CHARACTERIZATION OF COMPONENTS ISOLATED FROM ALGERIAN APRICOT SHELLS (*PRUNUS ARMENIACA* L.)

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Shells resulting from food processing and agricultural activities, such as hard shells of apricot, are considered as wastes and are generally used as fuel. However, this residue shows promise as lignocellulosic feedstock for biorefineries, for its conversion to liquid fuel or bio-products. This study is dedicated to the characterization and isolation of lignin, cellulose and hemicelluloses from apricot shells (AS). The chemical composition and thermal stability of AS after chemical treatment with solvents (ethanol-toluene), cellulose, hemicelluloses and lignin were analyzed by standard methods, *i.e.* Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Further, almost 50.2 wt% of a water-insoluble extract was obtained after the bleaching process, which showed the removal of lignin, and the final percentages for this extraction were 50.2 ± 0.34%, 26.5 ± 0.83%, 23.7 ± 0.29% and 35 ± 1% for holocellulose, cellulose, hemicelluloses and lignin, respectively. FTIR spectroscopy evidenced the structure of lignin, cellulose and hemicelluloses. Thermal analysis and the kinetic study suggested that cellulose had higher thermal stability than the other components, with the activation energy of 289.62 kJ/mol. Thus, our results indicated the high potential of AS to be used as an environmentally friendly material in a biorefinery, as well as in the modern polymer and chemical industries.

Keywords: apricot shells, lignocellulosic, chemical composition, holocellulose, cellulose, hemicelluloses, lignin, kinetic study, thermogravimetric analysis (TGA)

INTRODUCTION

The rapid increase in agricultural wastes is one of the major environmental concerns, since the disposal of these wastes on the soil or in landfills causes serious environmental problems. This problem has turned the researchers' attention towards the valorization of agricultural residues, as well as towards the development of recyclable or biodegradable products.[1,2] Thus, the generation of lignocellulosic residues as agro-industrial by-products poses a challenge from the point of view of environmental protection, as well as for the progress of a "green" economy.[3-5]

Lignocellulosics are the most abundant source of insufficiently exploited biomass on the earth. They mainly consist of three polymers: cellulose, hemicelluloses and lignin, representing the three main constituents of the cell walls of plants, in which they are not uniformly dispersed. The structure and quantity of these plant cell wall components vary according to the species, tissues and harvesting period.[2] In general, lignocellulosic biomass is composed of 40-50% cellulose, 25-30% hemicelluloses and 15-20% lignin, as well as a small amount of other extractives.[6]

Prunus armeniaca L. is classified under the *Prunus* species of the Prunaidea sub-family and the Rosaceae family. At present, the apricot is cultivated in a diverse area with suitable climates.

Algeria and Italy are the most important world producers of apricot, with annual yields of 205.000 and 263.132 tons, respectively.[7] Apricot has an important place in human nutrition and apricot fruits can be used as fresh, dried or processed fruit, while a part of the produce is destined to the processing industry for various products. Apricot kernels are used in the production of oils and have been exploited in cosmetics, as active carbon or pharmaceutical agents for several diseases, such as vaginal infections, tumors and ulcers.[8,9] As regards the application of apricot shells, so far, they have been used in their natural, alkali modified form or as activated carbon in biosorption experiments.[10] Also, they can be used to carry out fast pyrolysis and in plastic-panel production.[11]

It is important to mention that little information and research are available on the composition of apricot shells, while their possible valorization is envisaged with the efforts of developing novel materials, fuels and processes, using these lignocellulosic materials instead of fossil fuels.[12] In this context, it is useful to find the composition of the lignocellulosic biomass of apricot shells in order to consider their potential use for new applications in various fields, which can add value to this agricultural waste abundant in Algeria. This study has focused on identifying the components of apricot shells (AS), using a combination of standard analysis methods used in wood chemistry and spectral methods (FTIR), while the thermal stability of the compounds was evaluated by means of TGA analysis.

EXPERIMENTAL

Materials and methods

Raw materials, chemicals and pretreatment methods

Apricot fruits (*P. armeniaca* L.) were collected from the Menna region, located in Batna in the North East of Algeria. The apricot shells obtained were dried at room temperature during several days, ground by an electric mixer to a fine powder and sieved over a 20-80 mesh screen to maintain the size uniformity of powdered shells, as per previous National Renewable Energy Laboratory NREL standard methods.

