MORPHOLOGICAL AND MICROSTRUCTURAL ASPECTS OF SOME SPECIFIC VEGETAL BIOMASS AND THEIR STRUCTURAL COMPONENTS

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Abstract: *Biomass production has seen a significant increase in renewable energy in recent years and has obtained significant approach due the effect on environmental quality. Solid biomass is the renewable raw material with important industrial use and many studies are focused in developing and optimizing this type of fuels. Chemical composition influences the calorific power of biomass, mainly due to the calorific power of structural compounds and extractives. Pure lignin has a higher calorific value (22.2 MJ/kg - 28.5 MJ/kg) than pure cellulose (16.5-17.3 MJ/kg) and hemicelluloses (13.9 MJ/kg) and resin has a much higher heating value of about 39.5 MJ/kg. The permanent structure of the crown of fruit trees is diverse in strength and angle of insertion and requires the application of adequate pruning through which the trees to capitalize on the full production potential of the variety and ensure the crown a solid structure. Vegetable waste from plantations and orchards has not been used for energy purposes so far due to several constraints, the logistical nature being the most important. The objective of this paper is to present the morphological and the structural chemical components (lignin, cellulose, hemicelluloses) of the woody biomass resulting from the various agricultural fruit trees (cherry, sour cherry, quince, pear and apple) by using scanning electron microscopy (SEM Quanta 200 3D), X-ray analysis (Xpert PRO MPD) and FT-IR analysis in order to identify the aspect of the sample surfaces and the EDS chemical composition.*

Keywords: *vegetal biomass, morphological analysis, SEM analysis, XRD analysis.*

1. Introduction

Biomass is the biodegradable fraction of products, waste, and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste [Marian, 2013], [Marian, 2016]. 60 % of the renewable energy in European Union comes from biomass. In the sectors of transport biofuels and electricity its increase was the fastest between 2008 and 2015 [Di Fraia, 2020]. Biomass is the third largest primary energy in the world, after coal and oil. It remains the primary source of energy for more than half the world's population, and provides about 1250 million tons oil equivalent (mtoe) of primary energy which is about 14% of the world's annual energy consumption [Chen, 2009]. Its use has been encouraged and fuel has been mainly produced from forest residues such as: bushes and aerial parts of trees. These have an important role in the forest management. The use of these resources becomes more and more important and also an important alternative to

the fossil fuels [Tavares, 2020].Not only wood can be used as a resource of biomass. There other options like: food crops, algae, aquatic plants, herbaceous and woody plants. A disadvantage in the use of biomass for production of the renewable energy is its behavior on combustion. These contain various elements like Na, K, Ca which can have an influence on combustion and the resulted ash. A high content of these elements along with sillica components will result in the formation of sillicates. Due to the adhesion of these particles, heat transfer may be affected. [Rodríguez, 2020]. The most important energy use of solid biomass from forestry is home heating. According to Romania's reports based on art. 22 of directive 2009/28 /ec, the amount of solid biomass used for electricity production and transport is less than 1% of the total used at national level. Less than 0.1% of solid biomass consumed in romania comes from from energy crops, agricultural or household waste. [MMR, 2017].

Total area of the forrest fund which is administered by Romsilva, through 41 forestry directorates and the institute of forestry research and management (ICAS), within 323 forestry schools and 10 experimental bases, is about 3.5 million ha and represents about 50% of the national forest fund. The distribution of the forest fund by development regions indicates a concentration in a significant proportion of it in the central (19.4% of the total forest fund and north-east (18.2%) development regions, followed by the Western development regions (16.1%), North-West (15.2%), South-West-Oltenia (12.4%), South Muntenia (12.3%), South-East (8.1%) and Bucharest-Ilfov (0.4%) [MER, 2016]. According to the National Institute of Statistics, in Romania, the softwood species cover 1,917 thousand ha (respectively 29.9%), and the deciduous species, 4,501 thousand ha (respectively 70.1%). Individually, by tree species, the largest area is beech, which is found on 2,139 thousand ha, followed by spruce with an area of 1,480 thousand ha and oaks, with an area of 1,060 thousand ha.

