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ASSOC. PROF. DR. ALİ BOLAT

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Chapter 1

DIFFERENCES IN CHEMICAL AND MORPHOLOGICAL PROPERTIES OF SORGHUM STALK BY STEM HEIGHT AND COMPATIBILITY OF THESE PARTS TO PAPER PULP BY CHEMICAL METHOD

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INTRODUCTION

The main components of plants are cellulose, hemicelluloses, and, lignin. If a common name is given to all of the trees, shrubs, and other plants that contain these basic components, we can say that all of them are lignocellulosic raw materials. Benefiting from lignocellulosic raw materials has been going on since the existence of human beings, albeit for different purposes. Although nutrition and shelter come at the beginning of the benefit, it has changed according to the age in the historical process. There were periods of abundance and scarcity of raw materials according to the usage rate and drought and precipitation.

We can define other herbaceous and similar plants other than trees and shrubs as non-wood. Paper production from non-wood fiber raw materials dates back to ancient times. The most widely used of these raw materials are crop stalks. It is easier to obtain paper pulp from crop stalks than from wood. In the early years, the use of crop straw was purely due to its easy processing and the search for raw materials suitable for existing possibilities. Therefore, the technical suitability of the raw material has come to the fore.

As a result of technological developments, the demand for annual plants has decreased with the use of wood raw materials. The main reason for this is the abundance of forest resources in those years and the wood yielding more fibrous raw materials than a certain area. However, the demand for annual plants has increased due to the increase in the demand for wood raw materials, economic competition between countries, forest resources, and geographical locations of the countries. The increase in demand for wood raw materials prompts researchers to work to evaluate all kinds of fiber resources. Some are technically and economically appropriate, while others may not. For example, in a study, it was suggested that the chemical properties of rosemary stems show the characteristics of hardwood, but its fibers are not suitable for paper production and it is recommended to be used in composite board production (Odabaş Serin et al. 2017). Similarly, in a study examining the chemical and morphological properties of apricot wood and fruit endocarp, it was stated that fruit endocarp fibers are not suitable for paper production but can be used in the production of boards, apricot wood has similar properties to other industrial value hardwoods, and therefore it is a suitable raw material for pulp production (Gençer et al. 2018).

Today, due to the shortage of raw materials, the fact that annual plants are quickly sought raw materials in the paper industry is due to the search for raw materials suitable for economic opportunities.

The self-renewal time of raw material in nature is directly proportional to its abundance or scarcity in use. When the growth period of the trees is calculated, it takes a very long time in the biomass cycle. It takes a long time for the wood raw material that forms the roots, trunk, and branches of trees to be suitable for technical and economic use. Although fast-growing species such as poplar, pine, and pavlonia can be used in 10-12 years, this period can be extended to long periods such as 25-100 years in main forest trees. However, in annual plants, this period is limited to a few months and a maximum of one year. For example, in crop stalks, this period is limited to a maximum of 8-10 months. For these reasons, the supply of biomass is quite fast. While the main crops are wheat, barley, oats, rye, and paddy, the geography of the countries and accordingly the nutritional habits and economic level affect the planting rates of these plants. These crops are mainly cultivated for grain production. Biomass remaining from seed production is a very important fiber source.

The collectible biomass amount of some crops remaining from cereal production is given in Table 1.

Table 1. Collectible biomass of some crops remaining from cereal production (Atchinson, 1973).

Crops	**The amount of collectible biomass (ton/ha)**
Wheat	2.3-3.0
Rye	1.2-1.4
Barley	1.2-1.4
Rice	1.2-1.4
Oats	1.2-1.4

However, most of them have an important place in traditional animal nutrition. This situation creates market competition and sometimes prices are higher than wood prices. For this reason, it may be a solution to grow annual plants, which can obtain very high dry raw material per unit area, primarily to meet the need for fiber raw materials.

We can divide the fibers obtained from annual plants into four groups according to their sources.

1-Stem fibers of herbaceous plants: crop stalks

2-Outer stem tissue (bast) fibers: flax, hemp fibers

3-Leaf fibers: abaca, sisal hemp

4-Seed hairs: cotton

Paper can be made from any raw material containing fiber whose technical characteristics are suitable for pulp production, provided that the appropriate method is selected.

However, in order for a raw material to be used in pulp production, it must be considered economically as well as technically appropriate. In order for the raw material to be used in pulp production to be economically suitable, the majority of the fibers it contains must be suitable for pulp production, and the main factors such as the yield and accessibility of this raw material per unit area must be met.

Sorghum is an important agricultural plant due to its greater biomass efficiency compared to other plants. Sweet sorghum is an annual plant (Almodares and Hadi, 2009) in which higher amounts of biomass can be obtained (Barbanti et al. 2006). A study from Turkey indicated that sorghum is an appropriate plant for Turkey's geography and the hay yield of 4713.2 kg/da is very high (Keskin et al. 2005). It is understood that sorghum is an important fiber source when compared with the hay yield (Table 1) obtained from grains cultivated depending on the geography of the countries, which have an important place in human and animal nutrition.

On the other hand, studies in Turkey on coniferous forest trees indicated that; the biomass increase in forest stands is 217.50 kg/da for red pines aged between 0 and 50 years (Durkaya et al. 2009), 90.13 kg/da for Calabrian pine (Durkaya et al. 2010a), and 115.33 kg/da for Crimean pine (Durkaya et al. 2010b). Compared to some forests, these species are important in our country's forest products industry, trees growing in Turkey, sorghum biomass yield is quite high.

In a study, firstly the pith of the sorghum stems was removed, and then the remaining rind was extracted. It has been stated that this part is an important fiber source for pulp production (Belayachi and Delmas, 1995). Therefore, the rind is a convenient raw material in the paper and pulp industry (Billa et al. 1997). It has been stated that sorghum stalks are suitable for pulp production by soda (Gençer and Şahin, 2015) and kraft (Gençer and Hatıl, 2019) methods. suitable for pulp production by the deep eutectic solvent and, the pulp comparable to those of the soda and kraft pulps (Gülsoy et al. 2022).

The aim of this study was to investigate the different parts of the sorghum stalks and also to determine their anatomical and chemical properties by height. Based on its chemical and anatomical properties, it is aimed to determine whether different parts of the plant are technically and economically suitable for pulp production. For this purpose, we divided the sorghum stalks into three equal parts fine end (F), medium (M), and bottom end (B), and examined the technical and economic suitability of each part for pulp production.

METHODOLOGY

Sweet sorghum (*Sorghum bicolor* x *S. bicolor* var. *sudanense)*, was planted in Bartın. The plant stalks were harvested and dried on the semi-open porch by means of sunlight. After drying, stalks are cut into three equal portions. The portions of sorghum stalks are named fine end (F), medium (M), and bottom end (B). Then the portions of the sorghum stalks are cut into 5 cm sizes.

Sorghum samples were macerated by the chloride method (Wise and Jahn, 1952), and the preparations were evaluated from the aspect of their fiber lengths, fiber width, and lumen width by their measurement with a light microscope. For the chemical analysis, sorghum samples were ground in a Wiley mill according to the TAPPI T 11 os-75 (1975) standard and sieved; the samples that remained on the 60-mesh sieve were used for chemical analysis. Determination of alcohol solubility TAPPI T 204 cm-97 (1997) chemical components of the sorghum, *i.e.*, α-cellulose (Han and Rowell, 1997), holocellulose (Browning, 1967), and lignin TAPPI T 222 om-02 (2002) standards were used. Determining cold and hot water solubility TAPPI T 207 cm-99 (1999) standard was used.

RESULT AND DISCUSSION

Chemical analysis results of different parts of sorghum stalks are given in Table 2. When chemical properties of the fine end (F) of the sorghum stalks, presented in Table 2, it can be seen that holocellulose (H:79.0%) and α-cellulose (α-C:45.2%) contents are higher than that of other portions (M and B). This value was close to the holocellulose ratio of *Acer campestre* (78.53%) (Alkan, 2004), and the ratio of lignin was about 16%, which was close to the lignin value of Holm oak (16.3%) (Alaejos et al .2008). Alcohol solubility (AS:25.3%) hot water solubility (HWS:29.2%) and cold water solubility (CWS:27.2%) values of sorghum bottom end (B) are higher than that of other portions (F and M). Therefore, these ratios are decreasing from root (B) to end (F). This indicates that the lignification at the end (F) of the plant is less than the other parts. According to these results, the fine parts (F) of the sorghum stalk will be converted into pulp more easily than the other parts. This means less energy, less time, and less chemical use. The average value of the lignin content of wood species is around 20-25% (Rydholm, 1965). While water-soluble sugar is high in the pith, the rind is richer in lignin and fiber (Billa et al. 1997), Belayachi and Delmas (1995) found the holocellulose and lignin content in depitced sorghum samples to be 69.0% and 16.1%, respectively. Accordingly, different parts of sorghum stem are a more economical raw material than wood.

Table 2. Chemical properties of different parts of sorghum stalks.

Statistical properties↓	CP→ (%)	H	α-C	L	AS	HWS	CWS
Mean	F	79.0	45.2	14.9	14.0	18.3	15.9
	M	77.2	37.3	14.5	18.0	21.0	18.1
	B	77.3	39.4	13.8	25.3	29.2	27.2
Maximum	F	79.4	45.3	14.9	14.3	18.8	16.2
	M	77.4	37.8	14.6	18.4	21.3	18.2
	B	78.0	40.3	14.2	25.6	29.5	27.8
Minimum	F	78.7	45.2	14.9	14.1	17.6	15.5
	M	77.0	37.0	14.4	17.7	20.8	17.9
	B	77.4	38.9	13.3	24.8	28.9	27.6
Standard deviation	F	0.37	0.03	0.02	0.02	0.61	0.34
	M	0.25	0.41	0.06	0.32	0.26	0.13
	B	0.65	0.78	0.53	0.3	0.26	0.12
Coefficient of variation	F	0.47	0.08	0.20	0.20	0.34	0.90
	M	0.32	1.01	0.43	1.6	1.27	0.71
	B	0.83	2.0	3.80	1.7	0.90	0.45

CP: Chemical properties, H: Holocellulose, α-C: alfa-cellulose, L: Lignin, AS: Alcohol solubility, HWS: Hot water solubility, CWS: Coldwater solubility, S: Sucrose

Fiber characteristics such as fiber length, fiber width, and lumen width of different parts of sorghum stalks are given in Table 3.

Table 3. Fiber characteristics of different parts of sorghum stalks.

Statistical properties↓	MP→ (µm)	FL	FW	LW
Mean	F	863	10.64	2.50
	M	913	11.30	2.71
	B	1107	11.52	2.87
Maximum	F	1309	7.50	10.0
	M	1500	20.0	10.0
	B	1500	22.50	10.0
Minimum	F	550	7.50	1.25
	M	610	5.0	1.25
	B	700	7.50	1.25
Standard deviation	F	258	3.10	1.75
	M	264	3.42	2.71
	B	311	3.11	1.99
Coefficient of variation	F	29.9	29.1	29.3
	M	28.9	30.33	3.21
	B	28.1	26.99	0.69

MP: Morphologic properties, FL: Fiber length, FW: Fiber width, LW: Lumen width

Morphologic properties of the lignocellulosic material play a determinative role in the distinctive of the panel and paper to be produced. Table 3 presents morphological characteristics of different parts of sorghum stalks. The average fiber lengths of F, M, and B portions of sorghum stalks are 863, 913, and 1107 µm, respectively. The average fiber widths of F, M, and B portions of sorghum stalks are 10.64 µm, 11.30 µm, and 11.52 µm, respectively. The average lumen width of A, B, and C portions of sorghum stalks are 2.50 µm, 2.71 µm, and 2.87 µm, respectively. Also, the fiber length decreased from the bottom end of the stems to the fine end.

Gülsoy and Şimşir found fiber lengths fiber widths and lumen width values of 1250 µm, 24.00 µm, and 10.30 µm, respectively in fern stems (Gülsoy and Şimşir, 2018). Gülsoy and Uysal (2020) found that fiber lengths fiber widths and lumen width values of European aspen were 1180 µm, 24.25 µm, and 10.50 µm, respectively. Length of the fibers in cotton stalks were 1010 µm (Gençer et al. 2001), 1150 µm in rye straw (Usta and Eroğlu, 1987), 740 µm in wheat straw (Deniz et al. 2004) and, kiwi stem 1500 µm (Yaman and Gencer, 2005). In the examination of the morphological characteristics of fruit trees, the fiber length of fig and olive woods was found to be 830 µm (Odabaş Serin and Kılıç Penezoğlu, 2020a; Odabaş Serin and Kılıç Penezoğlu, 2020b). It has been stated that this value is 1100 in olive, 1160 in loquat wood (Topaloğlu et al. 2019), and 1200 µm in alder wood (Tırak Hızal and Erdin, 2016).

The fiber length in the leaves of sweet sorghum was measured as 1380 µm. The maximum fiber lengths of F, M, and B portions of sorghum stalks are 1309 µm, 1500 µm, and 1500 µm, respectively. It can be stated that sorghum fibers are suitable for pulp production. In general, the average length of the fibers of hardwoods is a little more than 1 mm (Suchsland and Woodson, 1986). The fiber length with a mean between 900 and 1600 µm is considered a "medium length" (IAWA, 1989). As can be seen in Table 2 sorghum fine end (F) fiber length is lower than "medium length". On the other hand, medium (M) and bottom (B) part fibers mean sorghum stalks are included in "medium length".

CONCLUSION

This study was carried out to propose a solution to the raw material problems experienced in the pulp industry. As a raw material, sorghum plant was used as a substitute for wood raw material in pulp production. For this reason, it is to determine whether there is a chemical and morphological difference from the bottom (B) end to the fine (F) end of the sorghum stems and whether the sorghum stem fibers are suitable for pulp production.

Three main problems of the paper industry today;

1. Raw material supply: This problem is that timber logs cannot be used in the pulp industry because they are expensive. In order to solve this problem, private enterprises can both make a profit for themselves and contribute to the production of raw materials by supporting the afforestation of empty areas with fast-growing species. In addition, the utilization of residual fibrous raw materials in agricultural areas or the production of plants such as hemp, reed, and sorghum, which are direct sources of fibrous raw materials, should be encouraged and benefit from agricultural support.

2. Energy cost: A decrease in energy consumption will reduce the cost per unit. Since the cooking time is shorter in pulp production from annual plants, the cost per unit of pulp will decrease. The low lignin ratio is an advantage in terms of chemical substance consumption and energy consumption in the delignification process in pulp production by chemical methods. With these properties, sorghum steam is suitable for pulp production by chemical methods.

3. Environmental pollution: The use of annual plants in reducing environmental pollution reduces the rate of chemicals to be used. Because the chemical substance used in converting annual plants into pulp, which is easier to cook than wood, is also decreasing.

Sorghum stalk has a high α-cellulose ratio and a low lignin ratio, hence it can easily be used in an alternative raw material pulping process.

Sorghum fine end fibers (F) are short and thin-walled cells. Thin-walled fibers can collapse easily. Then they should give high bonding areas and a smooth surface on the paper. Therefore, fibers of the fine end (F), which are short fibers, are found suitable for the production of writing and printing paper. Sorghum middle (M) end and bottom (B) end fibers have medium fiber length. On the other hand, these fibers give high mechanical resistance in paper production.

The fine end (F) of the sorghum stalk has more α-cellulose. In the case of pulping, the fine end (F) of the sorghum stalk has a higher yield than other portions. The main target of chemical pulping is to remove lignin located in the middle lamella. The bottom end (B) of the sorghum stalk has less lignin than other portions. Consequently, it can be easily delignification in the chemical pulping process than other in portions.

The fiber length of the fine (F) of the sorghum stems is similar to the fibers of fig and olive woods, the fiber length of the middle (M) part is similar to the fiber lengths of European poplar, and the bottom (B) part of the fiber lengths of loquat, alder and olive woods. Therefore, it can be a substitute fiber source to these wood species in pulp production.

According to the chemical and morphological findings obtained from sorghum stem parts, it can be used as a substitute raw material in the raw material shortage that may occur in the paper pulp industry. In addition, the fact that the stem of the sorghum plant can be fibrous more easily than wood and it is more environmentally friendly also stands out in the search for alternative fiber sources. Based on these data, the stem of the sorghum plant is technically and economically suitable for pulp production. For this reason, it is important to grow plants with a very high hay yield per unit area, such as sorghum, instead of the crops cultivated for vital needs in Table 1.

In addition, in this study, the raw material sources that are similar to the chemical and morphological properties of sorghum stalk and suitable for paper production were selected in the literature search. Compared to these sources, sorghum stalk is in a position to compete in terms of paper pulp production by chemical methods.

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Chapter 2

EFFECT OF STEM HEIGHT ON THE CHEMICAL COMPOSITION OF WOOD: A LITERATURE REVIEW

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INTRODUCTION

Wood chemical composition depends on tree species, tree age, radial and longitudinal location at the stem, climatic, and environmental conditions (Smook, 1992). In chemical terms, wood is defined as a three-dimensional biopolymer composite consisting of an interconnected network of cellulose, hemicelluloses, and lignin, and small amounts of inorganics and extractives. Generally, softwoods (coniferous species) have higher cellulose content (40-45%), higher lignin (26-34%), and lower pentosan (7-14%) content as compared to hardwoods (deciduous species) (cellulose 38-49%, lignin 23-30%, and pentosans 19-26%) (Rowell, 2005). The odor, strength, color, taste, hygroscopicity, density, and decay resistance of woods depending on the ratio of wood components (Panshin and de Zeeuw, 1980).