The dry powder of AS (20 g) was extracted with a 2:1 v/v ethanol/toluene (300 mL) mixture for 8 h to remove phenolics, pigments, wax and oils, followed by oven-drying at 50 °C for 24 h. The treated powder was used to find out the content of holocellulose, cellulose, hemicelluloses and lignin, and was stored at 4 °C for further analysis.

The chemicals used in the present study were the following: potassium hydroxide (>97%) purchased from Merck KGaA Company, Germany; sodium hydroxide (>99%) from Merck KGaA Company; nitric acid (>65%) from Chemical Company, Iasi; acetone (>99.8%) from Chemical Company; sulfuric acid (>96%) from Sigma–Aldrich; sodium chlorite (>25%, Synth) from Merck KGaA Company; glacial acetic acid (>99.8%) from Chemical Company, Iasi; ethanol (99.5%, Synth) from Chemical Company, Iasi; toluene (>99%) from Chemical Company, Iasi; hexane (>99.8%) from Chemical Company, Iasi.

Physico-chemical composition

The chemical composition, moisture (%) and ash (%) content of the apricot shells were determined according to the standard methods of NREL,[13] with the exception of holocellulose, which was determined by the sodium chlorite method.[14] The average of three replicates was calculated for each sample.

Isolation of acid insoluble lignin

An amount of AS extracted powder of 1 g was mechanically stirred in 15 mL of 72% H_2SO_4 (v/v) aqueous solution at 25 °C, in the powder/solution ratio of 1:15 (g/mL), for 2.5 h. The suspension was subsequently diluted with 200 mL of distilled water and heated at 90 °C for 1 h. Then, it was filtered on a sintered glass crucible G3 filter and washed with hot distilled water until neutral pH was reached. Finally, drying was carried out in an oven at 105 °C until constant mass was reached.

Isolation of cellulose and hemicelluloses

Separation of holocellulose

An amount of 5 g of extracted powder was mixed with 150 mL of distilled water, in the presence of 1.5 g of sodium chlorite and 10 drops of glacial acetic acid, for one hour at the temperature of 80 °C, under mechanical stirring. After 1 h, 1.5 g of $NaClO_2$ and 10 drops of glacial acetic acid were added to the mixture. The reaction was continued for 1 h and was repeated for 4 times. After the treatment, the holocellulose suspension was cooled in an ice bath, filtered on a sintered glass crucible G2 filter, washed with distilled water to neutral pH and then with acetone, and finally, was oven dried at 50 °C to constant mass.

Separation of hemicelluloses

An amount of 1 g of holocellulose was treated with 25 mL of potassium hydroxide (15%) for 2 hours at room temperature (25 °C). It was then filtered on a sintered glass crucible G2 filter, and the solid bleached phase obtained was cellulose, while the liquid fraction represented the hemicelluloses content. The liquid fraction was acidified with acetic acid to pH 5-6 and then precipitated in 5 volumes of ethanol. The residue obtained was filtered through a sintered glass crucible G2 filter, washed with ethanol and finally oven dried at 50 °C to constant weight.

Characterization

Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (Digilab Scimitar 2000 FT-IR) was carried out to study the structure of the isolated AS compounds after the treatment: lignin, cellulose and hemicelluloses, in the range of 400-4000 cm^{-1} at the resolution of 4 cm^{-1}. To obtain the spectra, thin transparent pellets were prepared by grinding and mixing for 20 s the dried samples with KBr in the ratio of 1:200 (w/w), followed by pressing under vacuum at a pressure of 75 kN cm^{-2} for 3 min.

Thermogravimetric analysis (TGA)

In order to examine the thermal stability of the samples (AS after treatment, cellulose, lignin and hemicelluloses) after different treatments, thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal (DTA) analyses were performed on approximately 2.4 to 4.4 mg of each sample, under air flow (20 cm^3min^{-1}), at a heating rate of 10 °C/min from 25 to 700 °C, using a Mettler Toledo TGA/SDTA 851. The processing of the obtained curves was done using Mettler Toledo STAR software. Constant operating parameters were kept for all the samples in order to obtain comparable data.