Romania enjoys a great diversity of tree species. Romania harvests approx. 60% of forest growth, compared to a European average of over 60%. In 2018, 19,462 thousand cubic meters (gross volume) of wood were harvested, with 1,146 thousand cubic meters more than in 2017. During 2017-2020, about 3.5 million cubic meters came from accidental products (wind gusts). Softwood species, especially spruce and fir, have a share of less than a third of the total wood mass, and deciduous species two thirds, of which beech has the largest share. The share of wood is distributed in Romania is distributed as follows: softwood represents 36.6% of the total volume of harvested wood, beech is in proportion of 33.8%, oak is 10.5%, various hardwood species (acacia, maple , ash, walnut, etc.) in a percentage of 11.3%, and the various soft species (linden, willow, poplar, etc.) in the amount of 7.8%.

In the state of art, the use of biomass in order to achieve heat properties leads to a decrease in the impact on the environment. This waste-based resource can lead to the obtaining of energy from alternative technologies in countries with rich agriculture, which would allow an economic development of those countries [Manrique, 2019]. Calorific power is one of the most significant characteristics of biomass. Many researchers have analyzed the energy properties of different types of biomass such as: cashew husks, coconut kernels, rice husks, wheat, corn, bioenergetic products, cardboard, paper, plastics, empty pine cones, spruce, as well as silver fir bark and stems [Aniszewska, 2014] [Demirbas, 2004] [Acar, 2012] [Nakkeeran, 2019] [Jóvér, 2018] [Bouabid, 2013]. Thus, by means of the calorimeter bomb, the generic calorific values were measured, a very important aspect for solid bio-fuels, because their chemical and physical composition is usually quite different [Toscano, 2009].

In the production of pellets, the amount of small particles in the raw mass is directly proportional to their mechanical strength [García-Maraver, 2011], which can decrease depending on a number of external factors.

Pellet suppliers consider compliance with all specific properties such as durability and characteristic particle size (particles smaller than 3.15 mm), fuel energy content and ash content. The properties of the pellets must be kept under control, otherwise significant deviations of the emissions in the environment and the longevity of the combustion systems may occur [Alakangas, 2002].

Studies conducted by various researchers have highlighted the influence of pelletizing parameters on different wastes from olive cutting [Zamorano, 2011] [García-Maraver, 2015]. Also, other studies [Miranda, 2009] analyzed the pelletization of forest waste based on oak. Research conducted by Filbakk et al. [Filbakk, 2011] has shown superior mechanical properties and a higher amount of ash at different proportions of wood and bark from the wild pine. Serrano et al. [Serrano, 2011] made barley straw pellets with different moisture values, in order to improve mechanical durability. Also, other researchers [Montero, 2014] [Mediavilla, 2009] made pellets from residual biomass of vines and cork, the ultimate goal being to optimize the pelletization flow with low energy consumption. According to several researchers the chemical composition of the structural compounds of biomass are presented in Table 1.

Table 1. *Main compounds in vegetal biomass*

	Species	**Cellulose, %**	**Lignin, %**	**Hemicelluloses, %**	**Reference**
1	Sweet cherry (Prunus avium)	45-47	18-21	32-37	[Popescu,2011]
2	Plum (Prunus domestica)	51-53	32-34	13-17	[Kiaei, 2014]
3	Apricot wood (Prunus armeniaca)	49-52	31-32	16-20	[Tajik, 2015]
4	Sour cherry (Prunuscerasus)	43	24	30.3	[Gallina, 2018]
5	Apple (Malus domestica)	36.5	18.6	28.7	[Tottingham, 1921]

The objective of this paper is to present the morphological and the structural chemical components (lignin, cellulose, hemicelluloses) of the woody biomass resulting from the various agricultural works of the fruit trees (cherry, sour cherry, quince, pear and apple) by using scanning electron microscopy (SEM Quanta 200 3D), X-ray analysis (Xpert PRO MPD), in order to identify the aspect of the sample surfaces and the EDS chemical composition.