Holocellulose is the total amount of polysaccharides in extractive-free wood. It contains cellulose, hemicelluloses, and minor amounts of other sugar polymers (pectin and starch) (Rowell et al. 2005). The main constituent of the woody cell wall is cellulose which is located mainly in the secondary cell wall. Cellulose is a homopolysaccharide and it is composed of β-D-glucopyranose units linked together by (1-4)-glycosidic bonds. Cellulose imparts high tensile strength and is not soluble in most solvents owing to strong hydrogen bonding and its molecular structure. In contrast to homopolysaccharide cellulose, hemicelluloses are heteropolysaccharides (Sjöström, 1993). Hemicelluloses are contributed to the structural components of wood by acting as supporting material in the cell wall (Rowell et al. 2005). Hemicelluloses from softwoods and hardwoods are different. In hardwoods, the predominant hemicellulose is xylan, with a small proportion of glucomannan. In softwoods, the main hemicellulose is galactoglucomannan. Softwoods contain only a tiny amount of xylan (Teleman, 2009). Hardwoods generally have higher hemicellulose content than softwoods. The molecular chains of hemicelluloses are branched and shorter than those in cellulose. (Fengel and Wegener, 1989).

Lignin, another component of the cell wall, is a three-dimensional hydrophobic polymer that fixes cellulose microfibrils and hemicelluloses together, thus giving the cell wall its “woody” properties. Lignin is polymerized from three phenyl-propane monomers (C9 units) called monolignols, namely p-coumaryl alcohol, sinapyl alcohol, and coniferyl alcohol (Henriksson, 2009). The three main types of lignin are characterized by differences in the degree of methoxyl substitution in C3 and C5 (Pereira et al. 2003). Lignin protects against pathogenic attacks (Raychaudhuri and Behera, 2022). In addition, lignin gives rigidity to the cell wall as it contains a higher proportion of carbon than cellulose and hemicelluloses (Meshitsuka and Isogai, 1996; Liu et al. 2017).

The term *extractives* cover the chemical compounds that can be extracted from wood with various polar or non-polar solvents. They are low molecular weight organic substances that are not components of the cell wall matrix and are responsible for color, odor, and resistance to fungi, insects, and marine borers (Panshin and de Zeeuw, 1980; Fengel and Wegener, 1989). The synthesis and accumulation of these protective compounds are carried out by living parenchyma cells, especially the ray parenchyma, during heartwood formation. Also, extractives represent a small proportion of wood below 10%, excluding tropical woods where this value may be higher. Although usually low amounts in a single species, extractives can contain hundreds of different molecules (Pereira et al. 2003). The lipophilic part of the extractives is often called wood resin. There are four main lipophilic compounds classes: steryl esters and sterols, fats and fatty acids, terpenoids including polyisoprenes and terpenes, and waxes (Jansson and Nilvebrant, 2009). Wood resin is a source of value-added chemicals. The basis of the turpentine industry is terpenes. The resin and fatty acids of many tree species cooked by the kraft pulping process are recovered in the tall oil and they are separated into pure fractions (Mutton, 1962). The composition of a water extract is very different from that of a hexane extract (Jansson and Nilvebrant, 2009). Cold-water removes gums, tannins, sugars, and coloring matter in the wood, hot-water also removes starches (TAPPI T 207, 2008). On the other hand, 1% NaOH removes the lignin, hemicelluloses, fatty acids, resins, waxes, and essential oils (Chow et al. 2008).

Ash is the inorganic part of the wood and is determined by incinerating (at 575 °C) of organic matter. Inorganic materials make up 0.1% to 0.5% of the oven-dry weight of wood in temperature zones and up to 3-4% in tropical woods. The main components of wood ash are calcium (Ca), sodium (Na), potassium (K), magnesium (Mg), silica (SiO_2), iron (Fe), and phosphate (PO_4) (Al-Mefarrej et al. 2011).

Knowing the chemical components of wood contributes to selecting wood for specific uses. Different types of wood (i.e., compression wood, tension wood, and heartwood) will behave according to their particular chemical properties in the pulping process. The availability and extent of chemical components are essential factors in determining the pulp quality of a wood variety. Compression wood is a poor quality source of pulpwood material due to lower pulp yield and degrees of delignification due to the higher lignin content (Pereira et al. 2003). High lignin content requires more pulping chemicals for delignification and produces weak fiber bonding (Casey, 1960). Also, it increases pulp beating time and hence energy consumption of the paper mill (Gulsoy and Eroglu, 2011). On the contrary, tension wood has a high cellulose content and is desirable for pulp yield and pulp brightness. On the other hand, the heartwood is more difficult to impregnate with pulping liquors due to its low permeability, resulting in more significant amounts of screened pulp rejects (Pereira et al. 2003). Heartwood has higher extractive content than sapwood (Gülsoy et al., 2021). The secondary wood component extractives cause problems during paper production, such as pitch problems, difficult bleaching, and brightness reversion (Pereira et al. 2003). As another secondary wood component, ash is considered undesirable in most industrial processes (Al-Mefarrej et al. 2011). Heartwood, sapwood, juvenile wood, mature wood, base wood, top wood, reaction wood, branch wood, and stem wood have different chemical structures. These differences are one of the most important factors affecting the use of wood as a final product. Therefore, this review covers a detailed summary of wood chemical composition differences along with SH of several tree species.

EFFECT OF SH ON WOOD CHEMICAL COMPOSITION OF WOOD

Many studies have been conducted on the effect of SH on the wood chemical composition of hardwood and softwood species. The results of some of these are summarized below in chronological order.

Cartwright (1941) examined the effect of SH on hot-water-soluble extractive content of western red cedar (*Thuja plicata* D. Don.) heartwood samples. They revealed that hot-water-soluble extractive content had negatively correlated with SH For example, the hot-water-soluble extractive content of outer heartwood samples was 8.31% at the bottom, 6.72% at the middle, and 4.19% at the top samples.

Nylinder and Hägglund (1954) examined the effect of sampling position (25%, 50%, and 75%) in the tree stem on the chemical composition of Norway spruce (*Picea abies* (L.) Karst.) wood. Klason lignin content was slightly decreased with increasing sampling position. It was found as 27.41% at 25% sampling position, 27.39% at 50% sampling position, 27.25% at 75% sampling position. Pentosan content was positively correlated with sampling position. It was determined as 7.51% at 25% sampling position, 7.55% at 50% sampling position, 7.87% at 75% sampling position. They found that ethyl ether-acetone-soluble extractive content of Norway spruce wood was increased with increasing sampling position. It was determined as 1.13% at 25% sampling position, 1.16% at 50% sampling position, 1.39% at 75% sampling position. The authors reported that the ash ratio of Norway spruce wood was slightly increased with increasing sampling position. Ash content was determined as 0.22% at 25% sampling position, 0.23% at 50% sampling position, 0.25% at 75% sampling position.

Uprichard (1963) studied the variation of extractive content with

SH of European larch (*Larix decidua* Mill.) and Japanese larch (*Larix leptolepis* Gordon). Wood samples were obtained from 1.0 feet to 74 feet of SH for European larch and from 1.0 feet to 84 feet of SH for Japanese larch. Methanol-soluble extractive content in both heartwood and sapwood negatively correlated with SH. In European larch wood samples, total extractive contents at 1 foot, 4.5 feet, 25 feet, 47 feet, 60 feet, and 74 feet of SH were 8.50%, 5.55%, 3.97%, 4.97%, 9.04%, and 8.03%, respectively. In Japanese larch wood samples, total extractive contents were 6.83% at 1 foot, 5.48% at 9 feet, 4.17% at 25 feet, 3.63% at 47 feet, 3.82% at 70 feet, and 3.20% at 84 feet.

Harris (1973) aimed to determine the variation of methanol-soluble extractive content with SH of heartwood and sapwood of lodgepole pine (*Pinus contorta* Dougl. ex Loud.). Wood samples were obtained from the butt, breast height, 5th, 10th, 15^{th,} and 20th internodes of the stem. Methanol-soluble extractive content in both heartwood and sapwood negatively correlated with SH. In heartwood samples, methanol-soluble extractive contents at the butt, breast height, 5th, 10th, and 15th internodes of the stem were 8.4%, 5.9%, 5.5%, 3.9%, and 2.8%, respectively. In sapwood samples, methanol-soluble extractive contents were 2.7% at the butt, 2.3% at breast height, 2.2% at 5th internodes, 2.1% at 10th internodes, 2.0% at 15th internodes, and 2.2% at 20th internodes. On the other hand, Chawla and Shanker (1974) revealed that hot-water solubility decreased with increasing sampling height in swamp mahogany (*Eucalyptus robusta* Sm.), and alcohol-benzene solubility showed an opposite trend.

Unkalkar et al. (1975) evaluated the influence of SH on wood components of *Eucalyptus hybrid* grown in India. Holocellulose, α-cellulose, and pentosan content had a positive correlation with SH. However, klason lignin content had a negative correlation. Holocellulose and α-cellulose contents were 72.6% and 38.6% at the bottom, 78.9% and 41.8% at the middle, and 80.4% and 41.8% at the top, respectively. The stem's bottom, middle, and top pentosan contents were 12.5%, 13.9%, and 15.8%, respectively. Klason lignin content at the stem's bottom, middle, and the top was 25.2%, 23.6%, and 23.0%, respectively. The highest 1% NaOH solubility was observed in the bottom part, followed by the stem's top and middle parts. The water (cold and hot) and alcohol-benzene solubility values were decreased from bottom to top. These results can be attributed to the negative correlation between SH and heartwood content. The authors noted that the heartwood ratio was found to be 40.5% at the bottom and 18.4% at the middle. There was no heartwood at the top position. Similar results were reported in *Eucalyptus urograndis* by Gominho et al. (2001). The brightness (Elrepho) of the wood meal at the stem's bottom, middle, and the top was determined as 25.0%, 33.2%, and 39.0%, respectively.

Wood brightness and color depending on the extractive content and the heartwood ratio. Ash content was significantly affected by SH. The highest (0.60%) and lowest (0.45%) ash content values were determined in wood samples at the top and middle of SH levels, respectively.

Krutul and Buzak (1986) found that alcohol-benzene-soluble extractives in sessile oak (*Quercus petraea* Lieb.) and Scots pine (*Pinus sylvestris* L.) were higher at the 6 m and 10 m SH of a tree than at 2 m. Stringer and Olson (1987) studied the relationship between SH and wood solubility values of black locust (*Robinia pseudoacacia* L.) located on Cumberland Mountain and Cumberland Plateau in Kentucky of USA. The authors noted that hot-water solubility values at 0%, 20%, 40%, 60%, and 80% of total tree height were 2.7%, 2.7%, 2.7%, 3.5% 3.0%, respectively. It was determined that except for 3.0% of these values, the others did not contain a statistical difference. Alcohol-benzene solubility values at 0%, 20%, 40%, 60%, and 80% of total tree height were 3.7%, 3.4%, 3.3%, 2.8%, and 2.7%, respectively. They also determined that ash content was 0.56% at 0% SH, 0.60% at 20% SH, 0.62% at 40% SH, 0.84% at 60% SH, and 0.87% at 80% SH.

Kasir and Al-Haialy (1987) studied the effect of three plantation regions (Ksiba, Noriya, and Dibis) on the holocellulose and lignin content and their variations throughout the stems of Australian pine (*Casuarina equisetifolia* Forst.) located in Iraq. They noted that the lignin content had high values at the lower positions of the stem and low values at the higher positions, while the holocellulose content had the opposite trend. Ethanol-benzene and 1% NaOH solubility of Australian pine grown in Iraq were higher at the lower parts of the stem than those of the upper parts.

Keith and Chauret (1988) examined the wood chemical composition at different SHs (breast height and 20% SH) of European larch (*Larix decidua* Mill.) located in Harrington (site A) and Petawawa (site B) stands of Quebec, Canada. The highest klason lignin contents at sites A and B were 29.54% at breast height and 27.74% at 20% SH, respectively. According to their results, hot-water and alcohol-benzene-soluble extractive contents in sites A and B were higher at breast height samples than those of 20% SH samples. However, these differences were statistically insignificant.

Voipio (1990) aimed to determine the effect of SH (20% and 80% of SH) on wood chemical components of several tree species from Kannus in the Ostrobothnia region of Finland. The studied tree species were Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* (L.) Karst.), European white birch (*Betula pendula* Roth), downy birch (*Betula pubescens* Ehrh.), European aspen (*Populus tremula* L.), grey alder (*Alnus incana* (L.) Moench.), and black alder (*Alnus glutinosa* (L.) Gaertn.). The author noted that glucose content in all studied tree species was decreased with increasing SH. The klason lignin content of these species had a linear correlation with SH level except for European aspen. Klason lignin content of black alder and grey alder was 21.0% and 21.0% at 20% SH and 22.1% and 23.5% at 80% SH, respectively. In European white birch and downy birch, the klason lignin content was 21.6% and 18.8% at 20% stem and 22.2% 19.8% at 80% SH, respectively. Klason lignin content of European aspen was 20.1% at 20% SH and 19.8% at 80% SH. Klason lignin content of Scots pine and Norway spruce was 25.5% and 27.8% at 20% SH and 27.0%, and 28.2% at 80% SH. The author reported that the total extractive content of species had a positive correlation with SH level. Total extractive content at 20% and 40% SH was 4.8% and 5.5% for black alder, 4.4% and 7.5% for grey alder, 4.2% and 5.8% for European white birch, 4.4% and 5.8% for downy birch, 3.2% and 4.5% for European aspen, 5.0% and 5.6% for Scots pine, and 3.5% and 5.4% for Norway spruce, respectively. The author reported that ash content positively correlated with SH except for Scots pine. Ash content at 20% and 40% SH was 0.3% and 0.4% for black alder, 0.4% and 0.6% for grey alder, 0.3% and 0.4% for European white birch, 0.3% and 0.4% for downy birch, 0.4% and 0.5% for European aspen, 0.3% and 0.3% for Scots pine, and 0.3% and 0.5% for Norway spruce, respectively.

Campbell et al. (1990) investigated the chemical variation in two varieties (*latifolia* and *murrayana*) of lodgepole pine (*Pinus contorta* Dougl. ex Loud.) collected from Missoula, Montana, USA. The holocellulose content of both varieties had a positive correlation (r = 0.48) with SH level. As known, juvenile wood has a high content of hemicelluloses and lignin and a low cellulose content compared to mature wood (Panshin and de Zeeuw, 1980). The authors claimed that this result could be attributed to the higher proportion of hemicellulose in the tree's juvenile wood at the top part. Conversely, the α-cellulose ratio of both *latifolia* (r = -0.51) and *murrayana* (r = -0.34) negatively correlated with SH level. They asserted that this result is probably owing to the higher ratio of slow-grown mature wood at the tree base. Koch (1987) noted that the specific gravity of wood decreased with increasing SH. In addition, cellulose forms the thicker secondary walls of mature wood cells at the base part of the tree (Riyaphan et al. 2015). Therefore, the α-cellulose content also decreased with increasing SH. The klason lignin content of both *latifolia* (r = 0.53) and *murrayana* (r = 0.43) showed an increasing trend from the base to the top of the tree. This rising trend in klason lignin could be ascribed to the higher proportion of juvenile wood at the top part of the stem. Juvenile wood had higher lignin than mature wood (Hodge and Woodbridge, 2004; Akgül and Tozluoğlu, 2009; Luo et al. 2021). The ethanol-toluene solubility had a negative correlation with SH in both *latifolia* (r = -0.51) and *murrayana* (r = -0.39). They found that the variation in extractive content with SH and diameter class is closely related to the mature heartwood ratio in the stem. Ash content in the *latifolia* and *murrayana* varieties of lodgepole pine was positively correlated with SH. In the *murrayana* variety, ash content ranged from 0.17% at 0% SH to 0.27% at 80% SH. In the *latifolia* variety, ash content at 0% and 80% SH was 0.17% and 0.26%, respectively. They claimed that the positive correlation between ash content and SH is probably related to a higher proportion of juvenile wood and more frequent knots and bases of branches at the top of the tree trunk.

Kumar (1996) observed that the chemical composition varied significantly with sampling height in forest red gum (*Eucalyptus tereticornis* Sm.) grown in India. There was a positive relationship with sampling height for holocellulose content and a negative relationship with klason lignin content. The author found that holocellulose content was 67.57% at 0% SH, 70.34% at 30% SH, 72.64% at 60% at SH, and 72.64% at 90% SH. Klason lignin content values at ground level, 30%, 60%, and 90% of SH was 29.27%, 27.69%, 26.46%, and 25.95%, respectively. Also, they observed that the hot-water-soluble extractive content varied significantly with sampling height. There was a negative relationship with sampling height for hot-water-soluble extractive content. The author found that hot-water-soluble extractive content was 14.55% at ground level, 12.27% at 30% SH, 12.02% at 60% SH, and 11.59% at 90% SH. Cold-water and alcohol-soluble extractive contents were high at the ground level, decreased up to 60% SH, and then increased to 90% SH. Cold-water and alcohol-soluble extractive contents at ground level, 30%, 60%, and 90% of SH were 13.77% - 10.59, 11.37% - 9.28%, 10.67% - 9.20%, and 11.07% - 9.77%, respectively.

