



## Chemical Changes in Historical Wooden Structures in Rize-Fırtına Valley

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**Abstract:** Studies conducted to determine the factors that cause damage in historical wooden buildings in our country are quite limited. Rize-Fırtına Valley, with a climate index higher than 65, is one of the regions with the highest rainfall in our country. The risk of decay in historical wooden buildings in this region due to the high climate index is quite high. As a result of this situation, the resistance properties of wood are negatively affected. Within the scope of the research, samples were taken from wooden mansions which are at least 150 years old in the region. Cellulose, lignin, and hemicellulose contents were determined in order to detect chemical changes occurring in the chemical structures of the wood samples. Thanks to the obtained results from this study, intervention/restoration methods may be suggested for the protection and sustainability of wooden materials in historical buildings.

**Keywords:** Fırtına Valley, Historical wooden structures, Chemical analysis, Cellulose, Lignin.

## Rize- Fırtına Vadisindeki Tarihi Ahşap Yapılardaki Kimyasal Değişimlerin Tespiti

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**Öz:** Ülkemizde tarihi ahşap binalardaki zarar yapan etmenlerin belirlenmesi amacıyla yapılan çalışmalar oldukça sınırlıdır. İklim indeksi 65'ten yüksek olan Rize-Fırtına Vadisi ülkemizde en fazla yağış alan bölgelerden biridir. İklim indeksi yüksek olan bu bölgede bulunan tarihi ahşap yapılarıdaki çürüme riski yüksektir. Bu durumun bir sonucu olarak ahşabın direnç özellikleri olumsuz etkilenmektedir. Bu bulgudan hareketle ülkemizin doğa ve kültür turizmi açısından popüler destinasyonlarından biri olan ve bu vadiye bulunan Rize ili Çamlıhemşin ilçesinde farklı yükseltilerdeki çeşitli tarihi yapılar araştırmaya dahil edilmiştir. Araştırma kapsamında söz konusu bölgede bulunan en az 150 yıllık ahşap konaklardan örnekler alınmıştır. Örnekler üzerinde meydana gelen kimyasal değişimleri tespit etmek amacıyla selüloz, lignin ve hemiselüloz tayini yapılmıştır. Bu değişimlerin yapılarıdaki elemanların taşıyıcı özellikleri üzerindeki etkisine bakılmıştır. Bu sonuçlar ışığında tarihi yapılarıdaki ahşap malzemenin korunması ve sürdürülebilirliği noktasında müdahale yöntemleri önerilebilecektir.

**Anahtar kelimeler:** Fırtına Vadisi, Tarihi ahşap yapılar, Kimyasal analizler, Selüloz, Lignin.

## INTRODUCTION

For centuries, wood has been used for the construction of numerous items that are now part of the cultural heritage due to their unique properties (strength, elasticity, thermal and sound insulation, color, odor, durability, etc.). Accordingly, wood is one of the oldest traditional construction materials used for religious and civil architecture in the Black Sea Region of Turkey.

As with all wood for all time, deterioration depends on a number of chemical and biological factors. Losses in mechanical strength due to deterioration raise concerns about shortening the life of wood. The degradation of wood can be accelerated as a result of its chemical or biological degradation, and this can be induced or accelerated by the outdoor effect (Almkvist and Persson, 2008; Sandström et al., 2005). It is extremely difficult to generalize the effect of degradation on the

material properties of wood and this is largely dependent on the wood. The type, age, environmental factors, rot mechanisms and other parameters active in the wood material, as well as the degree of exposure to oxygen, or its contact with the soil affect the life of the place of use (Highley, 1995; Thaler and Humar, 2013 ; Björdal, 2000).

Studies conducted to determine the factors that cause damage in historical wooden buildings in Turkey are quite limited. Chemical and physical change in weathering. How fast it will be does not only depend on the durability against rot and wood pests. It is an indication of how effective the weather conditions on the wood material is. It is the fiber loss caused by the deformation and the slow wearing of the damaged surface.

The factors of the special location of Rize-Fırtına Valley (climate, landscape and elevation) will have an effect on the physical, mechanical and biological properties of historical wooden structures. Climate indices was developed by the American Weather Forecasting Office to determine the decay risk for wood materials based on the climatic conditions of the environment as follows.

It was reported that the risk and risk of decay is relatively low in regions with a climate index of 35 or less, moderate in regions between 35 and 65, and the risk of decay of wood material in regions with a climate index of more than 65. The risk of decay in historical wooden buildings in this region due to the high climate index is quite high. Rize-Fırtına Valley, with a climate index higher than 65, is one of the regions with the highest rainfall with a 95-climate index in Turkey (Gezer, 2003). In the scope of this paper, two historical wooden mansions located in rural areas of Çamlıhemşin district were studied in detail.

