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CHARACTERIZATION OF CHESTNUT SHELL

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Abstract

The outer brownish shell (pericarp) that remained after the cottony structure was removed inside the sweet chestnut (*Castanea sativa* Mill.) fruit shell was characterized chemically and morphology. The study was focused on two ways; first is gravimetric analyses to determine main chemical composition of chesnut shell such as holocellulose, α-cellulose, and klason lignin and the second way was analytical analyses to identify the extractive composition and the amount. Main lignocellulosic compounds were determined as 45.3% holocellulose, 29.2% α-cellulose, 42.5% klason lignin. Extractive content was also 3.2%. Analytical results showed that MeOH:Water (95:5 v/v) extract contained 23.8% fructose, 16% glucitol, and 11.2% glucose. Gallic acid was found only 5% in the acetone: water extract. The fiber length, fiber width, lumen width, and fiber wall thickness of the samples were measured as 1.52 mm, 21.67 µm, 14.25 µm, and 3.71 µm, respectively. Chestnut shells, which are morphologically similar to hardwood fibers and contain a high amount of klason lignin, have significant potential for use as raw materials in different industries.

Key Words: Chestnut shell, cellulose, lignin, fiber properties

1. Introduction

Sweet chestnut trees as a hardwood species can grow to 30-35 m. Cultivated sweet chestnut trees are long-lived (up to 1000 years), and they may reach a significant circumference at breast height (up to 12 m). The sweet chestnut tree spreads from Southern Europe and North Africa to North-Western Europe and eastward to North East Türkiye, Armenia, Georgia, Azerbaijan, China and Syria. The altitude of chestnut tree in the world is between 200 and 1800 m. It covers more than 2.5 million hectares. Chestnut trees have always been cultivated for their wood and fruit (Avanzato, 2009; Conedera et al., 2021).

In 2020, worldwide production of chestnut fruit was 2.32 million tons. China is main supplier in the world, producing 1.74 million tons per year. Turkey produced approximately 76 thousand tons, accounting for 3.28% of the world's chestnut fruit production (FAOSTAT, 2022). In last years, there is a growing interest for the chestnut fruit. Because of its gluten-free form, it takes places in diets. In addition, the flour and marron glace production of chestnut has an important market. In parallel to production, an increased in the amount of chestnut shell, a by-product occurred. Shells composed of tannins, flavonoids and phenolic acids. With this chemical structure, it is used as tanning of leathers, coloring of wool and cottons and as an adhesive in wood industry (Husanu et al., 2020). As known flavonoids, have anti-allergic, anti-inflammatory and antioxidant activities. Because of these features, chestnut shells used in cosmetic and pharmaceutics as a natural preserver (Vazquez et al., 2008). Not only the extractive composition but also the lignocellulosic part could also be potential source for different area.

In order to convert this waste material into value-added products, its better to know more about it. There are some papers on the chemical composition (González López et al., 2012; He et al., 2016; Morales et al., 2018) and phenolic contents (Vázquez et al., 2008) of chestnut shell. Several authors also studied chemical composition (Moure et al., 2014) and fiber properties (Liang et al., 2021) of chestnut burs. From this point of view, we aimed to characterize the chestnut shell (pericarp), chemically and anatomically.

2. Material and Methods

Brown outer shells (pericarp) of sweet chestnut (*C.sativa* Mill.) fruits obtained from Yahyayazıcılar Village, Amasra district of Bartın province were used as raw material. The altitude is 30 m. Almost 5 kg of chestnut fruits was collected. Before the experiments, the white cottony structure inside the shell was separated manually with the tip of a knife. Shells grounded in a kitchen grinder were stored in glass jars till analysis.

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The chemical structure of the shell was investigated in two different ways, gravimetrically and analytically. To determine the amount of extractive material, the samples were extracted with MeOH:water (95:5 v/v) for 4 hours by using soxhlet apparatus. After processing, the MeOH:water portion was separated for further analytical studies and stored in deep freezers. The solid part was used in gravimetric measurements. Holocellulose (Wise & Jahn, 1952), α-cellulose (Rowell, 2005), and klason lignin (TAPPI T222 om-02, 2002) contents of samples were determined with relevant references. Each experiment was repeated three times.