Sharma (1997) studied the wood chemical composition at four heights of commercial bole (ground level, 30%, 60%, and 90% of SH) of black locust (*Robinia pseudoacacia* L.) grown in India. The wood samples taken from different tree spacings (0.60 x 0.60 m, 0.90 x 0.90 m, and 1.20 x 1.20 m spacing). Results showed that the klason lignin content was negatively related to the SH of black locust, while holocellulose content had a positive relationship with different height levels. In the 1.20 x 1.20 m spacing, holocellulose content was 63.22% at ground level, 64.96% at 30% SH, 68.00% at 60% SH, and 68.14% at 90% SH. Klason lignin content values at ground level, 30%, 60%, and 90% SH were 27.20%, 26.77%, 24.97%, and 22.60%, respectively. Similar trends were found for 0.60 x 0.60 m spacing and 0.90 x 0.90 m spacing. In addition, they revealed that all solubility values had a negative correlation with the SH of black locust. In the 1.20 x 1.20 m spacing, hot-water and cold-water solubility values were 6.22% - 5.51% at ground level, 4.94% - 4.43% at 30% SH, 4.13% - 3.52% at 60% SH, and 4.03% - 3.75% at 90% SH, respectively. Alcohol-benzene solubility values at ground level, 30%, 60%, and 90% SH were 4.17%, 3.81%, 3.10%, and 2.90%, respectively. Similar trends were seen in the 0.60 x 0.60 m spacing and the 0.90 x 0.90 m spacing. The trend in the solubility values can be ascribed to the high heartwood ratio of the bottom part of the stem.

Carvalho (2000) studied the chemical composition at the base and 4 m of SH of hybrid eucalyptus (*Eucalyptus urograndis* (*Eucalyptus grandis* x *Eucalyptus urophylla*)) wood grown in Brazil. He reported that the holocellulose and klason lignin contents were found as 74.10% and 22.20% at base and 73.76% and 22.59% at 4 m of SH, respectively. Also, he noted that the interaction between tree height and total extractive content was not significant (3.69% at base and 3.65% at 4 m of SH). In addition, Gominho et al. (2001) studied the total extractive content of heartwood and sapwood samples at different SH levels of hybrid eucalyptus (*Eucalyptus urograndis*) taken from Brazil. They found that total extractive content decreased from the base to the top in sapwood and heartwood samples. Total extractive content of heartwood samples was 8.99% at 5% SH, 8.01% at 25% SH, 6.60% at 35% SH, 6.11% at 55% SH, and 6.15% at 65% SH. In the sapwood samples, it was 4.64% at 5% SH, 3.71% at 25% SH, 3.15% at 35% SH, 3.03% at 55% SH, 2.69% at 65% SH, and 3.64% at 90% SH.

Orea-Igarza et al. (2004a) carried out an investigation on the effect of SH level on the chemical composition of red mahogany (*Eucalyptus pellita* F. Muell) at three different heights (25%, 55%, and 85% height level of the tree) of stem taken from the Forestry Company of Macurijes, in Pinar del Río province of Cuba. The results showed that variations in the axial direction were statistically significant for all the characteristics evaluated. The holocellulose content increased from 25% to 55% of tree height (from 78.70% to 80.68%) and decreased to 85% (from 80.68% to 78.70%). The cellulose contents at 25%, 55%, and 85% height levels of the tree were 40.91%, 43.19%, and 44.85%, respectively. There was a negative correlation between lignin content and SH level. Their results also showed that the toluene-ethanol (2:1), hot-water, and 1% NaOH solubility variations in the axial direction were statistically insignificant.

Orea-Igarza et al. (2004b) aimed to determine the relationship between wood chemical composition and SH level (25%, 55%, and 85%) of blue gum (*Eucalyptus saligna* Sm.) grown in Pinar del Río province of Cuba. They found that holocellulose content at 25%, 55%, and 85% height levels of the tree was 75.15%, 74.65%, and 71.50%, respectively. The effect of SH on cellulose and hemicelluloses content was statistically insignificant. They also revealed that lignin content at 25%, 55%, and 85% height levels of the tree was 24.90%, 25.40%, and 28.50%, respectively. Their results also showed that toluene-ethanol (2:1) solubility at 25%, 55%, and 85% height levels of the tree was 3.44%, 4.05%, and 8.58%, respectively. They also reported hot-water solubility values at 25%, 55%, and 85% height levels of the tree were 6.93%, 6.71%, and 5.86%, respectively. The 1% NaOH solubility values showed an increasing trend with SH (21.22%, 26.33%, and 30.23%). In addition, ash content was significantly affected by SH. The highest (0.30%) and lowest (0.23%) ash content values were determined in wood samples at 85% and 55% SH levels, respectively.

Carballo-Abreu et al. (2004) studied the wood chemical composition of lemon-scented gum (*Corymbia citriodora* Hook.) at three different heights (25%, 55%, and 85% height level of the tree) of commercial bole. The samples were taken from the Macurije region in Cuba's Pinar del Río province. The holocellulose content decreased from 25% to 55% of tree height (from 81.73% to 80.29%) and increased to 85% (from 80.29% to 82.61%). The opposite trend was observed in the lignin content (18.30%, 19.70%, and 17.40%). They also reported that syringyl -guaiacyl lignins differed in the different parts of the tree. The lignin in the higher part of the tree is less cross-linked than in other parts. The cellulose and hemicelluloses variations in the axial direction were statistically insignificant. In addition, the toluene-ethanol (2:1) solubility decreased from 25% to 55% of tree height (from 3.48% to 1.38%) and increased to 85% tree height (from 1.38% to 2.02%). The same trend was observed in hot-water solubility (4.18%, 1.62%, and 2.50%). They also noted a significant positive correlation between 1% NaOH solubility and SH level. In addition, it evaluated the ash content of lemon-scented gum (Carballo-Abreu et al. 2004) and red mahogany (Orea-Igarza et al. 2004a) at 25%, 55%, and 85% SH levels of the tree grown in Pinar del Río province of Cuba. The results showed that the effect of SH level on the ash content of both species was statistically insignificant.

Shanqing and Jianju (2004) studied wood chemical components of *Mytilania laosensis* and their variation along tree stem. The results showed that the differences in the cold-water extractives and holocellulose content at different heights along the tree stem were statistically insignificant. However, the contents of hot-water extractives, 1% NaOH extractives, cellulose, and lignin varied significantly along the tree stem. Hot-water extractives were low in the middle section but higher at the two ends. Cold-water extractives, 1% NaOH extractives, and lignin content tended to decrease with increasing SH, and holocellulose content increased. In addition, cellulose content was higher in the middle section than in the bottom and top sections.

Kostiainen et al. (2004) studied the effect of SH (breast height, 40%

SH, and top of stem) on the chemical composition of Norway spruce (*Picea abies* (L.) Karst.) at Flakaliden, Sweden. They noted that klason lignin and acid-soluble lignin ratio were lower at breast height and 40% of SH than at the top section of the stem. The α-cellulose ratio had an opposite tendency. The ratio of hemicelluloses decreased up to 40% SH and then increased to the top section of the stem. The authors also reported that acetone-soluble extractive ratios at breast height (1.98%) and 40% of SH (2.00%) were lower than at the top section of the stem (2.38%).

Adamopoulos et al. (2005) analyzed the variations in the chemical structure of sapwood and heartwood from the bottom, middle, and top of the stem of 35 to 37-year-old black locust (*Robinia pseudoacacia* L.). In the heartwood sample, lignin content at the bottom, middle, and top of SH was 25.73%, 20.03%, and 18.33%, respectively. In the sapwood sample, lignin content increased from the bottom to the middle of tree height (from 18.13% to 21.42%) and decreased to the top of tree height (from 21.42% to 19.64%). In the heartwood sample, hot-water solubility at the bottom, middle, and top of SH was 8.7%, 8.7%, and 9.8%, respectively. Hot-water solubility of heartwood samples decreased from the bottom to the middle of tree height (from 5.5% to 4.7%) and increased to the top of tree height (from 4.7% to 5.0%). The dichloromethane solubility variations of the heartwood sample in the axial direction were statistically insignificant. In the sapwood sample, dichloromethane solubility had a positive correlation with SH. They also reported a linear correlation between SH and ash content of sapwood and heartwood from the bottom, middle, and top of the stem of the black locust.

Silva et al. (2005) studied the axial variation of the wood chemical composition of rose gum (*Eucalyptus grandis* Hill ex. Maiden) located in Paraná of Brazil and reported that the highest holocellulose content was found at the top portion (70.13%), followed by middle (69.61%), and base portion (66.34%). They also noted that total lignin content was 28.59% at the base, 26.71% at the middle, and 26.41% at the top. They also noted that the highest total extractive content was found in the base portion (5.11%), followed by the middle (3.68%) and top portion (3.46%).

Olmos (2005) studied the holocellulose, α-cellulose, klason lignin content, and alcohol-benzene solubility values at different sampling heights (0.9 m, 8.9 m, 16.3 m, and 21.3 m) of the sapwood and the heartwood samples of Tasmanian blue gum (*Eucalyptus globulus* Labill.). Tasmanian blue gum is grown in the Santa Juana region of Chile. The author noted that the holocellulose content of the sapwood sample was 82.78% in 0.9 m, 83.09% in 8.9 m, 82.81% in 16.3 m, and 83.07% in 21.3 m. In the heartwood sample, it was 82.94% in 0.9 m and 83.08% in 8.9 m. α-cellulose content of both sapwood and heartwood samples negatively correlated with SH. She also reported that the klason lignin content of the sapwood sample was 17.51% in 0.9 m, 16.35% in 8.9 m, 17.78% in 16.3 m, and 17.92% in 21.3 m. In the heartwood sample, it was 20.37% in 0.9 m and 19.38% in 8.9 m. In the sapwood sample, alcohol-benzene solubility values were 1.15% in 0.9 m, 1.44% in 8.9 m, 1.67% in 16.3 m, and 2.27% in 21.3 m. The heartwood sample had 3.88% in 0.9 m and 2.84% in 8.9 m.

Carrasco (2005) studied the wood chemical composition of alpine ash (*Eucalyptus delegatensis* RT Baker) and determined the effect of SH on wood chemical composition. They revealed that holocellulose content had a positive correlation with SH. However, klason lignin content had a negative correlation with SH. Holocellulose and pentosane contents were 60.0% - 18.6% at the bottom, 62.6% - 22.1% at the middle, and 62.9% - 21.7% at the top, respectively. Klason lignin content at the bottom, middle, and top wood samples was 26.3%, 24.9%, and 24.0%, respectively. The authors also noted that total extractive content was irregularly changed with increasing SH. Total extractive content was 4.8% at the bottom, 3.7% at the middle, and 6.0% at the top.

Bodîrlău et al. (2007) investigated the effect of SH on the chemical structure of common oak (*Quercus robur* L.) harvested from Iasi of Romania. Holocellulose ratio decreased from 1.3 m (72.21%) to 8.0 m (65.32%) of tree height and increased to 15.0 m (71.22%) of tree height. The highest and lowest cellulose ratios were observed in 8.0 m (43.26%) and 15 m (38.50%), respectively. The klason lignin ratio had a positive correlation with SH. In addition, hot-water, 1% NaOH-soluble extractives increased with increasing SH. Alcohol-benzene-soluble extractives decreased from 1.3 m (3.13%) to 8.0 m (2.87%) of tree height and increased to 15.0 m (3.39%) of tree height.

Abdel-Aal et al. (2008) have determined that the stem base of Australian beefwood (*Casuarina cunninghamiana* Miq.) had the highest cellulose content than breast height and 50% SH. The same trend was observed in the total extractive content. Hemicelluloses and ash content positively correlated with SH.

Nazri et al. (2009) observed the effect of SH on the chemical composition of lead tree (*Leucaena leucocephala* (Lam.) de Wit) wood and reported that holocellulose content had positively correlated with SH, while klason lignin content was negative. The highest holocellulose content was found at the top sample (76.25%), followed by the middle (75.16%) and base sample (73.38%). Klason lignin content at the base, middle, and top of SH was 24.67%, 23.33%, and 21.03%, respectively. This declining trend in the klason lignin can be attributed to higher earlywood content at top wood than base wood. The earlywood contains less lignin than latewood

(Panshin and de Zeeuw, 1980; Fengel and Wegener, 1989). Their results also indicated that all solubility values in the axial direction were increased from bottom to top of the tree. The ethanol-toluene solubility was 1.73% at the bottom, 1.76% at the middle, and 2.11% at the top. Cold-water and hot-water solubility values at the bottom, middle, and top parts of the tree were 4.44% and 5.48%, 5.01% and 6.68%, and 5.97% and 7.91%, respectively. They also found that 1% NaOH solubility was increased along with axial direction from the bottom (15.54%) to the top (17.73%). They claimed that these results are due to the active cells at the top parts of the tree. Most of the extractives are located in these cells. In addition, they found that ash content had a negative correlation with SH. The ash content was 0.87% at the bottom, 0.70% at the middle, and 0.63% at the top. This result could be attributed to lower heartwood content and lower density of top wood. The heartwood has a higher density than the sapwood, and it has more ash (Xia et al. 2018).

Yadama et al. (2009) examined the effect of SH on the chemical composition of Sitka spruce (*Picea sitchensis* (Bong.) Carr.) chosen from Alaska's Kenai Peninsula, USA. The ratios of cellulose and hemicelluloses positively correlated with SH, while klason lignin had an opposite correlation. Cellulose and klason lignin ratios at the bottom, the middle, and the top parts of SH were 37.0% - 28.1%, 37.6% - 27.3%, and 43.7% - 27.0%, respectively. In addition, the ratio of hemicelluloses was 18.0% at the bottom, 18.5% at the middle, and 22.0% at the top of SH. Their results also revealed that extractive content increased up to the middle of SH then decreased to the top of SH. Extractive content at the bottom, the middle, and the top parts of SH were 2.07%, 2.93%, and 2.13%, respectively.

Krutul et al. (2010) studied the effect of SH on the chemical composition of common oak (*Quercus robur* L.) grown in Mazovia-Podlasie region of Poland. The wood samples were taken from the bottom, middle, and top parts of the stem in the vertical direction. The wood samples in the radial direction were taken from the pith adjacent heartwood, heartwood, sapwood adjacent heartwood, and sapwood. The authors found that the cellulose content of sapwood and sapwood adjacent heartwood of common oak decreased with increasing SH. A linear correlation between cellulose content and SH was observed in pith adjacent heartwood. The cellulose content of heartwood was 48.1% at the bottom, 48.8% at the middle, and 48.2% at the top. They also noted that klason lignin in all parts of the cross-section had a positive correlation with SH. The highest and the lowest klason lignin contents were found at the top sample of pith adjacent heartwood with 23.5% and the bottom sample of sapwood with 21.8%, respectively. They also reported that the highest and the lowest alcohol-benzene solubility values were determined in the bottom sample of pith adjacent heartwood with 4.2% and the bottom sample of sapwood with 3.1%, respectively.

Al-Mefarrej et al. (2011) studied the chemical components at breast height, 25%, 50%, and 75% SH of the lead tree (*Leucaena leucocephala* (Lam.) de Wit) planted in King Saud University of Saudi Arabia. They found that cellulose content had negatively correlated with SH, while hemicelluloses and klason lignin contents had positively. The cellulose content of the lead tree was 47.67% at breast height, 46.34% at 25% SH, 45.34% at 50% SH, and 43.60% at 75% SH. The hemicelluloses and klason lignin contents at breast height, 25%, 50%, and 75% SH were 20.79 - 31.52%, 21.31% - 32.33%, 21.99% - 32.65%, and 22.65% - 33.74%, respectively. The authors also reported that extractive content had an increasing trend with SH. It was 8.03% at breast height, 8.17% at 25% SH, 8.47% at 50% SH, and 8.78% at 75% SH. Ash content was negatively correlated with SH. It was 2.60% at breast height, 2.57% at 25% SH, 2.21% at 50% SH, and 2.21% at 75% SH.

Arantes et al. (2011) evaluated total lignin and total extractive contents, along with their longitudinal variations, in wood from hybrid eucalyptus (*Eucalyptus urograndis* (*Eucalyptus grandis* x *Eucalyptus urophylla*)) located in the Minas Gerais State of Brazil. Longitudinal specimens were taken from the 2%, 10%, 30%, and 70% of log height levels and commercial height. They also determined the effect of diameter class (14.2 cm, 11.4 cm, and 8.1 cm) on the total klason lignin of wood samples. They determined that total lignin content at 14.2 cm diameter class was 31.60% in 2% SH, 32.29% in 10% SH, 30.05% in 30% SH, and 30.34 % in 70% SH. They reported that total lignin content at 2%, 10%, 30%, and 70% SH level of 11.4 cm diameter class was 30.51%, 31.34%, 29.55%, and 29.50%, respectively. The authors also revealed that total lignin content of 8.1 cm diameter class was 33.11% at 2% SH, 29.64% at 10% SH, 27.27% at 30% SH, and 28.86% at 70% SH. The authors also evaluated the effect of diameter class (14.2 cm, 11.4 cm, and 8.1 cm) on the total extractive of wood samples. They reported that the total extractive content at 2%, 10%, 30%, and 70% SH level of 14.2 cm diameter class was 3.90%, 2.98%, 2.49%, and 2.77%, respectively. They determined that the total extractive content at 11.4 cm diameter class was 3.69% in 2% SH, 3.07% in 10% SH, 2.45% in 30% SH, and 2.52 % in 70% SH. The authors also revealed that the total extractive content at 2%, 10%, 30%, and 70% SH level of 8.1 cm diameter class was 4.19%, 3.00%, 1.98%, and 1.79%, respectively.