2. Materials and Methods

During the research, vegetable biomass was collected from the following types: sweet cherry, sour cherry, quince, pear and apple from different areas of the Republic of Moldova and the adjacent counties of the Prut river. All residues were coarsely crushed directly into the field. Subsequently, the biomass was dried by the natural conversion method in the drying plant of the UASM Solid Biofuels Laboratory up to m = 10 ± 2%, then it was crushed at the SV 7 hammer mill. Surface morphology was investigated by scanning electron microscopy (SEM FEI Quanta 200 3d - dual beam, equipped with energy dispersive X-ray spectroscopy analysis unit – Xflash Bruker, USA). X-ray diffractions (XRD) were performed using a XPERT PRO MPD 3060 facility from Panalytical (Netherlands), with a cu – X-ray tube (Kα = 0.154051 nm), 2 Theta: 10°-70°, step size: 0.13°, time/step: 51s and a scan speed of 0.065651 °/s. FT-IR spectra were recorded on solid samples in KBR pellets by means of a FT-IR bruker spectrometer with a resolution of 4 cm-1.

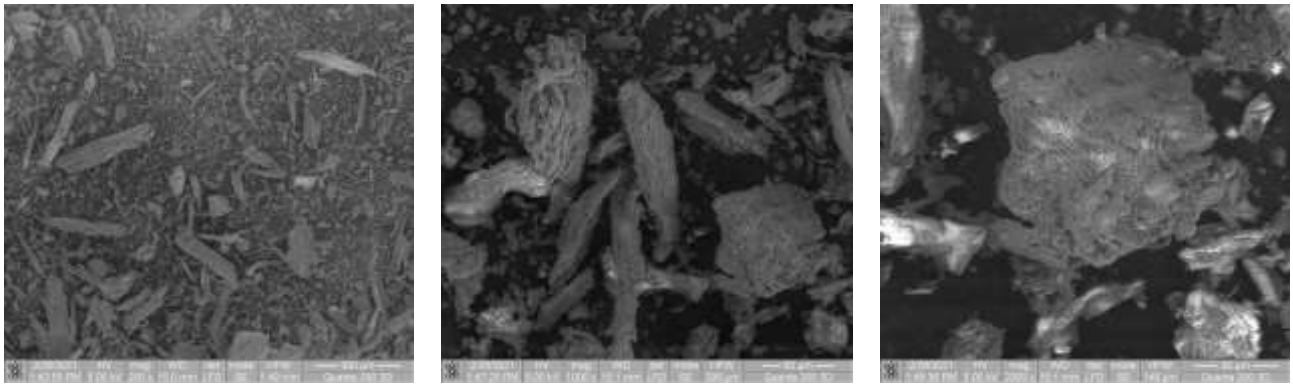
3. Results of the research and their discussion

3.1 SEM Analysis

Fig. 1-5 shows the SEM images at various magnifications, respectively 200x, 1000x and 2000x for the 5 types of vegetal biomass.