RESULTS AND DISCUSSION

Chemical composition of AS

The results of AS chemical composition analysis, obtained following standard NREL methods, are presented in Table 1. The ash content (2%) determined in this study was higher than those established by other research groups (0.55%, 1.67%, 0.3%, 1.0%),[15–18] but in the range reported for other investigated shells (nut shells: 1.2%-3.8%; almond shells: 1.54%-2.3%; cherry stones: 0.9%; grape seeds: 2.5%).[19,20]

Soxhlet extraction with organic solvents showed that the total extractive content (6.66 ± 1.5% based on dry AS) was higher than that reported previously by other researchers (0.74%-5.2%).[15,16,21]

In order to solubilize hemicelluloses and lignin, the alkali treatment was performed, while lignin residues were removed by the bleaching treatment. The yield of purification after the bleaching treatment was 50.2 ± 0.34%, which can be attributed to the removal of lignin and non-cellulose components. Figure 1 shows photographs of AS, before and after the bleaching treatment. The color of the raw apricot shell changed from brown to white, after bleaching. In Table 1, the chemical composition of the apricot shell is summarized. After bleaching and alkali treatments, the contents of cellulose, hemicelluloses and lignin were of 26.5 ± 0.8%, 23.7 ± 0.29% and 35 ± 0.34%, respectively. This indicated that the applied treatments were adequate for cellulose and hemicelluloses extraction and purification.

The lignin content reported for AS in previous works ranged from 23.4% to 51.43%.[16,17,19-21] Meanwhile, our results for the cellulose content are in accordance with those of other authors (22.4-39.8%).[16,17,19,21] These differences can be explained by a multitude of factors, such as differences in apricot species, climatic and geographical conditions, as well as in experimental methods.

Table 1
Proximate analysis and component analysis of the raw material

Parameters	Apricot shells
Proximate analysis (wt%, fresh basis)	
Moisture (%)	7 ± 0.5
Ash (%)	2.0
Component analysis (wt%, dry basis)	
AS treated material (%)	93.27± 1.5
Extractives (%)	6.66
Lignin (%)	35± 1
Holocellulose (%)	50.2± 0.34
Hemicelluloses (%)	23.7 ± 0.29
Cellulose (%)	26.5 ± 0.83

AS after organic treatment

AS after bleaching treatment (holocellulose)

Figure 1: Photographs of apricot shells (AS) before and after bleaching treatment

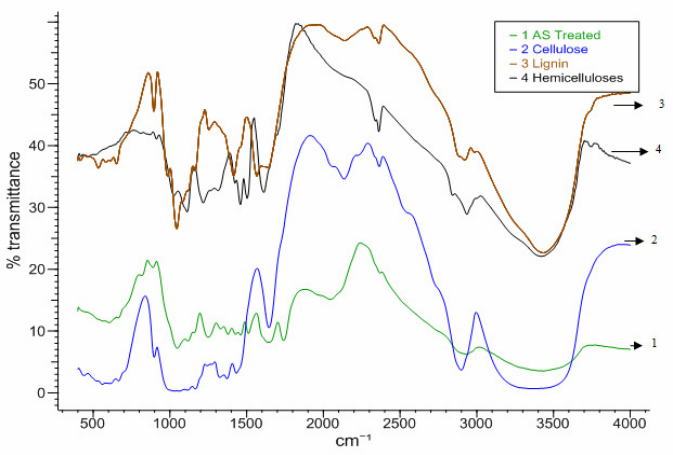

Figure 2: FTIR spectra of treated apricot shells (AS) (1), cellulose (2), lignin (3) and hemicelluloses (4)

Characterization of AS components

FTIR analysis

Structural analysis of lignin, cellulose, hemicelluloses and treated AS was performed by FTIR spectroscopy (Fig. 2, Table 2). FTIR spectroscopy is a suitable technique to find variations induced by different treatments on the molecular structure of materials.[22,23] The peaks between 3600-3000 cm^{-1} have been detected in all the spectra, and correspond to the OH stretching vibration of the -OH group and to the intermolecular hydrogen bonds.[24-26] The peaks between 2950-2850 cm^{-1} have been attributed to CH stretching vibration.[27]