Kumar et al. (2011) determined the ash content at different heights (0.15 m, breast height, and top of stem) of 2, 4, and 6 years-old samples of *Acacia auriculiformis* and Australian pine (*Casuarina equisetifolia* Forst.) acquired from the Mandya district of Karnataka in India. In all age groups of both species, ash content was recorded highest on top of the stem. The lowest ash content in all age groups of both species (except for two-year-old Australian pine) was observed in breast height samples. Ash content in 2 years-old Australian pine had a positive correlation with SH.

Rather (2012) aimed to determine the effect of SH and chemical components of forest red gum (*Eucalyptus tereticornis* Sm.) grown in India. He reported that while holocellulose content was increased with increasing SH, klason lignin was decreased. Holocellulose content and klason lignin content at 0%, 30%, 60%, and 90% of total SH were 66.13% and 31.15%, 67.66% and 29.43%, 69.88% and 27.45%, and 70.87% and 25.80%, respectively. The author also revealed that hot-water, cold-water, and alcohol-benzene solubility values negatively correlated with SH. Hot-water and cold-water content at 0%, 30%, 60%, and 90% of total SH were 15.92% and 12.04%, 10.00% and 10.24%, 9.17% and 9.21%, and 8.25% and 8.95%, respectively. He also noted that alcohol-benzene solubility was 9.15% at 0% SH, 8.21 % at 30% SH, 7.91% at 60% SH, and 7.33% at 90% SH.

Zaki et al. (2012) evaluated the effect of SH on the wood chemical composition of rubber tree (*Hevea brasiliensis* (Willd. ex A. Juss.) Müll. Arg.) clone RRIM 2009 and clone RRIM 2024. They reported that there was showed a decreasing trend in the holocellulose and α-cellulose content of the wood samples from bottom to top for both clones. However, there was an increasing trend in the klason lignin content of the wood samples. Holocellulose content of clone RRIM 2009 and clone RRIM 2024 was 58.93%-60.56% at the bottom, 57.71%-59.04% at the middle, and 56.34%-56.15% at the top, respectively. α-cellulose content of clone RRIM 2009 and clone RRIM 2024 was 39.75%-43.02% at the bottom, 38.54%-41.62% at the middle 36.09%-39.60% at the top, respectively. In addition, the authors noted that the klason lignin content of clone RRIM 2009 and clone RRIM 2024 was 16.90%-16.47% at the bottom, 17.35%-16.56% at the middle, and 17.64%-16.75% at the top, respectively. They also reported that both clones' hot-water, 1% NaOH, and alcohol-toluene solubility values were negatively correlated with SH. Hot-water solubility of both clones was slightly decreased with increasing SH, while alcohol-toluene and 1% NaOH solubility values were significantly decreased. The ash content of both clones had a negative correlation with SH. Ash content of clone RRIM 2009 was 0.85% at the bottom, 0.82% at the middle, and 0.73% at the top. In the clone RRIM 2024, ash content was 0.71% at the bottom, 0.69% at the middle, and 0.68% at the top.

Gonçalves and Lelis (2012) noted that cyclohexane solubility at 0%, 25%, 50%, 75%, and 100% SH of brown salwood (*Acacia mangium* Willd.) was 1.71%, 1.79%, 1.43%, 1.61%, and 0.43%, respectively. In addition, Oliveira et al. (2012) noted that ethanol-cyclohexane solubility and ash content of flowering yellow-ipe (*Handroanthus vellosoi* (Toledo) Matos) taken from trees planted in 1986 at the Estação Experimental de Luiz Antonio in Brazil was 3.53% in base, 3.73% in 1 m, and 3.19% in 2 m. They also noted that ash content was 0.60% in base, 0.61% in 1m, and 0.80% in 2m. Also, Neverova et al. (2013) examined the distribution of extractive substances along with the stem length of the Siberian larch (*Larix sibirica* Ledeb.). They reported that the highest values of flavonoids and the organic soluble extractive substances as a whole were observed in the bottom part of the stem. This value gradually decreased up to the top of SH.

Liu et al. (2013) investigated the variation of the chemical components along the stem of sawtooth oak (*Quercus acutissima* Carruth.) and Chinese cork oak (*Quercus variabilis* Blume) located in Hongya Mountain Forest Farm of China. They noted that the lignin content, cellulose content, alcohol-benzene solubility value, and ash content at base and 9.6 m SH of sawtooth oak were 24.51% - 25.92%, 43.59% - 45.90%, 5.06% - 4.60%, and 1.33% - 1.22%, respectively. On the other hand, the same components at base and 9.6 m SH of Chinese cork oak were 18.99% - 15.95%, 45.77% - 39.25%, 3.35% - 3.84%, and 1.34% - 0.94%, respectively.

Krutul et al. (2014b) aimed to analyze longitudinal variations in alcohol-benzene solubility and ash content of sapwood and heartwood samples of common oak (*Quercus robur* L.) obtained from Jabłonna Forest Inspectorate, Zegrze Forest District of Poland. They determined that the alcohol-benzene solubility of sapwood samples was 3.8% at the bottom, 4.1% at the middle, and 4.5% at the top. In the heartwood samples, it was 4.2% at the bottom, 4.9% at the middle, and 5.3% at the top. The authors also found that the ash content of sapwood samples was 0.51% at the bottom, 0.52% at the middle, and 0.53% at the top. In the heartwood samples, it was 0.35% at the bottom, 0.31% at the middle, and 0.40% at the top.

Hussin et al. (2014) aimed to determine the chemical composition of wood samples at the different SHs of batai wood (*Albizia falcataria* (L.) Fosberg) from Malaysia. The authors reported that holocellulose content was 85.22% at the bottom, 88.88% at the middle, and 88.76% at the top. These differences in the holocellulose content were not significant. Klason lignin content was 25.88% at the bottom, 26.95% at the middle, and 28.55% at the top, and klason lignin content increases from bottom to top of the stem were statistically significant. The authors also revealed no significant correlation between solubility values and SH. In addition, they stated that ash content was 0.86% at the bottom, 0.96% at the middle, and 0.88% at the top. While the bottom and the top samples were in the same statistical group in terms of ash content, the middle sample was different from the others.

Saffian et al. (2014) investigated the vertical variation of the wood chemical composition of rubber tree (*Hevea brasiliensis* (Willd. ex A. Juss.) Müll. Arg.) clone RRIM 2020 from Malaysia. They also determined the effect of planting density (500, 1000, 1500, and 2000 trees/ha) on the chemical composition of rubberwood. In the 500 trees/ha planting density, holocellulose, α-cellulose, and klason lignin content negatively correlated with SH. The authors revealed that the chemical composition of rubberwood clone RRIM 2020 was significantly affected by planting density and SH. In the 500 trees/ha planting density, hot-water solubility and alcohol-benzene solubility were 5.77% and 1.67% at the bottom, 4.08% and 1.34% at the middle, and 3.55% and 1.42% at the top. Ash content of rubber tree clone RRIM 2020 (planting density 500 trees/ha) was 0.58% at bottom, 0.47% at middle, and 0.43% at top.

Yunanta et al. (2014) examined the effect of SH on chemical components of light red meranti (kawang jantung) (*Shorea macrophylla* (de Vriese) Ashton), meranti melantai (seraya melantai) (*Shorea macroptera* Dyer.), and seraya daun tumpul (*Shorea retusa* Meijer) from Indonesia. The wood samples were taken from the bottom and top parts of the stem in the vertical direction and the inner heartwood, outer heartwood, and sapwood in the radial direction. According to their finding, the holocellulose content of outer heartwood and sapwood in the three species negatively correlated with SH. In the inner heartwood samples, while holocellulose content of *Shorea macrophylla* and *Shorea macroptera* were increased in the bottom part of the stem towards the top part, it was decreased in the *Shorea retusa*. They also reported that α-cellulose content of three species' inner heartwood, outer heartwood, and sapwood samples had a decreasing trend with increasing SH. In addition, klason lignin content in all cross-section parts of *Shorea macroptera* and *Shorea retusa* had positively correlated with SH. However, klason lignin of *Shorea macrophylla* had a decreasing trend with increasing SH. According to their study, hot-water, cold-water, and alcohol-toluene solubility values of *Shorea macrophylla* sapwood were increased with increasing SH. In addition, the alcohol-toluene solubility of Shorea macrophylla outer heartwood positively correlated with SH. 1% NaOH solubility values of sapwood, outer heartwood, and inner heartwood samples of *Shorea macrophylla* were decreased with increasing SH. The same trend was observed in the alcohol-toluene solubility of the inner heartwood of *Shorea macrophylla*. On the other hand, hot and cold-water solubility values of outer heartwood and inner heartwood of *Shorea macrophylla* had negatively correlated with SH. In the wood samples of *Shorea macroptera*, cold-water solubility values of sapwood, outer heartwood, and inner heartwood showed a decreasing trend with increasing SH. Also, the hot-water solubility of outer heartwood negatively correlated with SH, while sapwood and inner heartwood had a positive correlation. In all cross-section parts of *Shorea macroptera*, 1% NaOH and alcohol-toluene solubility values were positively correlated with SH. In the wood samples of *Shorea retusa*, hot-water, cold-water, 1% NaOH, and alcohol-toluene solubility values in all cross-section parts had a positive correlation with SH except for hot-water solubility of sapwood sample. Consequently, the authors concluded that solubility values depended on the wood sample's radial and longitudinal position.

Krutul et al. (2014a) evaluated the influence of SH on the chemical composition of the outer wood and pith zone wood of European white birch (*Betula pendula* Roth). According to their results, the cellulose content of outer wood and pith zone wood of European white birch was 49.6%-46.5% at the bottom, 50.2%-47.9% at the middle, and 50.1%-48.1% at the top, respectively. They also reported that klason lignin of exterior wood was decreased with increasing SH. It was increased in the pith zone wood. They also found that 1% NaOH solubility of outer wood was 28.4% at the bottom, 29.3% at the middle, and 30.0% at the top. In the pith zone wood, it was 30.3% at the bottom, 28.4% at the middle, and 28.1% at the top. Alcohol-benzene solubility was erratically varied in both inner and outer wood.

Latib et al. (2014) investigated the relationship between the SH and chemical components of burflower-tree (*Neolamarckia cadamba* Roxb.) wood harvested from Malaysia's Uitm Pahang Forest Reserve. The wood samples were obtained from the bottom, middle, and top trees. The authors found that tree height significantly affected holocellulose and klason lignin content. The holocellulose content decreased from the bottom to the middle of the tree (from 84.65% to 82.11%) and increased to the top of the tree (from 82.11% to 84.84%). The same trend was observed in klason lignin content (30.20%, 24.58%, and 30.92%). The authors also found that hot-water, 1% NaOH, and ethanol-toluene solubility were statistically significantly affected by tree height. However, its effect on cold-water solubility was insignificant. The ethanol-toluene solubility decreased from the bottom to the middle of the tree (from 2.54% to 2.24%) and increased to the top of the tree (from 2.24% to 2.58%). The same trends were determined in hot-water solubility (6.70%, 6.03%, and 6.94%) and 1% NaOH solubility (18.83%, 17.50%, and 18.33%). In addition, the axial position had no significant impact on the ash content of the burflower-tree.

Pramasari et al. (2014) studied the holocellulose, α-cellulose, and klason lignin content and alcohol-benzene solubility in the wood samples of the bottom, middle, and top parts of the 2- and 5-year-old teak *(Tectona grandis*

Linn. f.) taken from Cibinong Science Center Nurseries in Indonesia. They found that the holocellulose content of two aged samples and the klason lignin content of 5 aged samples decreased with increasing SH. However, the klason lignin content of 2 aged samples positively correlated with SH. Holocellulose content of five aged samples and α-cellulose content of both age groups varied irregularly from the bottom to the top. The authors also determined that the alcohol-benzene solubility values of two aged samples were 0.92% at the bottom, 1.11% at the middle, and 1.19% at the top. In the five aged samples, alcohol-benzene solubility values were 3.85% at the bottom, 5.86% at the middle, and 5.18% at the top.

Baptista et al. (2014) reported that klason lignin content of the tree of heaven (*Ailanthus altissima* (Mill.) Swingle) in the Serra da Estrela region of Portugal was 20.98% at 15% height level, 20.58% at 35% height level, 20.42% at 65% height level, and 22.83% at 85% height level. They noted that hot-water solubility was 2.93% at 15% height level, 2.96% at 35% height level, 3.12% at 65% height level, and 2.61% at 85% height level. 1% NaOH solubility values at 15%, 35%, 65%, and 85% height levels was 18.67%, 19.61%, 16.59%, and 19.49%, respectively. They also reported a linear correlation between ethanol solubility and height level. In addition, SH had no significant effect on ash content.

Johansson et al. (2015) aimed to determine the effect of SH on the chemical composition of the sapwood and the heartwood of Scots pine (*Pinus sylvestris* L.) wood. Wood samples were obtained from long-term field trials at Svartbergets experimental forests, Unit of Field-Based Research, of the Swedish University of Agricultural Sciences (SLU). In the sapwood sample, klason lignin content was 26.1% at breast height, 24.7% at 50% of SH, and 26.8% at 75% of SH. In the heartwood sample, klason lignin ratios at breast height and 50% SH was 24.4% and 25.0%, respectively. Also, they revealed that xylose and mannose amounts in both sapwood and heartwood were increased along with the increasing SH.

Muhcu et al. (2015) studied the effect of log position (0-3 m, 3-6 m, 6-9 m, 9-12 m, and 12-15 m) on the chemical composition of European larch (*Larix decidua* Mill.) wood obtained from Trabzon province, Black Sea region of Turkey. According to their results, the ratio of hemicelluloses had a positive correlation with log position, while cellulose and klason lignin ratios had a negative correlation with log position. It was evident from the results that variations in the axial directions were statistically significant for all the characteristics evaluated. Their results also indicated that log position significantly affected soluble extractive content. The ratios of hot-water, cold-water, 1% NaOH, and alcohol-benzene-soluble extractives were decreased with increasing log positions. On the other hand, ash content was increased with increasing log position. Ash contents at 0-3 m, 3-6 m, 6-9 m, 9-12 m, and 12-15 m were 0.23%, 0.31%, 0.40%, 0.51%, and 0.62%, respectively.

The influence of SH on the wood chemical composition of seven clones of rubber tree (*Hevea brasiliensis* (Willd. ex A. Juss.) Müll. Arg.) from Thailand was determined by Riyaphan et al. (2015). Wood samples were taken from 1.3 m and 6 m heights of 13 years old trees. According to the average chemical composition values of seven clones, the wood sample at the 6 m of SH had higher holocellulose (2.85%), α-cellulose (2.27%), hemicelluloses (3.62%), pentosan (6.36%), and lower klason lignin (1.99%). According to their results, the average hot-water solubility of seven clones was significantly increased with increasing SH (6.6% in 1.3 m and 6.1% in 6 m). The average alcohol-benzene solubility of seven clones was slightly increased (2.8% in 1.3 m and 2.9% in 6 m). In addition, the average ash content of seven clones of rubber tree was 0.9% in 1.3 m and 0.8% in 6 m.

Dwumaa (2016) aimed to determine the effect of SH on holocellulose, α-cellulose, hemicelluloses, and klason lignin contents of sapwood and heartwood of teak *(Tectona grandis* Linn. f.) grown in the Brong Ahafo region of Ghana. The wood samples were taken from the stem's bottom, middle, and top. They reported that holocellulose and hemicelluloses contents of sapwood and heartwood samples were increased with increasing SH, while α-cellulose and klason lignin contents were decreased. The bottom sample of heartwood and middle sample of sapwood had the lowest (63.07%) and highest (72.72%) holocellulose content. The highest (41.75%) and lowest (39.68) α-cellulose contents were observed in the middle part of the heartwood and the top part of the sapwood, respectively. The bottom sample of sapwood showed the highest klason lignin content (25.09%), whereas the top sample of heartwood showed the lowest klason lignin content (22.61%). The authors also noted that the effect of SH on α-cellulose and klason lignin contents of sapwood was statistically insignificant.

Marsoem and Irawati (2016) assessed the chemical composition of two Acacia species from Indonesia. They noted the klason lignin contents of earleaf acacia (*Acacia auriculiformis* A. Cunn. ex Benth.) and brown salwood (*Acacia mangium* Willd.) were significantly decreased from the bottom to the top of the stem. In the earleaf acacia, klason lignin content was 24.6% in the bottom, 24.3% in the middle, and 21.6% in the top. Klason lignin content of brown salwood was 23.3% in the bottom, 24.3% in the middle, and 21.6% in the top. In both species, klason lignin contents of bottom and middle samples were in the same statistical group. However, the top samples were in a different statistical group. In addition, they reported that alcohol-benzene solubility values of earleaf acacia and brown salwood were significantly decreased from the bottom to the top of the tree. The alcohol-benzene solubility values of earleaf acacia were 3.3%

at the bottom, 3.6% at the middle, and 2.3% at the top. They also noted that alcohol-benzene solubility values of brown salwood were 2.2% at the bottom, 3.7% at the middle, and 1.4% at the top. Extractive content values of brown salwood showed a statistically significant difference for each position in the stem. On the other hand, extractive content values of bottom and middle samples of earleaf acacia sample were in the same statistical group. However, the top samples were in a different statistical group. On the other hand, the ash content values at the bottom, middle, and top samples of earleaf acacia were 0.42%, 0.36%, and 0.25%, respectively. Ash content of brown salwood was 0.31% at the bottom, 0.25% at the middle, and 0.24% at the top. However, the authors noted that these differences in the ash content were not statistically significant.