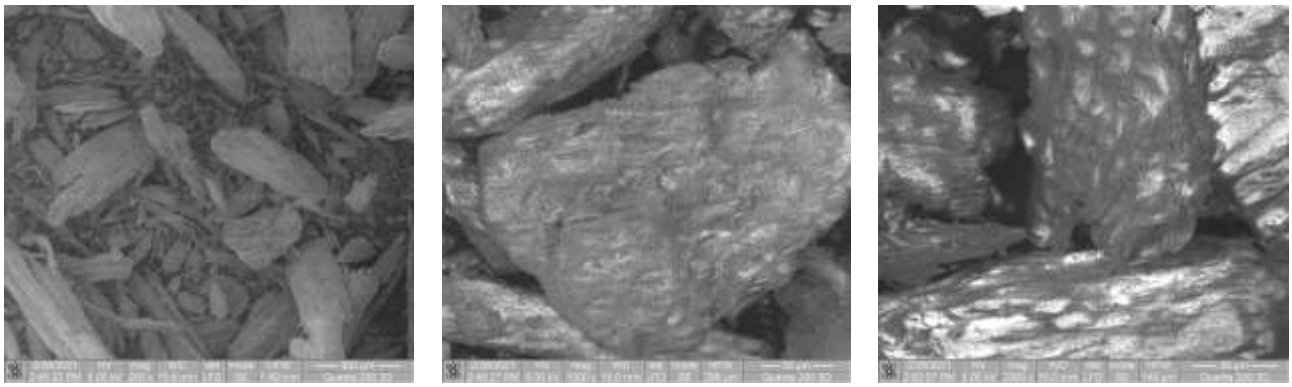
Sweet cherry

Figure 1: *Surface morphology of the vegetal biomass*



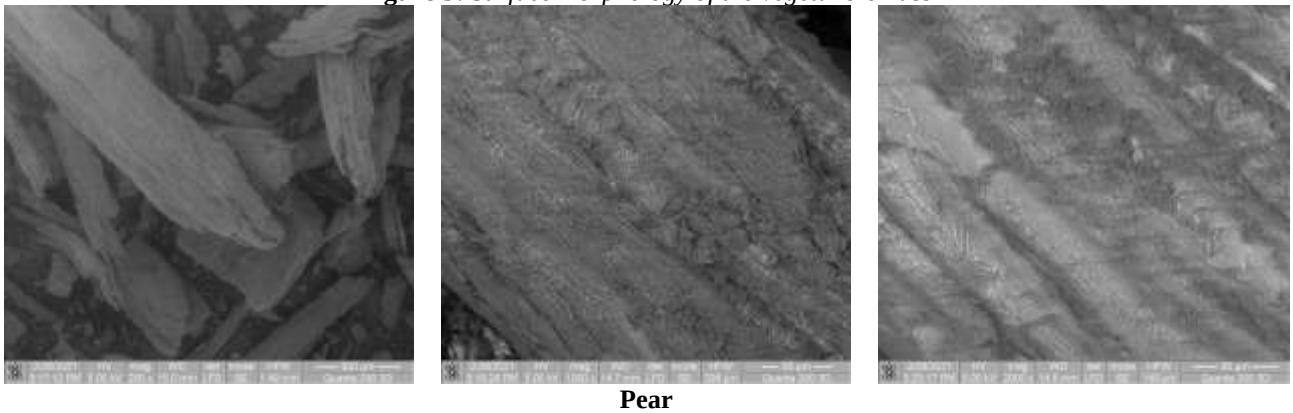
Sour cherry

Figure 2: *Surface morphology of the vegetal biomass*



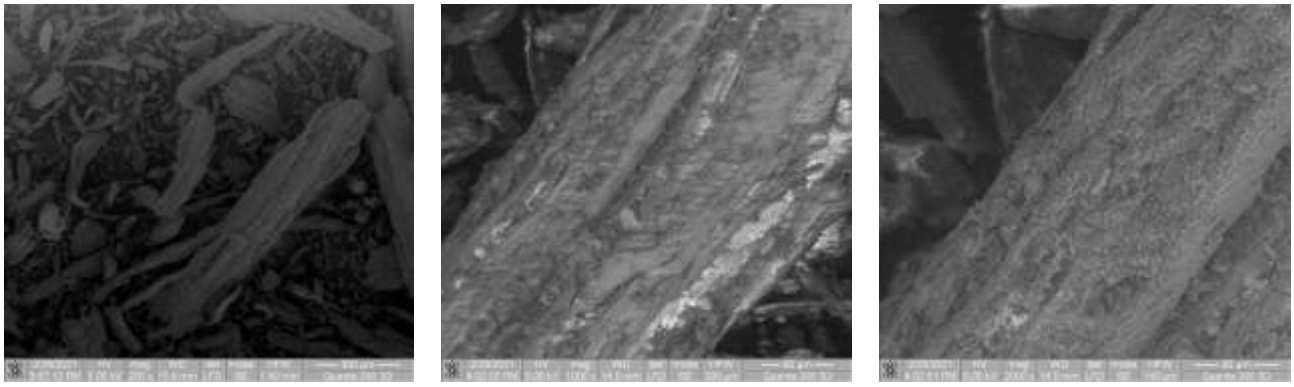
Quince

Figure 3: *Surface morphology of the vegetal biomass*



Pear

Figure 4: *Surface morphology of the vegetal biomass*



Apple

Figure 5: *Surface morphology of the vegetal biomass*

Table 2: *EDS chemical composition of the vegetal biomass*

	Sweet cherry	Sour cherry	Quince	Pear	Apple
C (wt.%)	46.66	50.79	44.10	47.47	48.61
O (wt.%)	53.34	49.21	55.90	52.53	51.39

Average elemental composition on 3 analysed surfaces per sample.

In Fig. 1, 4 and 5, respectively for sweet cherry, pear and apple are observed fibrous structures directed by the existing micellar structure. This structure exists in the the initial form of the trees. Also in some parts of the particles are observed some cleavage planes on the surface. Fig. 2 and 3, respectively quince and pear show granular structures with uneven dimensions and irregular surfaces. In all five analyzed structures, micropores with different shapes and distributions are highlighted.

According to the EDS results, a certain uniformity of the percentage of carbon and oxygen is observed, with higher carbon values for sweet cherry and lower ones for quince.

3.2 XRD Analysis

From the XRD analysis (Fig. 6) the 5 vegetal biomass samples present similar diffraction pattern highlighting specific cellulose, hemicelluloses and lignin peaks. The diffraction intensities are correlated with the percentages of compounds similar to those in Table 1. In Table 3 it is presented the crystallinity of the samples.

Table 3: *Crystallinity of the vegetal biomass samples*

	Species	Cr 101	Cr 10-1	Cr amorf	Cr 002	Cr. I., (A cr)/A total
1	Sweet cherry	14.81	16.41	19.98	22.18	42.4
2	Sour cherry	15.45	16.46	19.5	22.44	42.8
3	Quince	15.09	16.49	18.94	22.33	44.2
4	Pear	14.96	16.4	18.86	22.28	44.7
5	Apple	14.99	16.637	19.18	22.22	44.03