The absorptions at 3348, 2889, 1647, 1431, 1373, 1166, 1058, 1033 and 897 cm^{-1} are related to cellulose. The peak at 1647 cm^{-1} corresponds to the bending of the O-H groups upon the absorption of water. The absorption band of 1319 cm^{-1} was assigned to the bending vibrations of CH_2 in cellulose and the band at 1166 cm^{-1} represents the stretching of the anti-symmetric bridge of the C-O-C groups.[28]

The absorption band at 1033 cm^{-1} represents the morphological change in C-O. The absorptions characteristic of cellulose at 1431 cm^{-1}, 1058 cm^{-1} and 897 cm^{-1} resulting from -CH_2-(C6) bending, C-O pyranose ring vibrations and bending vibration of glycosidic bonds, respectively.[28-32] The disappearance of the peaks at 1716, 1502, 1508, 1558 and 1249 cm^{-1} is obvious after chemical treatment, revealing that lignin and hemicelluloses have been mostly removed. The peaks at 1502, 1508 cm^{-1} and 1249 cm^{-1} are related to C=C bonds in the aromatic rings of lignin and C–O–C stretching of hemicelluloses.[33–35]Generally, the bands at 1612 cm^{-1} and 1460 cm^{-1} are attributed to C=C groups, which are attributed to the aromatic ring and CH_3 deformation asymmetric vibration in the lignin structure, respectively. Also, the band present at 1417 cm^{-1} is related to the C-H group and bending of OH or CH in the hemicelluloses.[33,36]

Table 2
Characteristic FT-IR bands of the studied cellulose, lignin, hemicelluloses and treated AS samples in the 3800-800 cm^{-1} region

No	Band assignment	Wavelength number (cm^{-1})	Treated AS	Cellulose	Hemicelluloses	Lignin
01	OH intermolecular stretching	3433, 3421, 3348 (vs)	+	+	+	+
02	C–Hn stretching	2935, 2888 (s)	+	+	+	+
03	C=O stretching of various aromatic groups	1716, 1741 (w)	+	-	+	-
04	Absorbed O–H	1647 (w)	-	+	-	-
05	C=C of aromatic skeletal vibration (lignin)	1612 (s)	-	-	-	+
06	Conjugated C–O	1558 (m)	-	-	+	-
07	C=C of aromatic skeletal vibration (lignin)	1502, 1508 (s)	+	-	+	+
08	C–H deformation in lignin and carbohydrates	1460 (s), 1463 (s)	+	-	-	+
09	C–H deformation in lignin and carbohydrates	1417, 1431, 1427 (m)	+	+	-	+
10	C–H deformation in cellulose and hemicelluloses	1373, 1379 (m)	+	+	-	-
11	CH_2 rocking vibration in cellulose	1319 (m)	-	+	-	-
12	C–O linkage in guaiacyl aromatic methoxyl groups and acetyl groups in xyloglucan	1249, 1247 (m)	+	-	+	-
13	C-O-C stretching mode of the pyranose ring	1217 (s)	-	-	-	+
14	C–O–C vibration in cellulose and hemicelluloses	1165, 1166 (s)	-	+	+	-
15	C–O stretching	1112, 1114 (vs)	+	-	-	+
16	C-O stretching	1033 (vs)		+	-	-
17	C-O stretching mainly from $C_{(3)}$-O(3)H in cellulose	1051, 1058 (vs)	+	+	-	-
18	C-O stretching	1045 (s)	-	-	+	-
19	Glucose ring stretching, C_1-H deformation	897 (m)	+	+	+	-

(s) strong; (m) medium; (w) weak; (vs) very strong; (vw) very weak

Thermogravimetric analyses

The TG and DTG curves of treated AS, cellulose, hemicelluloses and lignin are shown in Figures 3 and 4. Table 3 summarizes the data regarding the decomposition of the samples: onset temperature (T_{Onset}), degradation temperature at maximum weight-loss rate (T_{peak}), temperature at which the thermal decomposition process ends (T_{end}) and weight loss (W%), obtained from the TG and DTG curves. Generally, the thermo-chemical decomposition processes of the samples can be divided into three stages: drying, depolymerization and char thermo-oxidation.