Wistara et al. (2016) evaluated the relationship between SH and chemical components of sapwood and heartwood sections of red meranti (*Shorea leprosula* Miq.) grown in Indonesia. Wood samples were taken from 7 m, 10 m, and 13 m of SH. The holocellulose ratio in both sections had a rising trend with increasing SH. The α-cellulose ratio in sapwood had a positive correlation with SH. The α-cellulose ratio in heartwood at 7 m, 10 m, and 13 m was 40.44%, 42.48%, and 40.60%, respectively. The ratios of hemicelluloses in sapwood were negatively correlated with SH. The ratios of hemicelluloses in heartwood were 26.33% at 7 m, 25.64% at 10 m, and 28.22% at 13 m. The klason lignin ratio of sapwood showed an increasing trend from bottom to top of the log, but heartwood showed an opposite trend. The sapwood part's hot-water, cold-water, 1% NaOH, and alcohol-benzene-soluble extractives decreased up to 10 m SH then increased to 13 m. Similar trends were observed in the heartwood part's hot-water and 1% NaOH-soluble extractives. Heartwood part's cold-water and alcohol-benzene-soluble extractives negatively correlated with SH. From 7 m to 13 m, the sapwood part's ash content was 0.31%, 0.29%, and 0.39%, respectively. Heartwood part's ash content negatively correlated with SH.

Yeh et al. (2016) determined the chemical composition of bottom and top samples of loblolly pine (*Pinus taeda* L.) juvenile wood harvested in Orange County, NC, USA. Total lignin contents were 28.5% at the bottom and 29.6% at the top samples. The glucose and mannose contents at the top sample were slightly lower than in the bottom sample. In addition, the bottom sample's galactose, xylose, and arabinose contents were higher compared to the top sample. They also noted that the alcohol-benzene-soluble extractive contents were 3.3% at the bottom and 5.1% at the top specimens. They claimed that this might be due to the living part (cambial part) in the top specimens being higher than the bottom specimens. Therefore, the amount of primary extractives (including metabolism-related compounds) is also higher.

Nordin et al. (2016) determined the ash content of lead tree (*Leucaena leucocephala* (Lam.) de Wit) procured from Tawau, Sabah in Malaysia and reported that it was 0.77% at the bottom, 0.91% at the middle, and 0.99% at the top. On the other hand, Udoakpan and Njoku (2016) aimed to determine the effect of SH on the klason lignin and the total extractive content of gmelina (*Gmelina arborea* Roxb.) and Caribbean pine (*Pinus caribaea* Moralet) grown in Nigeria. They reported that klason lignin values of both species had negatively correlated with SH. In the gmelina samples, klason lignin content was 30.75% at 10% SH, 26.30% at 50% SH, and 24.15% at 90% SH. In the Caribbean pine samples, klason lignin content was 29.22% at 10% SH, 26.96% at 50% SH, and 26.11% at 90% SH. In the gmelina samples, the total extractive content was 29.30% at 10% SH, 28.87% at 50% SH, and 28.03% at 90% SH. The total extractive content in the Caribbean pine samples was 13.65% at 10% SH, 13.32% at 50% SH, and 14.07% at 90% SH.

Rather et al. (2017) aimed to evaluate the effect of sampling height on wood extractives in high-density plantation of 25-year-old forest red gum (*Eucalyptus tereticornis* Sm.). The wood extractives (hot-water, cold-water, and alcohol-benzene solubility) were studied by taking from four different tree heights (ground level, 30%, 60%, and 90% of total tree height). The highest extractive contents were recorded at ground level and the lowest at 90% of total tree height.

Amini et al. (2017a) examined the chemical components of three different stem parts (bottom, middle, and top) of brown salwood (*Acacia mangium* Willd.). They noted that while holocellulose, α-cellulose and hemicelluloses ratios were increased in the lower part of the stem towards the upper part, the klason lignin ratio was decreased. Holocellulose ratio was 82.23% at the bottom, 83.95% at the middle, and 85.99% at the top. α-cellulose and hemicelluloses contents at the bottom, middle, and top were 47.00% - 35.22%, 48.16% - 35.79%, and 49.84% - 36.14%, respectively. They also found that klason lignin content tended to remain stable at the bottom (21.07%) and the middle (21.06%) samples, then significantly decreased at the top (17.23%). The extractive content of brown salwood was increased from the bottom to the top of the stem. Alcohol-toluene solubility was 1.40% at the bottom, 1.86% at the middle, and 2.05% at the top.

Amini et al. (2017b) studied the effect of SH on klason lignin content and ash content of the lead tree (*Leucaena leucocephala* (Lam.) de Wit) from Malaysia. They noted that the highest klason lignin (25.22%) was observed in the bottom of the stem, and the lowest (18.63%) was in the middle of the stem. Ash content had positively correlated with SH. It was 0.80% at the bottom, 0.95% at the middle, and 1.41% at the top.

Taş (2017) examined the relationship between SH (1.3 m, 2.8 m, and 4.3 m) and the chemical composition of Turkish pine (*Pinus brutia* Ten.) located in the Bartin province of Turkey. The author noted that SH did not significantly affect holocellulose content. His results also pointed out that SH exhibited a significant and negative correlation with α-cellulose and a significant and positive correlation with klason lignin. The author found that SH did not significantly affect hot-water-soluble extractives. His results also revealed that SH showed a significant and negative correlation with cold-water-soluble extractive content. In addition, the ash content of *Pinus brutia* (Ten.) increased up to 2.8 m SH then decreased to 4.3 m.

Kılıç Pekgözlü et al. (2017) aimed to determine the effect of sampling height on the chemical composition of European black pine (*Pinus nigra* Arn.) located in Bolu province of Turkey. Their study indicated that the holocellulose ratio was not statistically significantly affected by sampling height. However, the α-cellulose ratio was statistically significantly decreased with increasing sampling height, while the klason lignin ratio was statistically significantly increased. Holocellulose ratio was 73.09% at the base, 73.58% at the middle, and 73.48% at the top of the stem. α-cellulose and klason lignin ratios were found as 52.07%-24.77% at the base, 50.27%-25.48% at the middle, and 49.70%-25.74% at the top, respectively. They also noted that alcohol, hot and cold-water-soluble extractives positively correlated with sampling height, and variations in the axial direction were statistically significant for all the characteristics evaluated.

Putra et al. (2018) aimed to investigate the effect of SH on the wood chemical components of batai wood (*Albizia falcataria* (L.) Fosberg). They noted that holocellulose values of wood samples were irregularly changed from the bottom to the top of the stem. However, there was a negative correlation between SH and klason lignin content. Holocellulose and klason lignin contents at the bottom, the middle, and the top were 76.04% - 23.78%, 88.33% - 22.86%, and 69.17% - 16.69%, respectively. On the other hand, there was a positive correlation between extractive content and SH. They also noted that alcohol-benzene solubility was 2.34% at the bottom, 3.51% at the middle, and 3.83% at the top.

Rahman et al. (2018) aimed to determine the effect of SH on the wood chemical composition of burflower-tree (*Neolamarckia cadamba* Roxb.) from Pahang Forest Reserve, Malaysia. The chemical analyses were performed on the lower, middle, and upper parts of the stem. According to their results, the highest holocellulose (70.93%) and klason lignin (30.92%) contents were observed at the top of the stem, lowest values (68.44% and

24.58%, respectively) were in the middle of the stem. They also noted that solubility values were irregularly varied with increasing SH. Hot-water and cold-water solubility values were 6.70% - 5.65% at the bottom, 6.03% - 5.75% at the middle, and 6.94% - 5.54% at the top, respectively. 1% NaOH and alcohol-toluene solubility was 18.83% and 2.54% at the bottom, 17.50% and 2.24% at the middle, and 18.33% and 2.58%t at the top, respectively. In addition, ash content was 0.74% at bottom, 0.57% at middle, and 0.55% at top.

Topaloglu and Erisir (2018) investigated the change in wood chemical composition along the longitudinal direction (1.3 m, 6.3 m, and 12.3 m) of oriental beech (*Fagus orientalis* L.) and Caucasian fir (*Abies nordmanniana* (Stev.) Spach.) trees grown in Turkey. According to their finding, both species' holocellulose and klason lignin contents had a positive correlation with SH, while the cellulose content of both species had a negative correlation.

Raia et al. (2018) determined the effect of SH on holocellulose, klason lignin, and total extractive contents of rubber tree (*Hevea brasiliensis* (Willd. ex A. Juss.) Müll. Arg.) (clone RRIM600) grown in Paraná of Brazil. Holocellulose content was 70.60% at the base, 71.74% at the 1.5 m SH level, and 73.27% at the 3 m SH level. The authors noted that klason lignin content was 19.61% at the base, 19.06% at the 1.5 m SH level, and 18.46% at the 3 m SH level. They also reported that total extractive content was 6.00% at the base, 5.39% at 1.5 m SH level, and 4.42% at 3 m SH level. They also determined that ash content was 1.04% at the base, 1.11% at the 1.5 m SH level, and 1.18% at the 3 m SH level.

Hassan (2020) investigated the relationship between SH and wood chemical composition of lebbek (*Albizia lebbeck* (L.) Benth.) grown in Egypt. The cellulose, hemicellulose, total extractives, and hot-water and cold-water solubility values were significantly decreased with increasing SH. On the contrary, klason lignin content and ash content positively correlated with SH. Recently, Kılıç Pekgözlü et al. (2020) examined the effect of the SH on the polysaccharide composition of Turkish pine (*Pinus brutia* Ten.) wood. They reported that hemicelluloses content was 280 mg/g at 1.3 m SH and 282 mg/g at 2.8 m SH, whereas 300 mg/g at the top of the stem (4.3 m). Except for glucose and mannose, the amounts of all other sugar units were positively correlated with SH. For example, the xylose amount was 66 mg/g at 1.3 m, 68 mg/g at 2.8 m, and 74 mg/g at 4.3 m. The top of the trees contains more juvenile wood (Henriksson et al., 2009), juvenile wood has more xylose than that mature wood (Johansson et al. 2015).

CONCLUSIONS

In this study, variation of chemical composition along SH of trees was reviewed. Results showed that wood chemical components are generally affected by SH. Holocellulose, hemicelluloses, and ash ratios were generally positively correlated with SH. In contrast, wood's cellulose ratio, lignin ratio, and soluble contents (hot-water, cold-water, 1% NaOH, alcohol-benzene, acetone, *etc*.) generally had an opposite correlation. In some studies, the opposite results were obtained. These contradictory findings indicate that the differences in the chemical components along SH can be depended on factors such as tree species, environmental conditions, and sampling time. The chemical composition of the wood can predict the quality of wood-based products such as particleboard, fiberboard, and paper. This review hopefully may give an understanding for future researchers on small-diameter top wood in the sense of wood industries.

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Chapter 3

METAGENOMIC APPROACHES FOR FOOD SCIENCE AND TECHNOLOGY

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1. Introduction of Metagenomics and Foods

Metagenomics offer a molecular implement for investigating microorganisms without the need for a pure culture through the examination of DNA directly extracted from a sample. The DNA of all the microorganisms in a population could be analyzed by the help of this technique. Total metagenomics including DNA sequencing and analysis can reveal details on a variety of sample and better describe the microbial population in a particular habitat. It can not only identify the species that are present in a population but also provides insights about the metabolic processes and practical uses of the microorganisms. The combination of metagonomics with function-based screening methods improves the potency of this technique for identifying functional genes from uncultured microorganisms and finding activity of colonies that has been transferred to the host by the inserted environmental DNA (Langille et al.,2013).

Traditional microbiological methods generally have a start step obtaining a pure culture. However, these standard culturing techniques could provide less informations about the bacterial diversity in a targeted sample (Coughlan et al., 2015). The microbial world is much larger than what could be discovered by using traditional microbiological techniques, as demonstrated in recent developments of molecular microbiology. The novel techniques presents more promising attempts to reach the genetic data found in various species (Ling et al., 2015).

Two new DNA sequencing methods "the pyrosequencing and the parallelized ligation-mediated and bead-based sequencing" techniques have been evolved in 1990s. The combination of these two methods were known as "Next-Generation Sequencing" (NGS) techniques. Furthermore, commercially available sequencers were discovered and improved the possibility of high-throughput sequencing (HTS) of genes microbial ecosystems (Kergourlay et al., 2015).

Foods contain various type of microorganisms which are widely used in different food processings or destroyed during processing for sustaining food safety. The majority of the food microorganisms could be detected by several methods. The metagenomic methods allow to analyze all microorganisms by investigating the genomic data obtained directly from a food sample, to determine species, and to provide detailed information about microbial communities. Metagenomic-based approaches are considered as striking developments for food safety which offer the direct identification of whole microbial communities exitisting in different food samples (Billington et al., 2022). Moreover, the functional metagenomics has considerable potential in the food industry including, identification of enzymes, capability of monitoring some reactions which could be difficult to conduct or progress under harsh environmental conditions like temperature, pH, osmolarity and the discovery of bioactive components (Coughlan et al., 2015).

Metagenomics is currently used in the food industry with different purposes including taxonomic profiling of microbiological food products and supplements, to enhance culture methods, identifying pathogens and detection of some contaminants and enzymes. The targeted-amplicon analyses are beneficial for characterizing the changes in bacterial populations that arise throughout fermentation processes or during long-term storage of fermented products (Escobar-Zepeda et al., 2016). The probiotics also could be evaluated by targeted-amplicon analyses (Morovic et al., 2016). The ability of analyzing population dynamics provided by targeted-amplicon combined with shotgun metagenomics has also been used to enhance culture-based enrichment methods (Jarvis et al., 2015; Zilelidou et al., 2016).

This book chapter covers discusses available metagenomic methods for food processes and functionality of the metagenomic approaches combined with biotechnological application for food fermentation, modification of food enzymes and sustaining food safety.

2. Metagenomics in Food Fermentation

Fermentation is one of the most common food processing and preservation method. The fermented foods have been exhibited to have improved properties in comparison to the corresponding raw ingredients due to synthesis of microbial metabolites, elimination of allergens and biological activity of microorganisms (Marco et al., 2017). Fermented food products have been extensively analyzed by using metagenomics techniques. The detailed informations about communities could be collected by the help of metagenetics. Table 1 reports some studies related to fermentation of different food types. The spontaneous food fermentations are mostly achieved by activity of either lactic acid bacteria (LAB) or yeasts. NGS techniques are the foremost methods that promise to evaluate the evolution of microorganisms during natural fermentation processes (Kergourlay et al., 2015).

Kefir is known as a probiotic beverage and a dairy product fermented with both yeasts and bacteria. The metagenomics studies have revealed that the bacterial community of kefir grains is dominated by 3 species: *Lactobacillus kefiranofaciens*, *Lactobacillus buchneri*, and *Lactobacillus helveticus* (Nalbantoglu et al., 2014). Moreover, *Kluyveromyces* and *Saccharomyces* are found to be the dominant yeasts in kefir grains (Leite et al., 2012).

Sourdough starters are comprised of LAB and yeasts which are used for traditional bread production. It was observed that many taxonomic groups in sourdough could be determined by a quick evolution. However, after first day of bread fermentation, some species have seen to be subdominant which poorly identified by cultural methods, emphasizing the importance of metagenomics for understanding fermentation mechanisms of foods (Ercolini et al., 2013).

In recent years, NGS techniques have been commonly used to enlight fermentation process of seafoods. Especially in Korea, fermented seafoods are generally called as jeotgal. The natural fermentation of highly salted seafoods including oysters, shellfish, shrimp, fish and etc. are constitutent of jeotgal. Since the fermentation of shrimp, shellfish, cuttlefish, roe and tripe of pollack, and crab were mostly composed of *Lactobacillus* and *Weissella*, oyster fermentation had been achieved by a halophilic bacteria *Salinivibrio* (Jung et al., 2013b).

The production of cheese starts with lactic acid fermentation and continues with different ripening stages. While LAB are responsible for the early acidification process, the non-starter microbiota (particularly yeasts and molds) is participate in the formation flavor and aroma. The bacterial microbiota of several traditional cheeses including Irish cheese (Quigley et al., 2012), Croatian cheese (Fuka et al., 2013), mozzarella cheese (Ercolini et al., 2012), Herve cheese (Delcenserie et al., 2014), Poro cheese (Aldrete-Tapia et al., 2014) and Latin-style cheese (Lusk et al., 2012) had already been investigated by16S metagenetic analysis. The results of all these studies confirmed that the microbial diversity in accordance with classic microbiological culture. It was found out that 14 bacterial and 10 fungal genera which are in charge of cheese ripening and aging have been present in cheese microbiota. The microbial flora of cheeses were identified by HTS and prominent differences compare to classic microbiological methods were discovered (Kergourlay et al., 2015).

The bacterial and fungal populations of kombucha tea have been identified by the first culture-independent and high-throughput sequencing. It has been observed that *Gluconacetobacte*r is the major bacterial genus and the yeast populations of kombucha tea were found to be dominated by *Zygosaccharomyces* (Marsh et al., 2014).

A local Italian salame has been analyzed by HTS of 16S rRNA amplicons to characterize the total bacterial community. It has been stated that HTS techniques have the abilitiy of specifying strains that present in a certain food product (Polka et al., 2015).

The microbial community of fermented Halkidiki olives obtained from different regions has been determined by metataxonomic analysis.

It has been commited that the complexity of fermented olive microbiota was mostly associated with specific geographic areas (Argyri et al., 2020).