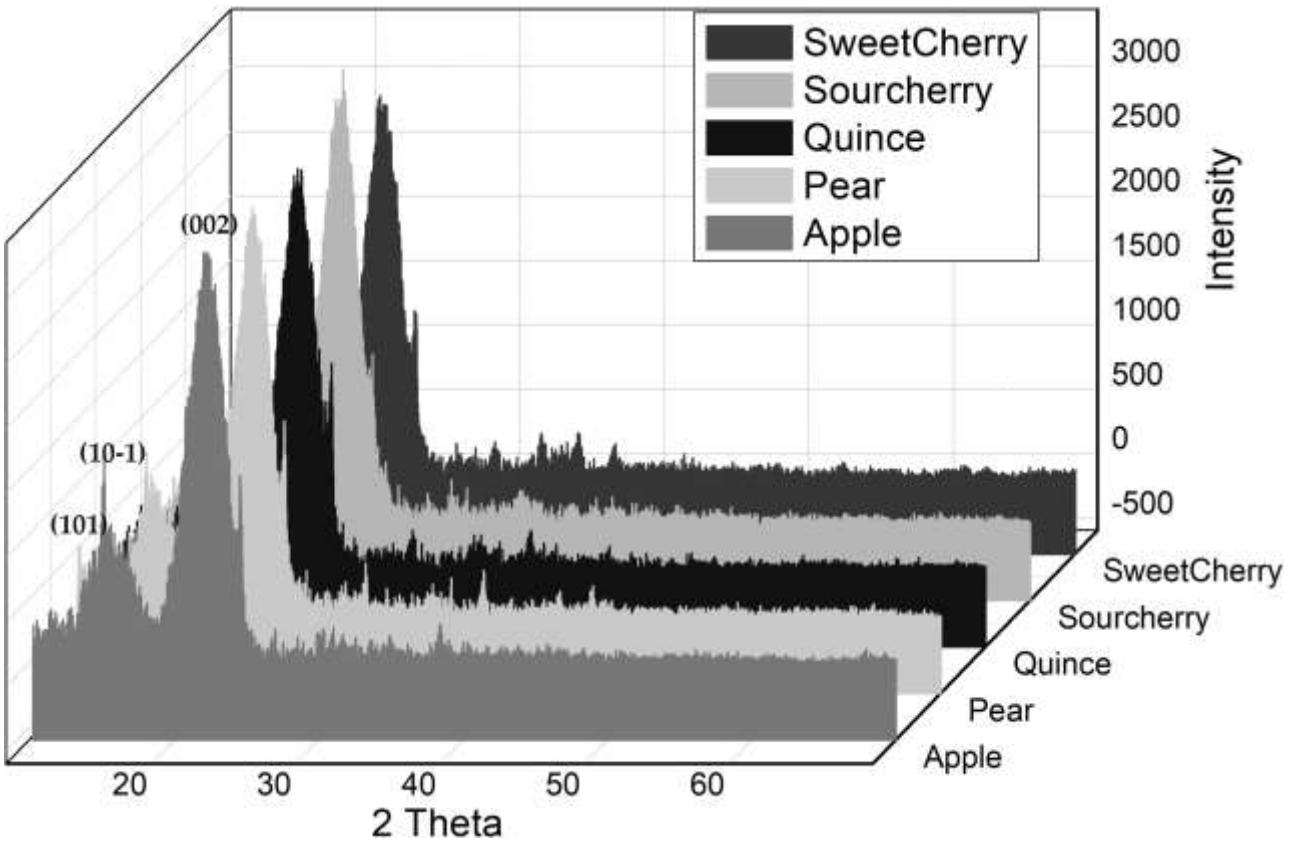


Figure 6: *XRD pattern of the structural compounds*

3.3 FT-IR Spectroscopy

FT-IR spectroscopy is a very useful technique for analyzing the structure of wood chemical components. FT-IR spectra recorded for different wood species are shown in figs. 7: 1-sweet cherry (prunu savium), 2-sour cherry (prunus cerasus), 3-quince, 4-pear (pyrus communis), 5-apple (malus domestica). In the 3800–2700 cm^{-1} region (fig. 7), strong hydrogen bonded (o–h) stretching absorptions and prominent c–h stretching absorptions were observed. It may be observed in fig. 7 that all bands in this region have different intensities in the spectra of wood samples.

The spectra of wood samples are very complex in the ‘‘fingerprint’’ region. Here we can find bands assigned to different stretching vibrations of the groups from the main wood components similar to ref. [Kondo, 2005] and [Nishiyama, 2003]. The bands at 1595, 1510, 1270 cm^{-1} are assigned to c=c, c–o stretching or bending vibrations of different groups from lignin. The bands at 1460, 1425, 1335, 1220, 1110 cm^{-1} are assigned to characteristic c–h, c–o deformation, bending or stretching vibrations of different groups for lignin and carbohydrates. The bands at 1735, 1375, 1240, 1165, 1060, 1030 cm^{-1} are assigned to characteristic c=o, c–h, c–o–c, c-o deformation or stretching vibrations of different groups from carbohydrates. However, in the different types of wood the positions and relative intensity of the bands are different. The relation between lignin and carbohydrates can be calculated by the ratio of some bands of the ft-ir spectra. As it is expected the lignin/carbohydrate ratio is different for all wood samples, as is evident from the increase of the 1505 cm^{-1} band assigned to lignin and decrease of the 1738 cm^{-1} band assigned to carbohydrates. The 1505 cm^{-1} band is used as an internal standard assigned to benzene ring stretching vibration for lignin.