The thermogravimetric curves recorded at a heating rate of 10 °C/min revealed a complex degradation mechanism, involving three to six stages. All the samples showed an initial small weight loss (<5%) between 30 and 150 °C. The 2.2 to 5.2% humidity is removed throughout the first stage, when the temperature reaches approximately 100 °C. For hemicelluloses, the first stage is an endothermic process, with a peak temperature of 135 °C, which is attributed to moisture evaporation, together with the release of some volatile components and subsequently, the decomposition of major components will initiate.

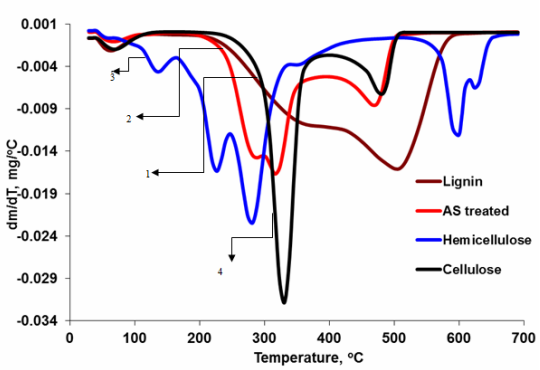

Figure 3: DTG curves of lignin (1), treated apricot shells (AS) (2), hemicelluloses (3) and cellulose (4)

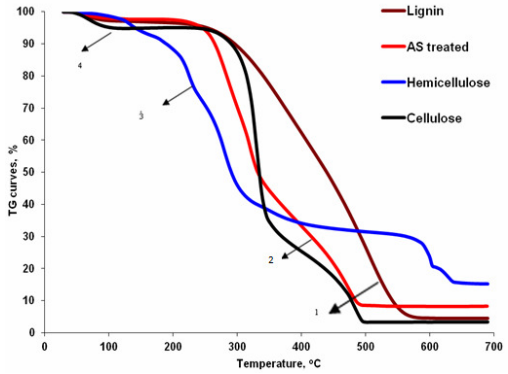

Figure 4: TG curves of lignin (1), treated apricot shells (AS) (2), hemicelluloses (3) and cellulose (4)

Table 3
Main thermogravimetric characteristics of cellulose, lignin, hemicelluloses and treated AS

Sample	Stage	T_{onset} (°C)[a]	T_{peak} (°C)[b]	T_{endset} (°C)[c]	W (%)[d]	Residue at 700 °C (%)
Lignin	I	45	63	90	3.00	3.77
	II	281	366	446	49.28	
	III	446	507	558	43.95	
Treated AS	I	44	67	118	2.27	7.27
	II	260	287	305	28.73	
	III	305	317	331	19.84	
	IV	331	470	488	41.89	
Hemicelluloses	I	124	135	155	8.89	14.48
	II	216	226	232	20.68	
	III	266	280	303	26.74	
	IV	303	353	406	12.62	
	V	588	600	604	11.21	
	VI	616	624	637	5.38	
Cellulose	I	50	74	97	5.15	2.76
	II	306	330	343	66.04	
	III	430	481	493	26.05	

[a]T_{onset} – temperature at which the thermal decomposition begins; [b]T_{peak} – temperature at which the degradation rate is maximum; [c]T_{endset} – temperature at which the thermal decomposition process ends; [d]W – mass loss percentage in each stage

The depolymerization of cellulose occurs in the temperature range from 300 to 340 °C, characterized by a most significant mass loss of 66%. This is followed by thermal oxidation, with a mass loss of 26%, which occurs within the temperature range from 430 to 493 °C.