Table 1 High-throughput sequencing (HTS) studies in different food fermentations

Targeted gene	Food type	Purpose of the study	Reference
16S rRNA gene of bacteria	Dairy Product	Monitoring ripening process of Italian cheese	De Filippis et al., 2016
26S rRNA gene of fungi	Fermented beverage	Must fermentation of Spanish grapes	Wang et al., 2015
16S rRNA gene of bacteria	Meat	Ripening of fermented meat (salami)	Greppi et al., 2015
16S rRNA gene of bacteria	Seafood	Traditional fermentation of shrimp	Jung et al., 2013a
16S rRNA gene of bacteria	Vegetables	Monitoring olive and brine fermentation	Cocolin et al., 2013
16S rRNA gene of bacteria and ITS1-4 of fungi	Fermented beverage	Traditional Japanese tea fermentation	Zhao et al., 2015
16S rRNA gene of bacteria	Dough	Fermentation of maize product	Elizaquivel et al. ,2015

3. Metagenomics in Food Processings and Storage

Food processing and preservation is a substantial topic for both food industry and consumers. The changes in microorganisms throughout processing and storage is an important challenge. The existence of a technique that have the ability of characterizing dominant and sub-dominant microorganisms has a great importance to set up either storage or processes conditions (Khan and Shatya, 2018).

The 16S rDNA pyrosequencing approach has been applied on fresh spinach samples in order to measure the effect of different storage times and temperatures. *Pseudomonas* and *Enterobacteriaceae* were the most significant spoilage bacteria existing after 15 days of storage period (Lopez-Velasco et al., 2011).

The bacterial diversity of chilled pork was analyzed by pyrosequencing of the amplified 16S rDNA during long-term storage. At the beginning of the storage period *Micrococcaceae* was the most abundant bacteria and then sharply reduced. *Aeromonadacae* and *Puniceicoccae* were reached highest levels at seven day of storage. *Lactobacillaceae* dominanted the whole microflora after 21 days of storage (Zhao et al., 2014).

The biofilms are one of the significant aspects that responsible for food contamination and also cause serious economic losses due to spoilage of foods. In particular, bacteria are able to form biofilms to be protected under environmental stress conditions. The biofilms produced by bacterial communities in four different food processing plants have been characterized by using 16S rRNA sequencing. *Pseudomonas* spp. and *Acinetobacter* spp. identified as the dominant bacteria which are extensively biofilm producers (Caraballo Guzman et al., 2019).

The microbiome and resistome of retail ground beef products without antibiotics were examined by 16S rRNA amplicon and target-enriched shotgun sequencing. The microbiome of ground beef samples were predominated by *Firmicutes* and *Proteobacteria.* Tetracycline resistance

has reached up to 90% of run mapped to resistance gene accessions in ground beef samples (Doster et al., 2020).

4. Metagenomics for Food Enzymes

Food processing requires a chain of stages starting with harvesting or slaughtering of raw materials to the final products. The need for enzymes for different industrial applications has increased since the enzymes are environmentally friendly and safe. The industrial enzymes that participate in food processes summarized in Table 2.

Table 2 Some enzyme groups and their application areas in food industry (Khan and Sathya, 2018)

Enzymes	The activity of enzyme	The application area in food industry
Proteases	Hydrolysis of proteins	Meat tenderization Breaking kappa-casein in cheese manufacturing Improving digestibility of wheat protein-gluten
Amylase	Degradation of starch and glycogen	Production of maltose and fructose syrup Increasing softness and volume of bread Reducing dextrin to fermentable monosaccharides for beer fermentation
Cellulase	Degradation of cellulose	Production of maltose and fructose syrup Increasing softness and volume of bread Reducing dextrin to fermentable monosaccharides for beer fermentation
Lipase	Hydrolysis of lipid components	Production of structural lipids Cheese ripening Enhancing quality of edible fats and oils
Pectinases	Degradation of pectine	Fruit juices clarification Improving quality of essential oils Production of modified pectin
Xylanase	Degradation of plant matter	Improving cereal processing and end product quality Dough conditioning
B-galactosidase	Breakdown of galactose	Degradation of lactose

Generally, industrial food processing are performed under undesired physicochemical conditions like, pH, pressure, water activity and temperature. Since the enzymes have proteinaceous structure, they are very disposed to denaturation reactions during food processings. Therefore, modification of enzymes that could be succeed under extreme conditions is highly required for food industry (Khan et al., 2013).

The extremozymes are defined as modifed enzymes that have the ability of performing under extreme conditions including lower water activity, poor oxygen concentrations, wide range of temperature, pH and pressure, higher salinity. The extremozymes are able to accelerate enzymatic reactions under intense conditions. Moreover, some enzymes that can catalyze enzymatic reactions under more than one harsh condition for instance combination of temperature and pH are known as polyextremohilic enzymes. These enzymes mostly synthesized by different bacterial groups containing thermophilic, psychrophilic, acidophilic, alkaliphilic, and halophilic bacteria (Liszka, et al., 2012).

The microbial enzymes have shorter loops with less number of prolines. Therefore it is easy to provide flexibility to the enzyme structures in order to prevent denaturation reactions. The molecular adaptation of enzymes to harsh environmental situations could be achieved by increasing hydrophilicity, changing content of amino acids, increment of more negatively charged residues, enhancing noncovalent interactions, larger catalytic sites (Siglioccolo et al., 2010).

Amylases are one of the commonly used enzymes of food industry with interesting characteristics properties. Amylases can catalyze reactions under various conditions such as lower or higher temperature, lower or higher pH. An endoacting amylase excluded from a metagenomic library exhibited no similarity to known amylases or amylolytic domains emphasizing that metagenomic screening provided different genes from extreme environments (Delavat et al., 2012).

The fact that thermostable bacterial and fungal proteases have significant challenges during processing and pursuing their properties during large-scale production have induced in higher industrial costs. Functional metagenomics has helped to eleminate these financial problems by expression of genes for unique enzymes from unusual environment (Neveu, et al., 2011).

Cellulases are used for different food processings including coffee manufacturing, oil and carotenoid extraction, production of juices and nectars, beer and wine fermentation. The phylogenetic analysis of cellulase exhibited only 50% analogy with respect to the available genes (Xia et al., 2013).

Moreover, the results of functional metagenome analysis of *Ascophyllum nodosum* showed 42% sequence similarity between β-glucosidase and cellulase genes (Martin et al., 2014).

β-Galactosidase enzyme hydrolyzes lactose of milk to glucose and galactose and mostly produced by *Aspergillus.* The alternative metagenomic sources of β-Galactosidase have been discovered by previous researches (Vester et al., 2014; Zhang et al., 2013).

Lipases or triacylglycerol hydrolases are widespread enzymes which hydrolyze triacylglycerols into glycerol and fatty acids. The commercial lipases are synthesized by *Candida, Pseudomonas, Mucor, Rhizopus, Geotrichum, Achromobacter, Alcaligenes, Arthrobacter, Bacillus, Burkholderia*, and *Chromobacterium.* A lipase enzyme with unique properties was explored by metagenomic library search (Sharma et al., 2012).The lipase enzyme having thermo- and alkali-stable properties and higher specificity for buttermilk triacylglycerols discovered from a metagenomic library (Chow et al., 2012).

Xylanases are the enzymes that mostly preferred by bakery and feed industries and take place in the production of functional foods. Xylanese enzyme has potential to improve biomass degradation have been found out in a previous study (Cheng et al., 2012).

Tannase enzymes are capable of removing tannins from green tea and used for the manucfacturing instant tea. A tannase enzyme was characterized from metagenomic library and utilized in removal tannins from green tea infusions (Yao et al., 2014).

5. Metagenomics for Food Safety

The application of metagenomics for food safety and quality advancement is still in progress. However, this technique suggests interesting possibilities for estimating the incidence or occurence of pathogens and spoilage microorganisms and the potency to identify unknown microflora (Billington et al., 2022; Brown et al., 2019; Jagadeesan et al., 2019). The NGS technology enables faster detection and prevention of foodborne outbreaks which relieved public health concerns. The NGS in food safety is performed in two ways:

1. The determination of the whole genome sequence (WGS) of a single microorganism

2. The application of metagenomics to a biological sample generating sequences of multiple microorganisms (Allard et al., 2016).

After the announcement of WGS microbial pathogens into surveillance of public health smaller and earlier outbreaks were detected, the source causing outbreaks was easily identified and the number cases related to outbreak increased (Carleton and Gerner-Smidt, 2016; Jackson et al., 2016). Moreover, WGS is started to be used for food industry to detect contamination throughout processings. The antimicrobial resistance of food pathogens and the microorganisms causing spoilage during storage could be analyzed by these methodology (Besser et al., 2018; Jagadeesan et al., 2019).

It is well-known that tomatoes are frequently source for human *Salmonella* infections. Shotgun metagenomics sequencing of enrichment media emphasized that *Paenibacillus spp.* are able to outcompete and kill *Salmonella* during the enrichment phase indicating that an alternative enrichment media should be utilized for prevention tomato contamination (Ottesen et al., 2013). Similar findings in *L. monocytogenes* and *E. coli* have shown the success of targeted-amplicon and shotgun metagenomics sequencing in enrichment techniques (Ottesen et al., 2016; Margot et al., 2016).

The potential safety risks of traditional Ghanaian fermented milk product were determined by 16S rRNA gene sequencing and shotgun metagenomic. It was found out that the major source for bacterial contamination was raw cow milk and *E. coli* and *K. Pneumoniae* are the identified pathogens that should be taken careful consideration for hygenity of the end product (Walsh et al., 2017).

The fresh bagged spinach samples spiked by *Escherichia coli* which producer of Shiga toxin were analyzed with shotgun metagenomic sequencing. The level of contamination has been reached aroun 10 CFU/100 g after 8 hours of enrichment. *Pseudomonas, Pantoea*, and *Exiguobacterium* were the key microorganisms that existed in bagged spinach samples (Leonard et al., 2015).

16S rDNA amplicon sequencing and whole genome shotgun sequencing were compared for the foodborne pathogen detection. The performance of shotgun sequencing was better for detection and characterization of species, genome assembly, abundance estimation. However, 16S rDNA sequencing revealed not only large deviations from composition of sample at the genus and species levels, but also the absence of many pathogenic species (Grützke et al., 2019).

6. Conclusion

The NGS technology is able to compete with microbiological culture and physiological examination. The ultimate elongation of the effect of NGS results in economical savings in the food industry. This cost savings is one of the benefits of food industry that this new technology is expected to provide. Functional metagenomic databases explaining nature's abundance of enzymes with improved properties have stimulated the evolving food-processing industries demands. Metagenomic techniques are quite beneficial for process monitoring and setting storage parameters. The metagenonic techniques provide accurate, rapid, and reliable results for food fermentations.

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Chapter 4

DEGRADATION OF WOOD AND RECENT DEVELOPMENT OF WOOD PROTECTION IN TURKEY

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INTRODUCTION

Wood material has superior properties compared to different engineering materials. For example, it can be given as providing good sound and heat insulation, being a renewable raw material, easy processing and shaping ability, high resistance/density ratio, and aesthetic appearance compared to other materials (Bozkurt & Erdin, 1997). Wood is an environmentally friendly natural material used in both structural and non-structural applications (Obata, Takeuchi, Furuta& Kanayama, 2005; Priadi & Hızıroglu, 2013). Wood maintains its importance due to its positive properties and has approximately 10.000 usage areas as a raw material (Ors & Keskin, 2001; Khalil, Bhat, Awang, Bakare& Issam, 2010). Wood material has a decomposition effect due to being affected by environmental conditions. In addition, wood material cannot be resistant to external climatic conditions (heat, light, humidity), mechanical effects, water intake, biological pests, and burning for a long time. In particular, the service life of the wood material, which is not protected at all, is shortened and forest destruction increases accordingly. For this reason, wood material must be protected by techniques such as impregnation, heat treatment, and varnishing. Physical, mechanical, combustion, biological, etc. of the unprotected wood material. resistance to such effects is weakened.

WOOD MODIFICATION

The term wood modification means changing or improving the negative properties of wood. An effective wood modification process increases the dimensional stability of wood and provides high resistance to fungal decay. It also reduces the water absorption of wood and increases resistance to weather conditions (Hill, 2006). In summary, wood modification is the physical, mechanical, biological, combustion, etc. of the wood material. It can also be expressed as prolonging the service life against the effects.

WOOD MODIFICATION METHODS

Many researchers have classified wood modification methods differently. In general, wood modification methods can be classified as:

- Chemical Modification
- Thermal Modification
- Surface Modification
- Impregnation Modification

Chemical Modification

The chemical modification process is the reaction that results in the formation of a covalent bond between any reactive group in wood cell wall polymers and the chemical substance. This can occur either by the formation of a single bond between a chemical substance and an−OH group or by cross-linking with two or more−OH groups (Hill, 2006).

Chemical modification has two purposes. These are to increase the strength of wood against decay and better dimensional stability (Rowell, 2005). It increases the resistance against rot fungi without using any toxic chemicals. Many factors make the chemical modification process even more attractive. For example, the toxic chemicals used in the impregnated wood material harm the environment. In addition, the commercial value of poplar, eucalyptus, and coppice woods, which do not have high commercial value and are not used due to dimensional stability problems, can be increased by chemical modification (Rowell, 2005). Chemical modification methods are classified as acetylating, furfurylation, N-methol (DMDHEU), and reactive oil applications.

Thermal Modification (Heat treatment)

Thermal modification aims to heat the wood material in the temperature range where chemical reactions are accelerated. Thus, it provides a permanent change in the chemical structure of the polymer compounds in the cell wall (Boonstra, 2008). This method, it is aimed to improve the wood's properties without giving any chemicals to the wood. The thermal modification takes place at temperatures between 180°C and 260°C. If the temperature is kept below 140°C, only the properties of the wood change, if this temperature is exceeded, undesirable destruction will occur in the wood. It was determined that many important substances in wood were destroyed because of heat treatment studies carried out at temperatures above 300°C (Hill, 2006). The application of thermal modification increases the performance of the wood because it changes the molecular structure of the wood. These increased wood performances are biological resistance against fungi and insects, low equilibrium moisture content, increased dimensional stability due to reduction in shrinkage and expansion, increased thermal insulation ability, paint adhesion, resistance to external weather conditions, decorative color variety, and extended use time. The heat treatment application also enables the use of lower-quality tree species, increasing their competition against higher-quality tree species and supporting sustainable forest resources. In addition to all these changes in wood, heat treatment is considered a good alternative to impregnation since it is obtained without adding chemicals harmful to humans and the environment (Wikberg, 2004). The mechanical and physical properties of thermally modified wood are permanently changed. This change is due to the thermal degradation of hemicellulose. This change begins at approximately 150°C and continues to change with increasing temperature. Temperature is the most important factor in thermal modification. In addition, wood species directly affect the result of heat treatment time, process atmosphere, pressure, moisture content, and even the distribution of temperature (Viitanen et al., 1994). Today, thermal modification is carried out in many countries in Europe with different names and methods. For example, Finland used steam to heat wood material and called it the "ThermoWood" method. The Netherlands called it the "Plato" method using hot air and steam together, Germany the "OHT" method using hot oil, and France the "Rectification and Perdur" method using an inert gas (Mayes & Oksanen, 2002). For example, the superior properties that the Thermo wood method brings to the wood material are shown in Figure 1.

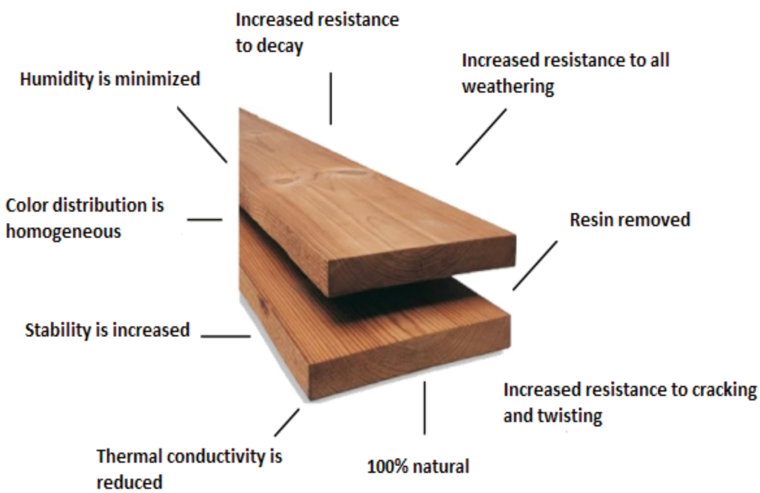

Figure 1: The superior properties of the ThermoWood method (URL-1, 2022).

Surface Modification

Some surface properties are among the physical properties of wood material. These properties can be listed as color, surface roughness, hardness, and gloss. Wood materials should have different surface properties depending on the purpose of use. Painting, varnishing, and coating are among the main types of surface modification. The wood material is a natural and sustainable and hydrophobic material. Surface modification not only improves the above-mentioned properties of the wood material but also protects the wood against environmental effects, increases the resistance against insects and fungi, extends the life of the wood, and gives it aesthetic properties.

Impregnation Modification

Impregnation modification is the process of impregnating the wood cell wall with chemical compounds or chemicals. In other words, it is the reaction of the material within the cell wall to become the proper form. For this reaction to occur, it is necessary to continue the impregnation process until the impregnating agent has penetrated into the wood cell. The molecules of the impregnating agents may be small enough to reach the interior of the cell wall. Detection of impregnation can be achieved by 2 basic mechanisms (Hill, 2006):

• Impregnation of the cell wall as a monomer (or oligomer) by sequential polymerization.

• Diffusion of soluble material into the cell wall by cascading operations to mix insoluble material.