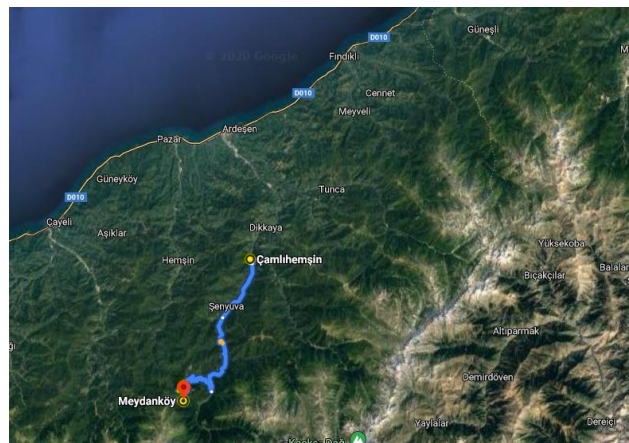
As high climate index results in high risks of decay in historical wooden structures, various historical buildings at different heights in Çamlıhemşin district of Rize province, which is one of the popular destinations in Turkey in terms of nature and cultural tourism and located in this valley are included in this study.

It is important to investigate the chemistry and structure of the material in order to detect structural changes and deterioration in historical wooden structures and to contribute to the protection and sustainability of wood. For this reason, in this paper, it was aimed to investigate the chemical changes in samples taken from historical wooden structures located at different elevations in the Rize-Fırtına Valley.

## MATERIALS AND METHODS

Two different areas were selected in Çamlıhemşin Rize for this study. Within the scope of the research, samples were taken from wooden mansions which are at least 150 years old in the region and are at different

elevations above sea level. Wood samples were taken from the south facing exteriors of historical wooden buildings and subjected to some chemical analysis. Those wooden houses studied in this project were constructed from chestnut (*Castanea sativa* Mill.). Chestnut is easily obtained from the close environment. In addition, natural durability of chestnut is very high. Therefore, it is the most preferred material in building such mansions.



**Figure 1.** General view of research area (Meydanköy- area 1; Çamlıhemşin-area 2).

Wood samples used in chemical analysis were mechanically chipped and ground in a laboratory type Willey mill. These samples were sieved according to the grain size that remained in the 60-mesh sieve in accordance with standard analysis methods. Since the samples were taken from different elevations above sea level, they were then placed in sealed nylon bags and stored separately. Samples taken from each house were subjected to chemical analysis in triplicate. The moisture content of the test samples was determined by drying in a n oven at  $103 \pm 20C$ . Following chemical analysis were conducted.



**Figure 2.** Historical some wooden buildings.

**Determination of moisture:** Moisture determinations of the wood samples used in the study were made before starting the chemical analysis. Moisture determinations were made according to TS 2471. Accordingly, 2g of sample was weighed on a precision scale and the first weight was determined and the sample

placed in the oven at  $103 \pm 20^\circ\text{C}$  was dried until it reached full dry weight. The samples taken out of the oven were cooled in a desiccator and their exact dry weights ( $M_o$ ) were determined by weighing on a precision scale.

The % moisture content of the samples was calculated using the following equation:

$$r = \frac{Mr - Mo}{Mo} \times 100 \quad (1)$$

r: Moisture of sample (%)

Mr: The weight of the sample in the damp state (g)

Mo: Weight of the sample in the dry state (g)

**Solubility in Alcohol-benzene:** Solubility processes in alcohol benzene were carried out to determine the proportions of substances such as oil, wax, resin and possibly ether-insoluble wood gum in the wood. Chemical analysis was carried out in triplicate by taking 10 grams from each sample group. For this, wood samples in 300 ml alcohol-benzene mixture were extracted for four hours in Soxhlet extraction device and the ratios of soluble substances were determined. Transactions were carried out according to the method in the TAPPI T 204 Om-88 standard (1988).

**Determination of Holocellulose content:** Holocellulose; it is the carbohydrate complex that remains after the lignin substance of the wood is separated. In the study, the most widely used and most reliable Chlorite Method was applied to determine the amount of holocellulose, which contains all of the carbohydrates in the wood. Three repetitive holocellulose determinations were made by taking 5 g from sample groups exposed to alcohol-benzene solubility. Chemical analysis was made according to Wise's chlorite method. As a result of the analysis, the samples were dried at  $103 \pm 2^\circ\text{C}$  and weighed. This weight was found to be holocellulose % in proportion to its original dry weight.

**Determination of Alpha-Cellulose content:** Approximately 2g was taken from wood dust previously extracted from alcohol benzene and used as a test sample. Alpha-cellulose determination was made according to the TAPPI T 203 OS-71 standard. Alpha cellulose ratio was determined using 17.5% NaOH on holocellulose samples. As a result, the amount of alpha cellulose was calculated as % compared to full dry wood. The crucible and the residue in it were weighed after drying at  $103 \pm 2^\circ\text{C}$ , cooling in a desiccator, and the ratio of alpha cellulose in percent (%) to the complete dry sample weight was determined.