For characterization of extractives two different solvent (MeOH:water and acetone:water) was used. Samples were extracted separately. Aliquots were analyzed by GC-MS (Shimadzu GC-MS-QP2010). The samples were silylated with pyridine: trimethyl chlorosilane: N, O-bis (trimethyl silyl) trifluoroacetamide (Kilic et al., 2011) and then analyzed in the GC-MS under the following conditions (Table 1).

Table 1. GC-MS operating conditions.

Column type	RTX-5MS (30m x 0.25µm x 0.25mm)
Carrier gas	He
Gas flow	1.10 ml/min
Ion source temperature	200 °C
Interface temperature	250 °C
Temperature program	120 °C (1 min./6 °C) 310 °C at 15 min.

Chlorite method was applied for the fiber maceration (Spearin & Isenberg, 1947). Shells were cut into small pieces and fiber length, fiber width, fiber lumen width, and fiber cell wall thickness of 50 randomly selected fibers were measured. The flexibility ratio [(lumen width/fiber width) × 100], slenderness ratio (fiber length/fiber width), and Runkel ratio [(2 × cell wall thickness)/lumen width] were calculated using the measured fiber dimensions.

3. Results and Discussion

The gravimetric results of the main compounds, found in the chestnut shell are given in Table 2. As seen they are compatible with the previous literature. Almost, 42% of the main structure was composed of lignin, a sustainable smart resource in the nature. With this feature, lignin content of chestnut shell is similar to hazelnut and peanut shells (Gullón et al., 2018). González López et al. (2012) determined the lignin as 44.9% in the shell part. However, Boran Torun et al. (2019) has found the lignin in the cupula of chestnut 22.95%, almost half of the shell value. On the other hand, the cupula contained more holocellulose than shell part. Extractives were found as 3.2%. It is considered that differences between the values of extractives in Table 2. are due to the solvent type. In this study MeOH:water (95:5v/v) was used. Both in our study and in González López et al. (2012) polar solvents, which are used for phenolic compounds, were preferred.

Table 2. Main compounds found in the chestnut shells (%).

	This study	**Morales et.al (2018)**	**González López et al. (2012)**	**Dönmez et al. (2016)**	**Boran Torun et al. (2019) cupula**
Extractives	3.20±0.04	1.5	9.9	10.76	4.35
Holocellulose	45.3±3.7	-	-	49.39	59.08
α-cellulose	29.2±0.9	25.6	25.2	40.03	-
Klason lignin	42.5 ±3	36.4	44.9	34.82	22.95

MeOH:water and acetone:water (95:5 v/v) extracts were analyzed with GC/MS to determine the phenolic compounds. Chromatograms are given in Figure 1. Identified compounds and the amounts were summarized in Table 3. Two different polar solvent was used. It was aimed to detect phenolic compounds in these two aliquots. Nevertheless, only gallic acid, which was found only 5%, was detected. More than 70% of two aliquots was sugar units. Xylitol, fructose, galactose, glucose and non-identified units (MW.437) are forming the content.