• For the impregnation process to be effective, the impregnation substance must not be washed under the conditions of use. However, washing the impregnation is not the priority. This is because in some conditions the impregnating agent can be chemically bonded to the polymeric components of the cell wall, although this is a washing process. The impregnation material should not be toxic because it is removed from the cell wall by burning, composting (the process of obtaining fertilizer from wastes) or all recycling processes while in all ambient conditions and the cell wall (Hill, 2006). The basic principle in impregnation modification; is based on the principle of bonding the cell wall by reacting with a chemical substance. This method is provided by 2 mechanisms (Hill, 2006):

• Polymerization of the impregnated monomer (or oligomer) by suitable chemical methods.

• Making the soluble chemicals insoluble in wood with appropriate methods after the wood is impregnated.

• In the wood impregnation method, boron, copper, plant extract, etc. different materials are used.

The example of impregnated wood is given in Figure 2, and the superior properties that the impregnation method brings to the wood are given in Table 1.

Figure 2: The example of impregnated wood (URL-2, 2022).

Table 1: The superior properties that the impregnation method brings to the wood.

It protects the wood from damage such as fungi and insects.
It extends the life of the wood by protecting it against weather conditions.
Increases the amount of sapwood.
It allows the use of perishable wood species.

PHYSICAL DEGRADATION OF WOOD

Corrosion

Various natural events such as wind, heavy rains; Damages caused by birds, ants, and various animals or humans constantly wear out the wood material. Although this wear takes place slowly and over a long period, it causes erosion on the material surface (Bozkurt, 2008).

Weathering

Wood, exposed to external weather conditions without adequate protection, undergoes some chemical and physical changes. Color loss caused by factors such as gases in the air, sunlight, rain, wetting, and drying succession; Fiber loss because of cracking and the gradual erosion of the destroyed surface are some of the negative effects of weather conditions. As a result of these effects, the worn material becomes weaker against other risks (Bozkurt, 2008).

Biological Degradation of Wood

Fungi

Fungi are by far the most extensive element of degradation in any structure (Mankowski & Morrell, 2000). The risk of fungal attack can be examined in 3 parts:

- Short-term soaking, which facilitates the formation of mold,
- Moderate soaking, which allows the colonization of rot fungi that can survive for many years in dry wood,
- It is the long-term ingress of moisture that allows the entry of rot fungi that degrade the wood (Wang et al., 2018).

Decay rates in wood material are typically a function of humidity, temperature, and wood species. Many rot fungi could ability to invade wood material. However, colonization is most affected by wood properties and moisture (Duncan & Deverall, 1964). The rot in wood can be classified in the broadest sense as follows.

White Rot

Type I: All cell wall components, but initially hemicellulose and lignin are particularly destroyed (Phellinus pini, Heterobasidion annosum).

Type II: All cell wall components are destroyed equally at all stages of rot (Tramates versicolor, Irpex lacteus) (Yıldız, 2000).

Brown (Brown) Rot

First of all, cell wall carbohydrates are destroyed, and modified lignin remains (Coniophora puteana, Gloeophyllum sepiarium, Serpula lacrymans) (Yıldız, 2000).

Soft Rot

Type I: Cell wall carbohydrates, especially in the S_2 layer of wood, are destroyed and longitudinal cavities are formed.

Type II: The cell wall from the cell space in leafy trees and the S_2 layer in coniferous trees are almost gnawed and the cell wall carbohydrates especially in the S_2 layer are destroyed (Chaetomium globosum, Alternaria alternata) (Yıldız, 2000). The destruction of wood by brown rot fungi is shown in Figure 3.

Figure 3: Damages to wood by brown rot fungi (Turner, 2008).

Bacterias

Bacteria are commonly found on wood exposed to very different environments and are divided into two degrading and non-degrading species. While some of the degrading bacteria only degrade the passage membranes, others actively destroy the lignocellulosic structure of the wood cell wall (Sivirkaya, 2003).

Insects

Insects that damage wood materials can be grouped into two groups insects that digest wood as food and insects that use wood as a shelter (Amburgey, 2008). Wood-digesting insects such as termites and the larvae of wood-boring beetles use wood as a food source for all or part of their life cycle (Jones & Eggleton, 2010). Insects that destroy wood according to the selection of nutrients and their characteristics are generally as follows. Insects that eat the wood in fresh wood are called primary insects, insects that infect dry wood are called secondary insects, and insects that damage rotten wood are called tertiary insects. For example, the shipyard beetle Hylecoetus dermestoides, the hardwood or sapwood beetle Lyctus linearis, and the house goat beetle Hylotrupes bajulus are some of the wood-damaging insects (Yıldız, 2000). *Hylotrupes bajulus* (L.) is from the family Cerambicidae and is the only wood-damaging member of this large insect family. The preferred wood moisture for Hylotrupes larvae is 15-25% (Amburgey, 2008). An image of the insect pests that damage the wood material is given in Figure 4.

Figure 4: Damages caused by insect pests on wood material (URL-3, 2022).

Termites

The two most important termite groups that can attack wood material are subterranean termites and dry wood termites. Both subterranean and drywood termites are found in North America. Subterranean termites, one of the two groups, are the most destructive. These are available in large numbers in the United States. Their quantity makes them a critical insect for bulk timber use. Subterranean termite workers forage randomly from the soil and usually enter through ground burrows after the building is built and form colonies on buildings. Drywood termites (Kalotermitidae) nest in low-humidity wood. Colonies of subterranean termites are usually larger than colonies of these termites. However, drywood termites are very difficult to detect. Therefore, they can cause significant local damage (Wang et al., 2018). Subterranean termites (Rhinotermitidae) can be extremely aggressive, exploiting cracks in the foundation to attack untreated wood and migrate upward through the wood. A mass termite attack on wooden structures can often be problematic as it will be difficult to detect without any intervening supervision. Wood preservation techniques will be essential for the performance of structures built in termite-dense areas (Morris, 2000). An image of wood material after the termite attack is given in Figure 5.

Figure 5: An image formed in wood material after termite degradation (URL-4, 2022).

Sea Pests

Wood material used in the marine environment is degraded by microorganisms and sea creatures. Although microorganisms decompose the surface of the wood material in the marine environment, the main damage is done by wood-driller organisms. Wood-driller organisms are divided into two groups: mollusks and crustaceans. Important wood-destroying organisms in the group of mollusks are Teredinids and Pholads. The most important genera of wood-piercing crustaceans are Limnoria, Sphaeroma, and Chelura. The most important factors affecting the spread of wood-driller organisms are seawater temperature and salinity (Sivrikaya, 2004). An image of sea pests on wood material is given in Figure 6.

Figure 6: An image created by sea pests on wood material (Cetin, 2009).

CHEMICAL DEGRADATION OF WOOD

Wood may undergo chemical degradation by various environmental factors. The reason for this is acid or alkaline environmental conditions or electrochemical reactions occurring in the wood itself (Bozkurt, 2008). The negative effects of acid and alkaline environmental conditions on wood occur in different ways. The acid cleaves and hydrolyzes the glycosidic bonds in polysaccharides. First, hemicellulose decomposes, then cellulose molecules break off from the main chain as monomers. In summary, acids make wood brittle easily (Ridout, 2013).

Wood burns when high temperatures are reached during combustion, which is another negative feature of wood. When wood is gradually heated, changes begin to occur in its structure, and these changes increase with increasing temperature. During combustion, first hemicellulose (180-350 °C), then cellulose (275-350 °C) and lignin (250-500 °C) decompose (Kim et al., 2006). The thermal stability of lignin is thought to be due to its heavily cross-linked structure and high molecular weight (Yang et al., 2006).

RECENT DEVELOPMENTS IN WOOD PROTECTION IN TURKEY

Gunes and Altınok (2022), determined the behavior of wooden carrier beams modified with tannin and treated with pre-heat treatment in different climatic conditions. For this purpose, Specimens prepared from Scots pine (*Pinus sylvestris* L.), oak (*Quercus petraea* L.), and chestnut (*Castanea sativa* Mill.) woods were impregnated with acorn tannin and pre-heat treated for 2 hours at 150ºC and 160ºC. Bending strength and modulus of rupture tests were applied after the specimens were conditioned at 20ºC temperature and 65% RH, 40ºC temperature, and 35% RH, 10ºC temperature, and 50% RH, respectively. As a result, the highest increase in bending strength was determined as in modified with tanninScotch pine specimens at 150ºC compared to the control specimens. Accordingly, it can be suggested to use Scotch pine wood in the manufacture of lightly loaded wooden house columns and beams and other structural elements.

Percin, Doruk, and Altunok (2022), as a pre-treatment acorn (valex) (Quercus ithaburensis), red pine bark (Pinus brutia Ten.) and oak thuja (galex) (Quercus infectoria Oliver) extracts after being impregnated with aqueous solutions. investigated some physical and mechanical properties of processed spruce (Picea orientalis) wood. Test specimens were impregnated with 10% tannin solutions before heat treatment. After pre-impregnation, the test specimens were heat treated at 150 °C, 175 °C, and 200 °C for 2 hours. The effects of impregnation and heat treatment on air-dry density, pressure strength parallel to fibers (CS), bending strength

(MOR) and modulus of rupture (MOE) were analyzed. As a result, it has been determined that the impregnation solutions have a positive effect on the mechanical properties of the untreated specimens and somewhat limit the resistance losses caused by heat treatment at low temperatures. However, the resistance losses increased with increasing temperature.

Atilgan, Peker, and Atar (2022), aimed to apply the resin developed from organic resins, which does not contain hardeners and harmful solvents, suitable for food and drug contact, on wood material, and then to determine the color and gloss changes of the wood. Specimens prepared from Scots pine (*Pinus Sylvestris* L.), Oriental beech (*Fagus Orientalis* L.), and Anatolian chestnut (Castanea sativa Mill.) as wood material were coated with resin and hardened at 60, 80, and 100°C temperatures. According to the data obtained; Total color change (ΔE), among wood species, is highest in Scotch pine, lowest in chestnut, highest in terms of drying temperature degree of 100°C, lowest in 60°C, highest in wood species and drying temperature interaction level in Scotch pine at 100°C (54.80), the lowest chestnut was measured at 60°C (29.60). The gloss change was determined as the highest in Scotch Pine (86.98) and the lowest in chestnut (82.37) wood at 60° angle.

Tan, Sirin, and Baltas (2022) impregnated sea mussel shell (*Chamelea gallina*) dusts at different concentrations on the woods of Eastern spruce (*Picea orientalis* (L.) Link.) and Anatolian chestnut (*Castanea sativa* Mill.). Combustion, adhesion, thermogravimetric analysis (TGA), and limiting oxygen index (LOI) test measurements were performed on these specimens. According to the TGA results, the residue amount in the spruce wood specimen was the highest at 5%, while the residue amount in the chestnut wood specimen was the highest at 15%. With increasing amounts of mussel shell dust, the limiting oxygen index values increased in both tree species. As a result, the impregnation of wood specimens with mussel shell dust improved the combustion resistance of the wood.

Altay, Toker, Baysal, and Babahan (2022a), investigated the surface properties such as color, gloss, and surface hardness changes of Oriental beech (*Fagus orientalis* L.) impregnated with borax, boric acid, ammonium sulfate and then coated with polyurea/polyurethane and epoxy resins. According to the results, all specimen groups gave negative lightness values after accelerated weathering. It was determined that the color stability of the epoxy resin-coated specimens was higher than the polyurethane/polyurea hybrid resin-coated specimens. In general, impregnation before coating reduced the gloss losses of the specimens after accelerated weathering. In addition, the impregnation process before being coated with epoxy and polyurethane/polyurea resins improved the surface hardness values of Oriental beech after accelerated weathering.

Altay et al. (2022b), applied a secondary coating of polyurethane/polyurea (PUU) hybrid resin and epoxy resin (EPR) to Oriental beech (*Fagus orientalis* L.) wood impregnated with boron compounds and ammonium sulfate. Then, the boron leaching test and SEM (Scanning Electron Microscopy) analyzes were applied to the specimens. According to boron leaching test results, specimens coated with polyurethane/polyurea (PUU) hybrid resin gave the most positive results against boron leaching. In the SEM analysis, it was determined that the boric acid (BA) impregnated and epoxy resin (EPR) coated Eastern beech wood showed a smoother surface than the other specimen groups.

Altay, Toker, Baysal, Babahan, and Kilic (2022c), investigated the fire and mechanical properties of Oriental beech wood impregnated with boron compounds and ammonium sulfate and then coated with epoxy and polyurea/polyurethane resins. According to the results they obtained, it was determined that the polyurethane/polyurea and epoxy resin-coated Oriental beech wood had higher compressive and bending strength parallel to the fibers than the untreated and uncoated (control) group. Along with the impregnation process before the polyurethane/polyurea and epoxy resin coatings, the compressive and bending strength of the Oriental beech parallel to the fibers decreased to some extent. The weight loss and temperature values of the polyurethane/polyurea and epoxy resin-coated oriental beech on fire were found to be higher than the untreated and uncoated (control) group. However, impregnation before polyurethane/polyurea and epoxy resin coatings improved the combustion properties of Oriental beech wood.

CONCLUSIONS

Increasing the service life of wood materials has been an ongoing process for years. Methods such as impregnation, heat treatment, and surface coating were used as wood preservation methods. For example, to protect unprotected wood material against environmental factors, partial charring of wood material has been used throughout history. Later, wood was impregnated with various vegetable, animal, and mineral oils. In addition, it has been tried to prevent rotting by keeping the wood material as dry as possible. Over the years, people have impregnated wood by using materials such as creosote and copper to protect the wood. In addition, people have realized that impregnation material is less harmful to the environment and human health. Later, they benefited from boron compounds. Later, the method of impregnating wood with plant extracts was also developed. In addition to impregnation, the heat treatment method has been used for years to keep the wood drier and prevent it from rotting and deforming. In addition, varnishes, paints, varnishes, epoxy resins, polyurethane/polyurea resins, etc., are used as surface coating agents. substances have been used. Today, many substances continue to be developed for wood preservation purposes.

As a result, as the human population increases, consumption increases in parallel. People should be as careful as possible to keep the life of the materials they use as long as possible. For example, when we think about the wood sector, while the human population was not very high in the past, forest destruction was limited to that extent. The massive material used in furniture was ubiquitous. As the population increased over time and consumption increased in parallel, forest destruction also increased. Later, when access to wood material was limited, people started to produce artificial plate materials from wood scraps. Efforts were made to minimize deforestation and environmental damage by extending the service life of the currently used solid material as much as possible.

In this context, in this study, the importance of wood preservation is emphasized and the latest wood preservation methods in Turkey are indicated in the literature. According to the data taken from the literature, the protective materials and methods used in the studies and the physical, mechanical, combustion, etc. of the wood material. properties such as improved. As stated in the literature, new preservatives are developed every day. In this way, the importance of wood preservation is emphasized. In addition, in the future, substances that extend the service life of wood and that are least harmful to human health should be developed.

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Chapter 5

INVESTIGATION ON POPULATION STRUCTURE AND GROWTH CHARACTERISTICS OF ROACH (*RUTILUS RUTILUS* L., 1758) FROM KARASU STREAM (IĞDIR, TÜRKİYE) AND SOME WATER QUALITY PARAMETERS OF THAT STREAM

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1. Introduction

While the whole world and Turkey are preparing for the 2000s, the problem of inadequate and unbalanced nutrition due to protein deficiency, which is more common especially in underdeveloped and developing countries, has brought to the agenda to benefit more from fisheries resources. It is estimated that our population will reach 70 million in 2000. In this case, aquaculture is an important alternative for our people to meet the animal protein deficit and to solve the balanced nutrition problems (Atay et al., 1995). In order to take the right steps on aquaculture, first of all, it is necessary to know the existing resources well and to organize fishing or breeding accordingly (Aras et al., 1995).

With 906.118 hectares of natural lakes in various regions with different climates, around 180,000 hectares of dam lakes and a 145,000 km long river network, Turkey is in an important rank among the world countries in terms of water resources and, accordingly, aquaculture potential (Aras et al., 1995). This potential is much greater for the Eastern Anatolia region (Kuru, 1975) where the Euphrates, Tigris, Çoruh, Aras and Muzur originate and where 65% of Turkey's Lakes located, around 40 freshwater fish species live present an important situation.

A large part of Turkey's inland fishery consists of carp. The share of common carp (*Cyprinus carpio*) and pearl mullet (*Chalcalburnus tarichi*) belonging to this family in our inland fishery is around 60%. If other species and subspecies of the family in question are added, this ratio can rise up to at least 70% (Aras et al., 1995).

The genus Rutilus, belonging to the family Cyprinidae, is generally distributed in Europe, North and West Asia and western North America. There are 4 species of this genus living in the inland waters of our country. It is seen that researches about this fish are mostly systematic (Kuru, 1971; Kuru, 1975; Geldiay and Balık, 1999).

Libosvarsky and Saeed (1983), in their study on the roach (*Rutilus rutilus*, L. 1758) fish found in the Morivan region of Czechoslovakia, determined that the growth of this fish was fast in the first years of its life, reaching up to 40 mm. In the aforementioned study, they found that the growth in the following years varied in both sexes, and the annual increase in growth in length varied between 19-33 mm in males and 19-38 mm in females. In the same study, the length of the captured specimens varied between 16 to 19 cm and the length-weight relationship of the male and female individuals forming the population found to be $W=0.00439xFL^{3.60}$ with r=0.96, and $W=0.01349xFL^{3.272}$ with r= 0.95, and age-length relationships determined as L= 481.2x(1-exp (3.60 -0.07179(t+0.22124)), L=609.6x(1-exp (0.053901(1+0.24104)), respectively.