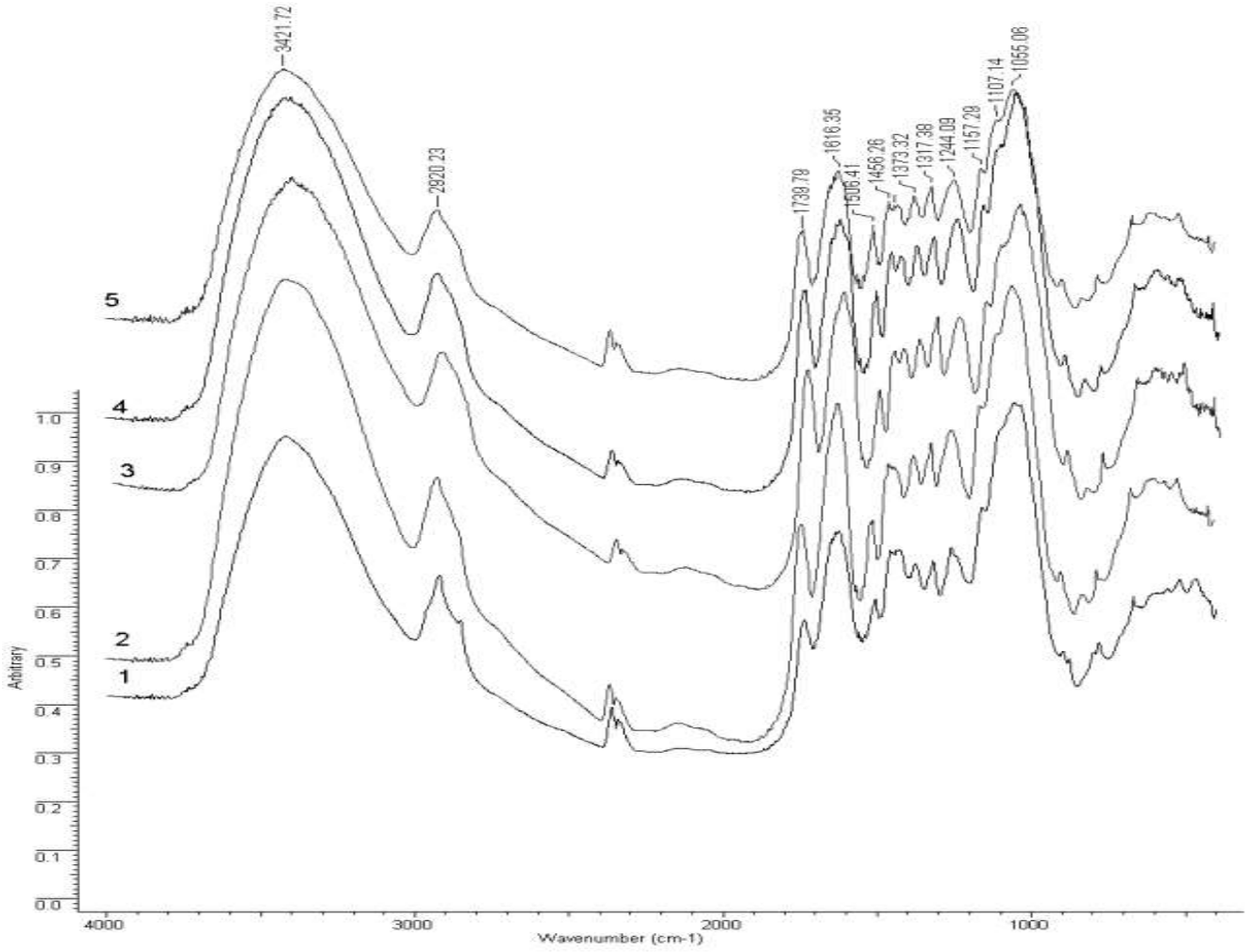


Figure 7: *FT-IR pattern of the vegetal biomass*

4. Conclusions

Biomass production has seen a significant increase in renewable energy in recent years and has obtained significant approach due the effect on environmental quality. The performed studies reveal that the vegetal biomass has a fibrous structures with micropores. Also the EDS chemical analysis presents similar values of carbon and oxygen for all 5 samples. The FT-IR analysis present complex spectra in different regions, where bands assigned to different stretching vibrations of the groups from the main wood components.

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