The amount of residue obtained at 700 °C is 2.76%, which is close to the value indicated in the literature when the first weight loss step of cellulose is observed between 220 and 300 °C, followed by the second one in the range of 300-475 °C. These two steps are related to the different initial mass of cellulose of 62 and 28%, respectively.[37,38]

When the moisture has been removed, lignin decomposition takes place in two stages at a temperature at which the degradation rate is maximum: 366 °C and 507 °C, respectively. The amount of residue obtained when the thermal oxidation process is over is 3.77%. In most of the literature, DTG plots reveal two peaks for lignin decomposition, apart from the peak associated to dehydration.[39]

Compared to lignin, the treated AS sample decomposes throughout two stages in the 260-331 °C temperature range, which may be associated with the decarboxylation and depolymerization processes. The thermal oxidation process takes place at temperatures above 380 °C and ends at about 490 °C, resulting in an amount of residue of 7.27%.

For hemicelluloses, the degradation process starts at a temperature of about 216 °C and is carried out in a three-step sequence up to 406 °C, when a stable intermediate is formed. Its decomposition takes place in two stages at a temperature higher than 588 °C, with T_{peak} = 600 and 624 °C. In the case of hemicelluloses, the amount of residue obtained is much higher than that for the other samples under analysis. As also shown in the literature, the lowest thermal stability has been noted in the case of hemicelluloses.[40-41]

The difference in the decomposition temperature of the various compounds (treated AS, hemicelluloses, cellulose and lignin) can be explained by the variation of their chemical structure. Hemicelluloses generally degrade rapidly, with pyrolysis between 210 and 350 °C. Cellulose pyrolysis occurs later, around 350-400 °C, while lignin degradation will cover the entire temperature range.[30] The DTG curves shown in Figure 3 and the main thermogravimetric characteristics described in Table 3 reveal that cellulose has good thermal stability, followed by lignin, treated AS and hemicelluloses.

Taking into account the temperature at which the thermal decomposition begins, the following thermal stability series has been established: hemicelluloses < treated AS < lignin < cellulose.

The kinetic data processing was performed by applying the Freeman-Carroll method.[42-43] This method allows calculating the activation energy, pre-exponential factor and reaction order from a single TGA curve by Equation (1):

$$\frac{d\alpha}{dt} = A \cdot e^{-\frac{E_a}{RT}} (1-\alpha)^n \quad (1)$$

where $d\alpha/dt$ = rate of reaction in s^{-1}, A = pre-exponential factor, E_a = activation energy in J mol^{-1}, R = gas constant = 8.31 J mol^{-1} K^{-1}, T = sample temperature in K, α = conversion degree and n = order of reaction. The kinetic parameters corresponding to the beginning stage of the degradation process are presented in Table 4.

Table 4
Kinetic parameters of cellulose, lignin, hemicelluloses and treated AS

Sample	n	Ea (kJ/mol)	lnA	ΔT (°C)
Lignin	0.39±0.012	52.17±0.55	4.38±0.12	270-355
AS treated	0.71±0.010	144.67±1.18	26.73±0.27	265-310
Hemicelluloses	0.90±0.089	200.37±2.10	44.26±0.51	220-240
Cellulose	0.89±0.017	289.62±2.57	53.51±0.531	320-340

The kinetic study carried out reveals the much higher thermal stability of cellulose, as the activation energy in the thermal decomposition onset stage is 289.62 kJ/mol, unlike the activation energy values of the other analyzed materials, which range between 52 and 200 kJ/mol. Our results are in accordance with those found by other researchers on the pyrolysis kinetics study of palm kernel shells (130.04-235.59 kJ/mol) and hazelnut husk (103.04-162.06 kJ/mol). They explain the decomposition kinetics as process occurring in several stages: by the degradation of

hemicelluloses and cellulose, as well as the slow thermal degradation of lignin.[44]

CONCLUSION

This work reports on the extraction of the main components of apricot shell biomass. FTIR spectroscopy and TGA have been used to characterize them. The removal of lignin has been confirmed by the absence of the peaks at 1502, 1508 and 1612 cm^{-1} in the FTIR spectra, suggesting the great efficiency of the bleaching process. TGA revealed that the cellulose extracted from the apricot shells has good thermal stability, followed by lignin, treated AS and hemicelluloses. The analysis of the FTIR spectra evidenced the structure of cellulose, hemicelluloses and lignin, which confirmed that apricot shells (AS) are a lignocellulosic biomass source with relatively high cellulose, hemicelluloses and lignin contents. This makes apricot shells (AS) an interesting and advantageous material for various valorization methods.

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