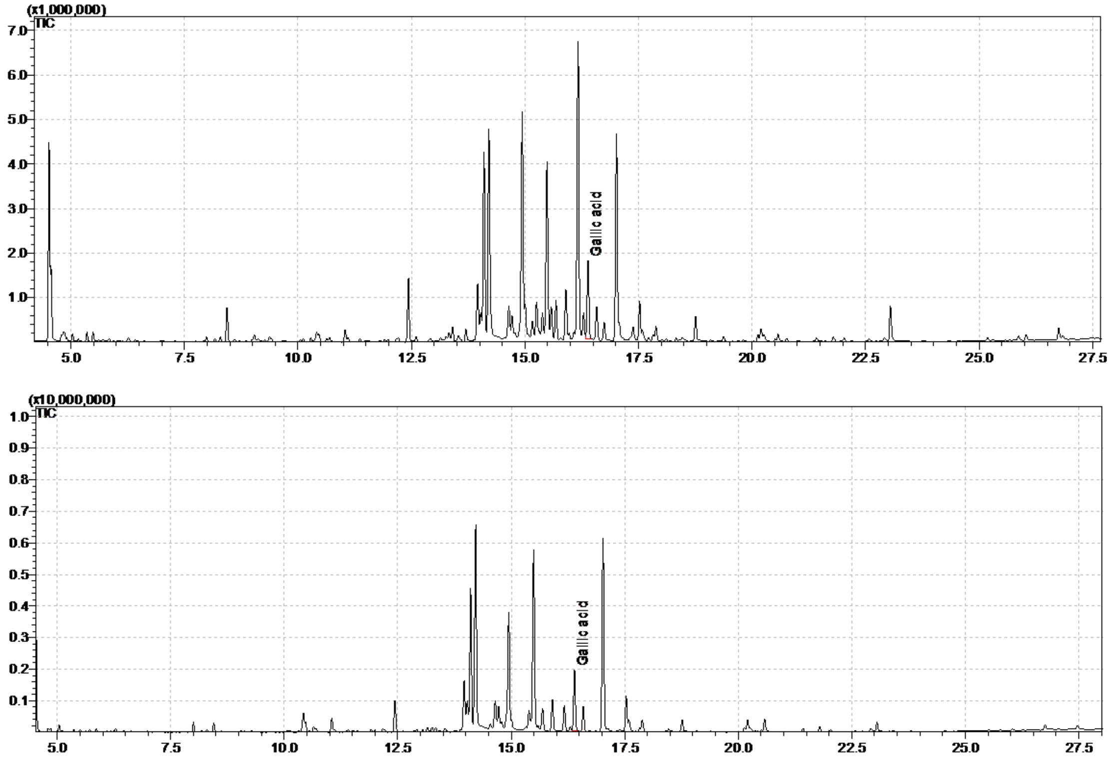

Fig. 1. The chromatograms of MeOH:W (upper) and Acetone:W (bottom) extracts of chestnut shell.

Fructose was the most abundant sugar units (23.2-18.8%) in the chestnut shell. This sugar also detected in the flowers of *C. sativa* as 5 g/100g. (Barros et al., 2010). Glucose with the amount of 17.1-11.2% is the second important sugar unit. However, Gullón et al. (2018) found the amount of glucose as 20.6%. Glucitol, known mainly as Sorbitol, was determined 16.1% in the MeOH extract. In the acetone:water extract the amount was 2%. Glucitol found in different fruits like apple, pear, and peach (Lenhart & Chey, 2017)

Table 3. The amount of chemical compounds determined in the MeOH:W and Ace:W extract of chestnut shell.

No	RT	Name	MeOH:Water (%)	Ace:Water (%)
1	12.43	Xylitol	3.15	2.5
2	13.95	Sugar (MW 437)	3.34	4.68
3	14.02	Sugar (MW 437)	1.48	11.93
4	14.09	D-Fructose-1	10.37	-
5	14.20	D-Fructose-2	12.84	18.78
6	14.93	n.i	13.5	11.3
7	15.00	Sugar (MW 437)	1.55	-
8	15.48	α-D-galactopyranose	9.92	16.6
9	15.58	Galactoside	1.63	-
10	15.68	D-Galactose	2.15	2.08
11	15.90	Myo-Inositol	2.88	2.64
12	16.16	Glucitol	16.15	2.03
13	16.38	Gallic acid	4.06	5.2
14	16.58	Inositol	1.87	2.12
15	17.01	α-D-glucopyranose	11.23	17.12
16	17.52	16:0	2.04	3.01
17	23.05	D-Glucuronic acid	1.84	-

