should be noted that the most significant information is contained in the first part of the spectra, in the wavelength range between 7500  $\text{cm}^{-1}$  and 4000  $\text{cm}^{-1}$ .

As in Figure 1, the dotted lines in Figure 2 are used to highlight chemical differences between hardwood and softwood assigned to lignin, hemicellulose, cellulose, and extractive compounds.

In Table 3, the most relevant wavelengths for the discrimination of hardwood and softwood samples are reported. It can be noted that the most important differences between hardwoods and softwoods are linked to hemicellulose and lignin components, consistent with literature results.<sup>21–25</sup> With respect to lignin, softwood contains significantly more guaiacyl units than hardwood, which is composed by a mixture of syringyl/guaiacyl units.<sup>11</sup> Hemicelluloses are mainly composed by 80%–90% of 4-*O*-methylglucuronoxylan in hardwoods, while 60%–70% glucomannans and 15%–30% arabinogalactan are the main constituents in softwoods.<sup>26</sup>

**3.2. PCA.** PCA was carried out on the spectra to investigate the variance in the spectral data. It was of interest to see if this variance would hold information about biomass origin and source. In particular, it was of interest to see if it was possible to discriminate between wood and bark samples and to evaluate the blends at different levels of bark concentration.

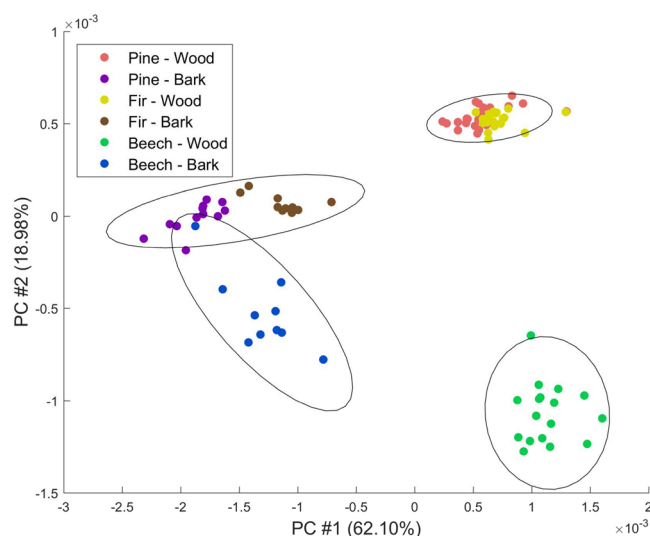
PCA results are presented in Figure 3. The score plot of the two first principal components (PCs) clearly shows that wood and bark samples were well-separated along PC1: bark samples have negative PC1 scores, whereas wood samples have positive PC1 scores. Looking at Figure 3, it is clear that, along PC2, there is a separation between hardwood and softwood. This separation is more evident for wood samples than for bark samples, because of the high heterogeneity of the latter one.<sup>6</sup> In this regard, it is possible to see that a beech bark sample falls into the softwood bark grouping; this is probably due to the high variability of the



**Table 3.** Near-Infrared (NIR) Absorption Band Assignment Associated with the Main Spectral Differences between Hardwood and Softwood (The First Column Refers to Numbers Associated with Spectral Differences Highlighted in Figure 2)

No.	measured wavenumber (cm <sup>-1</sup> )	bibliography wavenumber (cm <sup>-1</sup> )	assignment <sup>a</sup>	compound <sup>b</sup>
1	5982	5980	first OT C <sub>ar</sub> -H str. <sup>20</sup>	L
		5981	first OT C-H str. <sup>36</sup>	L
2	5893	5890	first OT C <sub>ar</sub> -H str. <sup>20</sup>	L
3	5805	5800	first OT C-H str. <sup>10,20</sup>	H
			first OT C-H str. (aromatic associated C-H) <sup>36</sup>	L
4	5230	5236	second OT C=O str. <sup>20</sup>	H
5	4964		holocellulose <sup>37</sup>	C, H
6	4813	4808	O-H str. + C-H def. <sup>10,20</sup>	C
7	4682	4686	C <sub>ar</sub> -H str. + C=C str. <sup>20</sup>	L, E
			C-H str. + C=O str. in acetyl groups <sup>20</sup>	H
8	4632	4625	C-H str. and C-O str. <sup>38</sup>	L, H
9	4405	4405	O-H str. + C-O str. <sup>20</sup>	C
10	4358	4365	C-O str. + O-H str. or C-H <sub>2</sub> bend. + C-H <sub>2</sub> str. <sup>20</sup>	C
11	4285	4283	C-H str. + C-H deformation <sup>20</sup>	C, H, xylan
		4282	C-H str. + C-H <sub>2</sub> deformation combination band (and second OT of C-H <sub>2</sub> str.) <sup>20</sup>	C
12	4243	4240	O-H deformation or C-H deformation and C-H str. or C-H <sub>2</sub> str. <sup>38</sup>	C
13	4189	4195	lignin <sup>20</sup>	L
14	4158		cellulose <sup>37</sup>	C