**Determination of Lignin content:** When wood is treated with strong acids, carbohydrates are hydrolyzed and residual lignin is obtained. Since chestnut contains a high percentage of tannins, samples were treated with alcohol to

remove tannins. Then cellulose was removed using with 72%  $\text{H}_2\text{SO}_4$  and lignin was obtained as the final product. For the determination of lignin, some extractives remaining undissolved in the samples must be removed together with lignin first. For this, standard alcohol extraction was applied to the samples. For the determination of lignin, 1 g of air-dried samples, which were extracted from alcohol before, will be transferred to a beaker and 15 ml of 72%  $\text{H}_2\text{SO}_4$  are poured on it and kept at  $12-15^\circ\text{C}$  for 2 hours. At the end of this period, the mixture in the beaker was transferred to a 1-liter flask and the amount of liquid in the flask was 560 ml so that the acid concentration was 3%. The residue was filtered through the crucible and washed with hot distilled water. The residue obtained was dried in an oven at  $103 \pm 2^\circ\text{C}$  and calculated in proportion to the initially used sample weight. TAPPI T211 om-02 standard method (2002) was used to determine the amount of lignin.

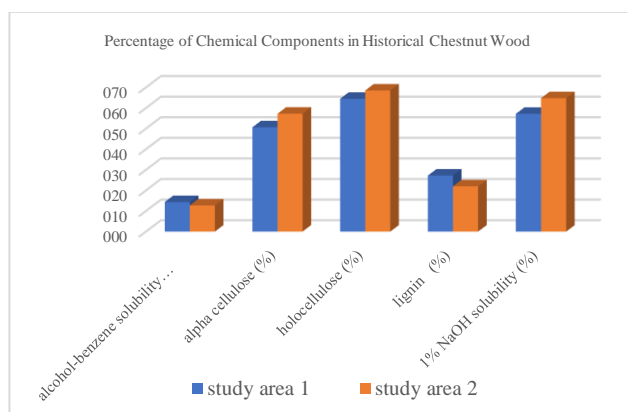
**Solubility in 1% NaOH:** The experiment carried out in accordance with the TAPPI T212 om-02 standard (2002), 2 g of air-dry sample with a sensitivity of 0.0001 g was placed in a 200 ml Erlenmeyer, then 100 ml of 1% NaOH solution was added with a pipette. The mouth of the Erlenmeyer was closed with a small flask, placed in a water bath at  $100^\circ\text{C}$  and kept in the water bath for one hour. It was mixed four times at the 5th, 10th, 15th and 25th minutes. At the end of this period, the residue in the flask was filtered by vacuum on a tared crucible and then washed with 10% acetic acid and hot water, the crucible and its contents were dried at  $103 \pm 2^\circ\text{C}$  and cooled in a desiccator and weighed.

## RESULTS AND DISCUSSION

Chemical analyses of samples taken from historical wooden building at different elevations were conducted and the results are shown Figure 3. Similar results were obtained from the percentage of alcohol-benzene solubility in the samples. While the highest percentage of alpha-cellulose was found in the sample taken from the first region; the lowest percentage was found in the sample from the second region. Holocellulose percentage was higher in the sample taken from the second region, when compared to the sample taken from the first region. With regard to 1% NaOH solubility of the samples, it was higher in the second region.

**Table 1.** Percentage of Chemical Components in Historical and original Chestnut Wood.

Experiments	Study Area 1		Study Area 2		"Chestnut wood"
	x	Std	x	Std	
Alcohol-benzene	14,34	0,11	12,71	0,03	19,84
Alpha cellulose	50,66	1,10	57,22	4,02	53,35
Holocellulose	64,50	0,67	68,51	0,70	68,00
Lignin	27,22	0,87	21,95	0,81	25,23
1% NaOH solubility	57,18	0,76	64,74	0,84	32,90



**Figure 3.** Percentage of Chemical Components in Chestnut Wood taken from Historical Wooden Structures.

It was reported that percentage of holocellulose, cellulose, lignin, alcohol-benzene solubility and 1% NaOH solubility of newly cut chestnut wood were 68%, 53.35%, 25.23%, 19.84% and 32.90%, respectively (Akgün, 2005).

The results showed that rather than main wood components, alcohol benzene solubility and 1% NaOH solubility dramatically changed in wood samples taken from historical buildings regardless of their locations. The reason for lower alcohol-benzene solubility was that extractives might have washed out from wood due to the rain and other climatic conditions. The reason for higher 1%NaOH solubility in wood samples taken from historical buildings could be because of weathering, UV degradation and insect infestation.

## CONCLUSIONS

(1) The results of study area-1 showed that percentage of cellulose, holocellulose, lignin, alcohol-benzene solubility and 1% NaOH solubility of chestnut wood were 50,66%, 64,50%, 27,22%, 14,34% and 57,18%, respectively.

(2) The study area-2 results revealed that 57.22%, 68.51%, 21.95%, 19.84% and 32.90%, respectively, were the percentage of cellulose, holocellulose, lignin, alcohol-benzene solubility and 1% NaOH solubility of newly cut chestnut wood.

(3) The results showed that rather than main wood components, alcohol benzene solubility and 1% NaOH solubility dramatically changed in wood samples taken from historical buildings regardless of their locations. The reason for lower alcohol-benzene solubility was that extractives might have washed out from wood due to the rain and other climatic conditions. The reason for higher 1%NaOH solubility in wood samples taken from historical buildings could be because of weathering, UV degradation and insect infestation.

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