The comparison of fiber properties of some lignocellulosic materials and chestnut shell are given in Table 4. Liang et al. (2021) noted that fiber length, fiber width, and slenderness ratio of chestnut burs were 1.06 mm, 17.51 µm, and 60.54, respectively. The fiber length of chestnut shell was significantly longer than those of some hardwood species such as poplar, oak, beech, and maple. Also, chestnut shell had longer fibers than some fruit tree such as avocado, pomegranate, kiwi, hazelnut, cherry, and apricot. Fiber width of chestnut shell had the similar to that of hardwood species. Chestnut shell had fibers similar to the fiber lumen width of the black pine cone. The cell wall thickness of chestnut shell was narrower than hardwood and fruit tree species (Table 4). On the other hand, chestnut shell had higher slenderness ratio and flexibility ratio, and lower Runkel ratio than those of hardwood and fruit tree species. This result can be explained by longer fibers of chestnut shell. Also, it can be attributed to narrower cell wall thickness of chestnut shell. More flexible and longer fibers resulted in paper with high strength.

Table 4. Comparison of fiber properties of some lignocellulosic materials and chestnut shell.

Sample	**FL (mm)**	**FW (µm)**	**FLW (µm)**	**FCWT (µm)**	**SR**	**FR**	**RR**	**Reference**
Chestnut shell	1.52	21.67	14.25	3.71	70.14	65.76	0.52	This study
Chestnut bur	1.06	17.51	-	-	60.54	-	-	Liang et al. (2021)
Castanea sativa	1.06	21.1	11.6	4.7	50.1	54.8	0.8	Alkan (2004)
Populus tremula L.	1.10	23.90	11.40	6.30	46.0	47.70	1.10	Gulsoy & Tufek (2013)
Quercus robur L.	1.17	20.50	9.56	5.50	-	-	-	Gülsoy et al. (2005)
Fagus orientalis L. (sapwood)	1.16	20.20	5.70	7.70	57.43	28.22	2.70	Gülsoy et al. (2021)
Acer campastre L.	0.58	25.00	16.30	4.40	-	-	-	Eroğlu & Gülsoy (2008)
Bracken stalks	1.25	24.00	10.30	6.85	52.08	42.92	1.33	Gülsoy & Şimşir (2018)
Black pine cone	1.25	31.10	13.70	8.70	40.19	44.05	0.56	Gulsoy & Ozturk (2015)
Pomegranate wood	0.75	20.95	11.65	4.65	35.58	55.61	1.60	Gülsoy et al. (2015)
Apricot wood (sapwood)	0.69	12.08	5.69	3.19	55.09	50.37	0.97	Gençer et al. (2018)
Avocado wood	1.06	25.78	16.18	4.80	41.00	63.00	0.59	Altunışık Bülbül & Gençer (2021)
Wield cherry wood (sapwood)	1.11	20.35	10.50	4.93	54.56	51.60	0.90	Gençer & Gül Türkmen (2016)
Kiwi wood	1.58	35.97	22.30	6.84	44.03	61.99	0.61	Yaman & Gencer (2005)
Hazelnut pruning	1.04	22.20	13.66	4.30	-	-	-	Gençer & Özgül (2016)

FL: Fiber length, FW: Fiber width, FLW: Fiber lumen width, FCWT: Fiber cell wall thickness, SR: Slenderness ratio, FR: Flexibility ratio, RR: Runkel ratio

4. Conclusions

The chemical composition and fiber morphology of chestnut (*C.sativa* Mill.) fruit shell were evaluated in this study. The results showed that chestnut shells had longer fibers, higher slenderness, and flexibility ratios compared to some hardwood and fruit trees. According to these results, chestnut shell can be used in paper production. Chestnut shell has a high lignin content (44.5%) and saccharides (23.2% fructose, 17% glucose). The amount of extractives are only 3% in the MeOH:water extract of chestnut shell.

Today, chestnut fruit shell utilizes only as a fuel. Actually, its high lignin and oligosaccharide content can be renewable resource for different areas. Its extractives can also be used as a natural antioxidant.

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