<sup>a</sup>Legend: str., stretching; bend, bending; OT, overtone. <sup>b</sup>Legend: L, lignin; H, hemicellulose; C, cellulose; E, extractives.

**Figure 3.** Score plot of the two first principal components (PCs).

bark, especially that of beech. In order to investigate the degree of variability even further, more samples are needed.

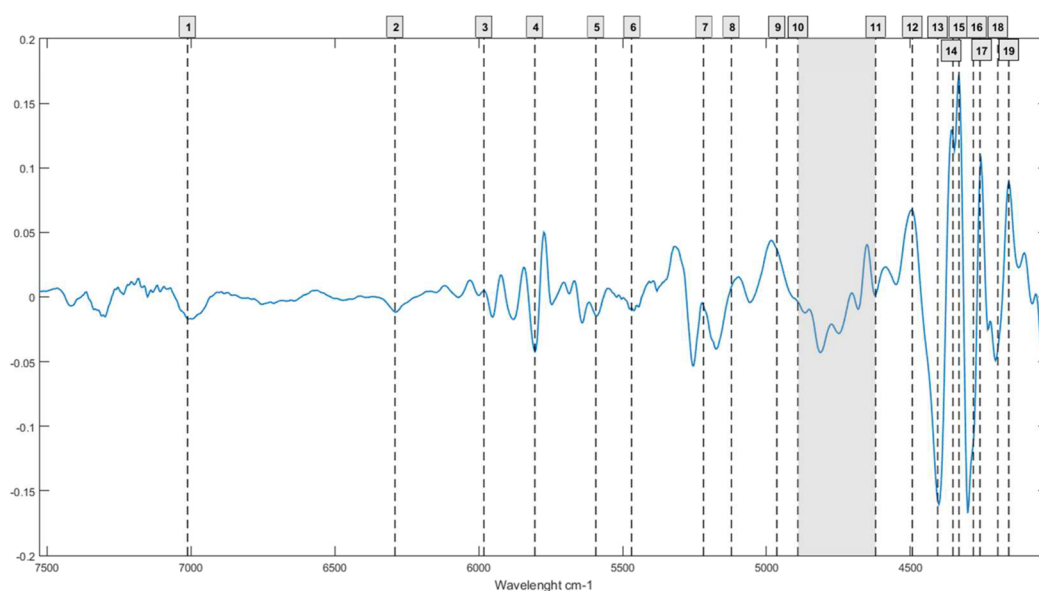
Only a sample of pine, a sample of fir, and a sample of beech appear outside the 99% confidence limits (ellipsoids), hence

PCA could be considered to be a powerful tool not only for differentiating between bark and wood samples, but also between hardwoods and softwoods.

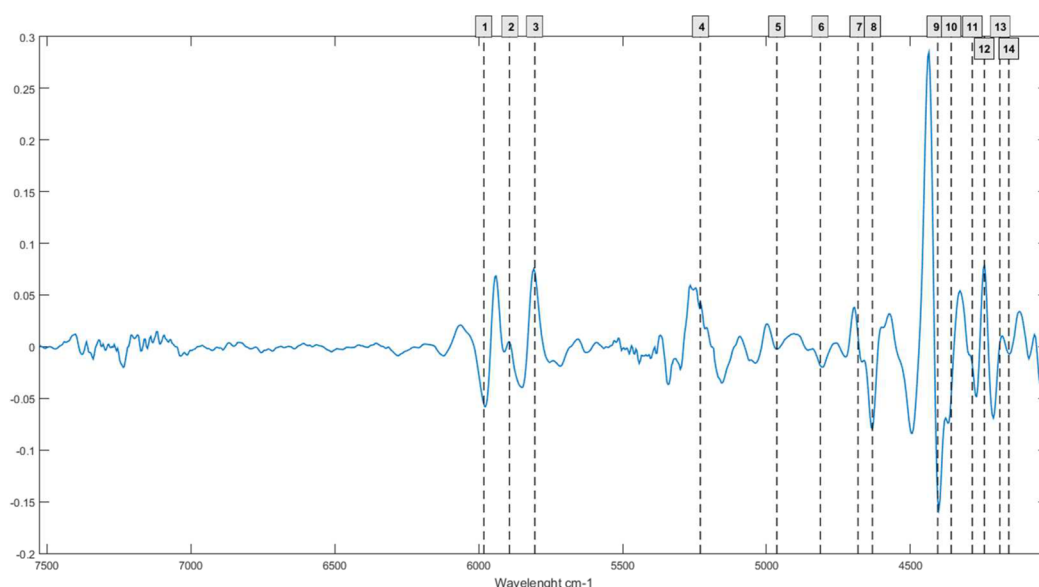
The loadings are investigated to determine which variables characterize the different clusters. A high peak in the loading plot indicates an important effect of the corresponding wavenumber and variation of the spectra due to chemical changes, while a small peak means that the impact of the factor is minimal.<sup>10</sup> However, please note that, since the data has been pretreated with the second derivative, peaks in the raw spectra appear as valleys in the loadings.

Relevant wavenumbers were investigated in order to identify the compounds associated with the discrimination between bark and wood (Figure 4) and softwood and hardwood (Figure 5).

The characteristic spectral bands, as marked on Figure 1 and in Figure 2, can also be detected in the loading plot. In accordance with the separation in the score plot, the first loading was used to interpret the differences between wood and bark and the second loading between hardwood and softwood. In Figure 4, it is possible to observe that bands at 7012, 6291, 5982, 5593, 5469, 5219, and 5122 cm<sup>-1</sup> have a minimal impact on the discrimination between bark and wood samples. It is important to note that the characteristic band of water at 5219 cm<sup>-1</sup> has a minimal loading impact, demonstrating that the moisture content between samples is similar and did not affect the discrimination.



**Figure 4.** First loading. Important wavenumbers for discrimination between wood and bark are labeled with numbers (the same as in Table 2).



**Figure 5.** Second loading, with the important wavenumbers for the discrimination between hardwood and softwood labeled with numbers (the same as in Table 3).

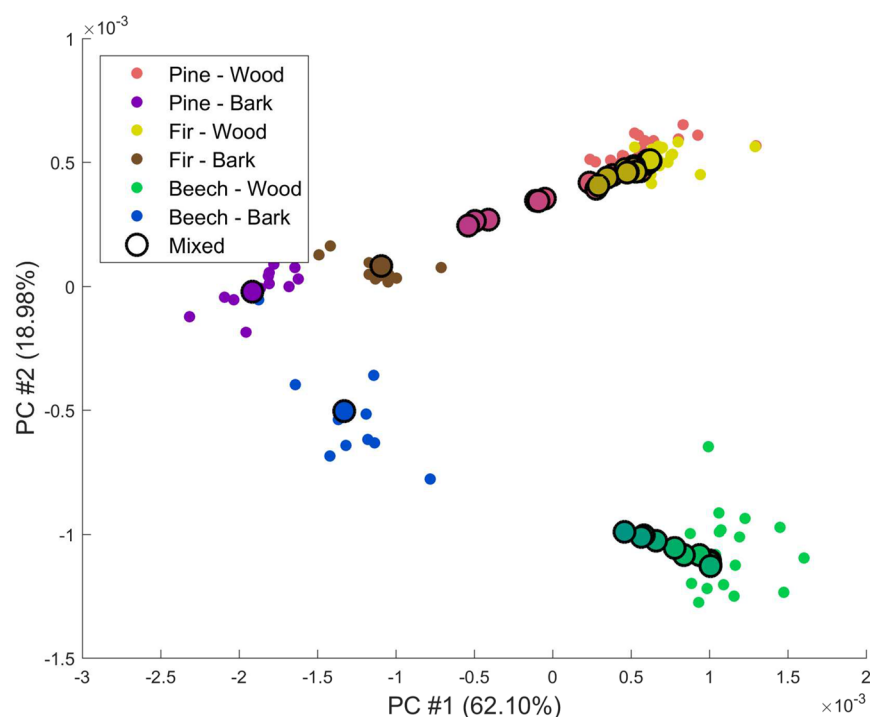
Instead, bands that are located at 5805 (H, L), 4964 (C, H), 4493 (C, H), 4358 (C), 4405 (C), 4331 (C, H), 4281 (C), 4252 (C) 4196 (C, H) and 4158 (C)  $\text{cm}^{-1}$ , which are associated with high peaks in the loading plot, are important variables for the discrimination of the two clusters. Also, the range between 4890 and 4620  $\text{cm}^{-1}$  seems to be important, especially the two bands at 4651 and 4636  $\text{cm}^{-1}$ .

Not all the variations of the spectra detected in Figure 2 seem to be significant for the discrimination between hardwoods and softwoods. Looking at the loading plot (Figure 5), it is possible to observe that bands at 5982 (L), 5805 (H, L), 5230 (H), 4682 (L, E, H), 4632 (L), 4358 (C), 4405 (C) and 4243 (L)  $\text{cm}^{-1}$  show high peaks, meaning that these peaks are discriminative for the difference between the two clusters, while bands at 5893, 4964, 4813, 4285, 4189, and 4158  $\text{cm}^{-1}$  have minimal impact.

The focus in this paper has been on the exploration of the NIR data. If a designated discrimination model was of interest, it

would be necessary to build such a model (i.e., PLS-DA<sup>27</sup> or SIMCA<sup>28</sup>). However, since the separations between the different classes are as clear as they are already in the PCA, the authors have no doubt that such a model would perform well. In addition, more wood species could be taken into account, on the basis of the future established objective.

In order to inspect the performance of the PCA model, spectra of blends at 10 levels of concentration (from 2% to 20% (w/w)) were projected in the PCA score plot (Figure 6). Each blend is composed by mixing the bark and wood average samples of each species (i.e., fir, pine, and beech). The different blends are grouped between wood and bark clusters and particularly the blends with high wood content are in agreement with their known composition percentages. It is possible to see that there is a linear trend related to bark and wood content and that the blends are located along the lines of connection of the different average samples.



**Figure 6.** Projection of blends between wood and bark at different levels of concentration in the PCA score plot.

It is also evident that blends with high bark concentration are well separated both from wood and bark grouping. Conversely, those with low bark concentration fall in the wood grouping.

Taking into account UNI EN ISO 17225-2, the pellet is mainly divided in three quality classes, according to its ash content (i.e., A1, A2, and B). The limit between A1 and A2 quality classes is an ash content of 0.7%.

Literature reports that debarked wood has an ash content of ~0.3%,<sup>29–32</sup> while bark contains 2%,<sup>29,30,33–35</sup> meaning that a maximum bark content of 20% could be added without changing the quality classification (A1).

For this purpose, since the model developed is able to recognize 20% bark content in blend samples at a 99% confidence interval, this tool could be used by operators of the sector for the pellet quality recognition. Furthermore, the linear trend in the blends along the axis of pure wood to pure bark suggests that building a regression model with the purpose of estimating the amount of bark in wood samples is fairly straightforward. However, because of the limited samples in this project, such a model has not been made; instead, it will be part of a future study.

#### 4. CONCLUSIONS

The results of this work clearly show that Fourier transform near-infrared (FT-NIR) analysis coupled with PCA method could discriminate samples not only between bark and wood but also between hardwood and softwood. The discrimination is mainly linked to differences in material compounds, i.e., cellulose, hemicellulose, lignin, and extractives. In particular, bark has a higher concentration of lignin, extractives, and inorganic material than wood, and therefore has a substantially smaller polysaccharides content. On the other hand, the discrimination between hardwood and softwood is due to the content and composition of lignin and hemicellulose.

According to CEN/TC 335, the determination of the quality of a solid fuel is very important and the identification and characterization of chemical composition give useful information

during its investigation and application. In particular, the origin and source of the material are attributes that are difficult to determine with the traditional chemistry but are very important for biofuel traceability. Consequently, the development of the FT-NIR technique, in combination with multivariate data analysis, could be an important tool for the energy sector providing a very fast biofuel traceability and pellet quality class.

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##### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

##### Author Contributions

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##### Notes

The authors declare no competing financial interest.

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