Penczak and Koszalinska (1993), in a study they carried out on 425 *Rutilus rutilus* (L. 1758) in the Narew River in the Northeast of Poland, found that this fish, which is an omnivorous species, is more intensely concentrated in regions with high organic pollution than in uncontaminated or less polluted regions. They found that they reached the highest values in length and weight in these regions. In these areas polluted with organic materials; they found BOD (Biochemical Oxygen Demand) as 12, COD (Chemical Oxygen Demand) as 16, ammonium nitrogen as 2.8 mg dm^3 and iron as 0.8 mg dm. In the same study, they determined that the dominant age group in the population was 6+ (25.64%).

In a study on the roach (*Rutilus arcasii* Steindachner, 1886) fish living in the Moros and Ucero rivers in Spain, it was reported that the females in the Moros River live up to 5+ years, while the males live up to 4+ years. These values were 6+ and 4+, in the Ucero river, respectively. Age-length relationships for Moros and Ucero populations were determined as L=120.1x(1-exp (-0.2668(t+0.007)) and L= 133.3(1-exp(0.2668(1+0.007)), respectively. Length-weight relationships were changed in both populations according to the seasons (summer and fall) and were calculated for Moros ve Ucuro populations as $W=0.0147x(FL)^{3.11}$ and $W=0.0187x(FL)^{3.021}$, $W=0.0119x(FL)^{3.212}$, $W=0.0160x(FL)^{3.004}$, respectively. It was observed that the condition coefficient of both populations varied between 1.8-2 and this value, which was high during the breeding period, showed a sudden decrease after breeding. It was determined that age at first maturity was 2 + and, the length of matured females was shorter than the matured males in both rivers. It was reported that the egg diameter was getting increase with age and reproduction begins in early April and continues until the beginning of June. It was determined that the egg production varied between 1594325 individuals/individual and the difference between habitats was not statistically significant. The relationship between egg production and length was found to be Log F= - 1.7825+2.6801 Log L (r=0.839) (Rincon and Lobon Cervia, 1989).

Bastl (1995) found that male and female individuals reach first sexual maturity at 77-90 mm (SL) and 58-80 mm (SL) lengths, respectively, in a study on the roach (Rutilus rutilus L., 1758) fish living in the Dunebe river. In the same study, it was determined that spawning took place in April-May, when the water temperature reached 11-19 °C.

It is known that there is natural hybridization in the Cyprinidae family, and these hybrids encountered were reported as *Chondrostoma polylepis x Rutilus lemmingi*, *Rutilus rutilus (L.) x Abramis brama* (L.), *R. rutilus* (L.) x *B .bjoerkna* (L.), *R. rutilus* (L.) x *S. erythrophtalmus* (L.), and *R. rutilus* (L.) x *A. alburnus* (L.) (Kuru, 1975; Elvira vd., 1990; Adams and Maitland, 1991).

One of the studies that was carried out on the Karasu Stream of the Iğdır Plain and some fish species in the environment, and the average condition coefficient (K) of Caner (*Barbus capito capito*) fish living in these waters was found to be 0.84. The ratio of head and ovary weight to live weight was 15% and 4%, respectively. He calculated the meat yield as 65.29. In the same study, some chemical properties of Karasu Stream were determined as pH 7.76, Sodium (Na) 3.09 me/lt, Potassium (K) 5.79 me/lt, Chlorine (Cl) 2.56 me/lt and Sulphate (SO4) 0.72 me/lt (Akyurt, 1986).

Emekçi (1994) found the Condition factor (K) of freshwater chub (*Leuciscus cephalus* L., 1758) living in Sarıyer Dam Lake to be between 1.263 and 1.805. In a study conducted in Akşehir Lake, the average condition value of freshwater mullet (*Leuciscus cephalus* L., 1758) was determined as 1.576 ± 0.011, 1.595 ± 0.017 for females, and 1.557 ± 0.013 for males (Altındağ, 1996).

Karataş (1995) determined the meat yield of freshwater mullet (*Leuciscus cephalus* L., 1758) as 73.88% in males and 71.96% in females. In the same study, it was found that the meat yield of Whiskered fish (*Barbus plebejus*) was 75.84% in males and 75.88% in females.

In the face of rapid population growth, insufficient land resources and over-consumption of many stocks in the seas have brought more use of fresh water resources to the agenda (Larkin, 1992). In this context, for the first time in our country, a study was conducted on the determination of some physical and chemical properties of the Iğdır Plain Karasu Stream, which is one of the important sources in the Eastern Anatolia Region, and the population structure and some growth characteristics of Rutilus rutilus fish belonging to the Cyprinidae family living in this water. We believe that it will shed light on future research.

2. Material and Method

2.1. Materiel

2.1.1. Research Area

This study was carried out in the close upstream part of the Karasu Stream, which flows next to Kazım Karabekir Agricultural Enterprise (longitude: 44.6022 latitude: 39.8974), which is located at zero distance to the Iranian border of TİGEM (Approximately 55 km from the city center of Iğdır Province) (Figure 1).

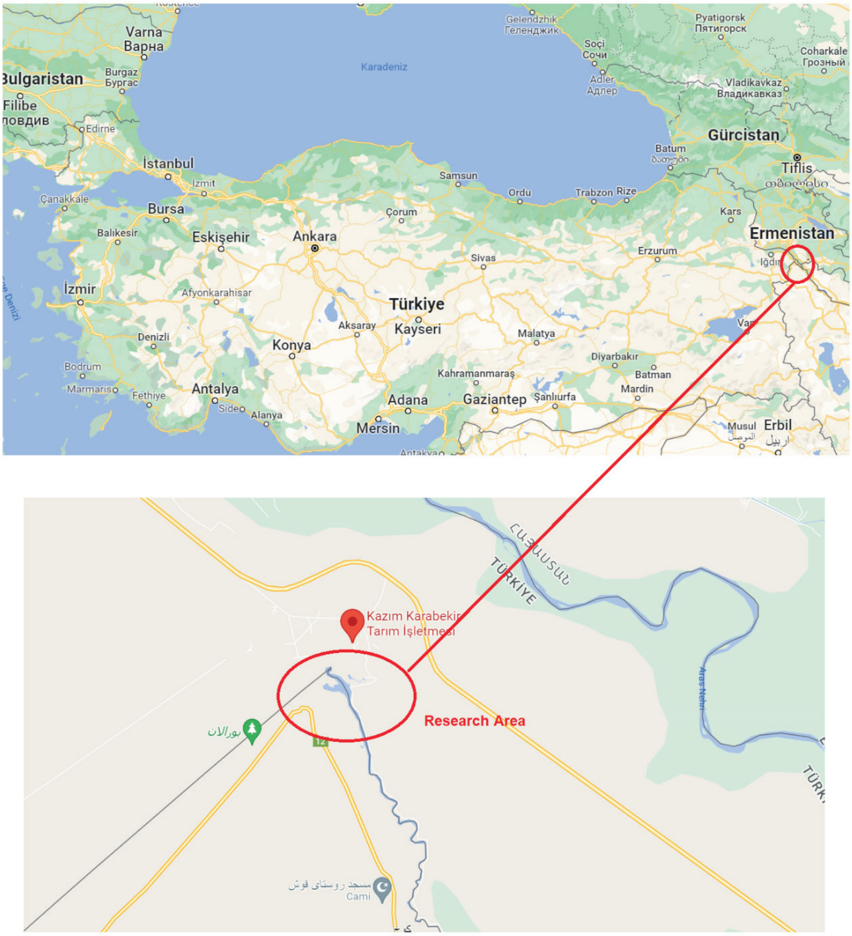

Figure 1. *Research Area*

The Iğdır plain has a microclimate character in the Eastern Anatolia Region, where the continental climate is dominant. The fact that it is surrounded by many high mountains and the height of the plain is 850 m above sea level results in a mild climate. In the plain, summers are hot and dry, and winters are cold. Most of the lands of the Iğdır plain are in desert character and the salt concentration of the drainage waters is quite high. The average annual precipitation in the plain is 233.7 mm, and the percent of precipitation by seson was 40% in spring, 14% in summer, 24% in autumn and 22% in winter. Average annual temperature is 11.6°C, average relative humidity is 62% and average annual evaporation is 1094.9 mm (Canbolat, 1990). With this appearance, the Iğdır Plain has the characteristics of a region very suitable for hot water fishing (Akyurt, 1988).

The Karasu Stream, from which fish and water materials are taken, consists of the waters formed as a result of the melting of the snow on

Mount Ararat, and the majority of the waters coming out of the ground. Therefore, Karasu Stream has the characteristics of a spring water.

2.1.2. Fish material

In the study, the fish called in scientific *Rutilus rutilus* (L., 1758) that found naturally in the Karasu Stream was used (Figure 2). Detected diagnostic features, D. III 9-11, A: III 9-11, P. I 15-18, V: II 7-8, L.lat: 40-46, L. tran: 7-8/3 -4 and pharyngeal teeth: 6-5; 6-5; 5-5, and the findings were in parallel with the findings of Kuru (1975), Geldiay and Balık (1999).

Figure 2. *Rutilus rutilus (L., 1758) from research area*

The fish, who's Turkish, English, French and German names are Kızılgöz balığı, Roach, Gardon and Plötze, is slightly flattened from the sides and covered with large scales. Head length is always less than body height. The eyes are lower and their diameter is 3.5-4 times the length of the head. The mouth is terminally located and relatively small. Dorsal fin starts roughly flush with ventral fin and its free edge is curved slightly inward. The caudal fin is deeply forked and the lobes are pointed. It can be up to 45 cm in length. The color is greenish gray on the back, sometimes with yellowish or bluish reflections. The flanks and abdomen are usually silvery white. The iris of their eyes is always red. Except for the dorsal and caudal fins, the tips of the others are orange red. With this feature, it is similar to *Scardinus erythrophtalmus*, which is called the first wing. In particular, there are many forms of various body parts that show great variation in terms of proportions and color. Although it is a fish that lives in rivers in general, it can sometimes be seen in lakes with abundant vegetation (Kuru, 1975, Balik and Geldiay, 1999).

2.1.3. Auxiliary Tools and Equipment

Scales for total weight, carcass weight and head weight taken from fish samples (with an accuracy of = 0.001g), size board (±1 mm) for fork length measurements, compass (± 0.05 mm) for head length and back height measurements, dissection scissors for sex determination and tweezers, microscope for age determination, mercury thermometer ± 1°C for temperature measurements, Hanna brand pH meter device was used for pH and electrical conductivity measurements.

2.2. Method

2.2.1. Research Plan

The research was carried out for 5 months between March 1997 and July 1997, and a total of 160 roach (*Rutilus rutilus* L, 1853) fish were caught from the same habitat during this period. Four samples were taken to determine the water quality.

2.2.2. Fishing Method

Gill nets with 15 mm, 20 mm and 30 mm mesh openings (two knot ancestors) were used for fishing.

2.2.3. Temperature, Electrical Conductivity and pH Measurements

Due to the temperature, electrical conductivity and pH properties that can change quickly, the measurements were made by us in the study area. The water temperature was measured with a precision mercury thermometer of ±1 °C, 2 m inland from the shore and at a depth of 10 cm. pH and electrical conductivity measurements were made with a Hanna brand portable-handheld digital pH meter with a sensitivity of 0.01 and working with a battery.

2.2.4. Analysis of Water Samples

Water, 2 m from the shore, from a depth of 10 cm, was taken into standard black 1l-piece bottles after rinsing 3-4 times with water (Anonim, 1976). The water samples taken were analyzed in the Soil-Water Analysis Laboratory of Erzurum Village Services X. Regional Directorate.

2.2.5. Age and Sex Determination

Age determination was made from stamps, which were recommended to be easy and practical, taking into account the previous studies (Çelikkale, 1991). With the help of tweezers, 10-20 scales were taken from the area between the lateral line and the dorsal fin and placed in a petri dish and kept in 4% NaOH plum for two hours. Then NaOH was removed and sufficient amount of water was added. The flakes are soaked in water for 30 minutes. Waiting is sufficient to remove the NaOH from the environment thoroughly. After removing the water in the environment, the flakes were soaked in 96% ethyl alcohol for 15 minutes to evaporate the remaining water. The fish scales were fixed with a clamp and fixed between the lamella and the age rings were read with the aid of a binocular microscope. Sex determination was made by observing the gonads by dissection of the abdomen (Nikolsky and Birkett, 1963; Çelikkale, 1991).

2.2.6. Condition Factor

In this study, "Fulton Condition Factor", which is the most widely used today and based on isometric growth, was used. The condition factor, which gives information about the nutritional capacity of the environment in which the fish live, is calculated using the $K = (W/L^3) \times 100$ equation where K = Condition factor, W-=Fish weight (g), L = Fish length (cm) (Ricker, 1975, Atay, 1989).

2.2.7. Determination of Population Structure and Growth Characteristics

2.2.7.1. Determination of Length and Weight Frequencies

Frequency and percent frequency distributions were obtained to determine population structure for all the fish sampled, according to the length and weight groups of the individuals, taking into account the different sex.

2.2.7.2. Length-Weight Relationship

The relationship between the length (L) and weight (W) of a fish is usually expressed by the equation $W = aL^b$. In the equation, values of the exponent 'b' provide information on fish growth.

2.2.7.3. Meat Yield (% Carcass Weight) and Proportional Head Weight (PHW)

Meat yield was calculated with the following formula (Aras, 1988)

% Meat yield = (Carcass Weight/Total Weight) x100

The following form was used to calculate the proportional head weight (Erdem, 1988).

PHW= (Head Weight/Total Weight) x100

2.2.8. Statistical Analysis

The mean, variance, standard deviation, standard error, regressions, correlations, comparisons, significance tests (t test), fit test (Ki-square test) of the population parameters were determined by known statistical methods. The most used ($p=0.05$) in biological research was chosen as the level of importance (Düzgüneş et al., 1983, Yıldız and Bircan, 1994).

A package program called "Statistica for Windows" was used in the calculations.

3. Results and Discussion

3.1. Some Physical and Chemical Properties of Water

Some physical and chemical properties of the water are given in Table 1.

Table 1. *Some Physical and Chemical Properties of the Water from Sampling Location*

Parameter	March-97	April-97	May-97	July-97	Mean
Ca^{+2} (mg/l)	92	70.40	89.60	84.0	84
Mg^{+2} (mg/l)	15.36	19.20	6.72	60.0	25.32
Organic Matter (mg/l)	0.56	2.24	1.20	2.00	1.29
pH	7.73	7.64	6.96	7.13	7.35
Conductivity (µmhos/cm)	1300	800	900	580	895
Hardness (FrS)	29	25	27	46	31.25
Total Alkalinity (mg/l $CaCO_3$)	298	258	286	115	139.25
Water Temperature (°C)	15	17	16	18	16.50
Air Temperature (°C)	9.5	32	23	29	23.38

3.1.1. Temperature

Air and water temperature values taken monthly throughout the research are given in Table 1. The lowest water temperature was 15 °C in March-1997, the highest 18 °C in July-1997, and the average was 16.5 °C.

Water temperature in streams depends on evaporation, energy input and output, and heat exchange between the surface of the water and the air. Spring waters have high temperatures because they do not come into contact with the air much. When the air temperature rises in summer, the temperature of the spring waters decreases inversely with the air temperature (Barlas et al., 1996).

The research site is very close to the main source and there are many secondary sources in the area where the measurements were made. Therefore, as can be seen from Table 1., it is out of the question that the air temperature has much effect on the water temperature over the months and at various times of the day.

Although carp can generally take food at water temperatures between 8-28 °C, the temperature at which they can best evaluate the feed is at temperatures above 18-20 °C (Çelikkale, 1988; Aras et al., 1995). In this case, it is seen that the roach (Rutilus rutilus) fish population could be fed all year round, but their development may be slow.

3.1.2. pH

The pH values of the hunting area water measured directly in the study area are given in Table 1. When the pH value was analyzed by months, the maximum pH was 7.73 in March and the minimum 6.93 in May.

The pH value limits of the water in carp breeding are 5.5-10.8 and the optimal value is 7-8 (Çelikkale, 1988). As seen in Table 1., the pH value determined as 7.35 on average in the research water is within the optimum limits, and it is close to the pH value found by Akyurt (1986) for the same water. Our findgins were close to Dipsiz lake (pH value between 6.76-7.05) that shows the spring water feature (Şen and Toprak, 1996). It was thought that the changes in the pH value according to the months may be caused by the precipitation, since the examined water has the characteristics of spring water.

3.1.3. Calcium (Ca) and Magnesium (Mg)

Calcium and magnesium contents of water samples are shown in Table 1. The amount of calcium varied between 70.40 mg/l (April-97) - 92 mg/l (March-97) and was determined as 84 mg/l on average. The amount of magnesium varied between 6.72 mg/l (May-97) and 60 mg/l (July-97) and was found to be 25.32 mg/l on average.

Calcium values were generally in parallel with hardness degrees by months, and calcium values by months were found to be higher than magnesium values. Calcium and magnesium are minerals that create hardness in water and are needed by aquatic organisms, and calcium values are generally higher than magnesium values (Uslu and Türkman, 1987).

3.1.4. Hardness

The hardness values determined in the water samples during the research are given in Table 1. The hardness ranged from 25 FrS (April-97) to 46 FrS (July-97). The average hardness value was calculated as 31.25 FrS.

It is thought that the reason for the rapid increase in the hardness value in July was due to the rain falling the day before the water sample was taken. Since the hardness of a water is closely related to the dissolution of the minerals in the soil that the water has come into contact with, the hardness of the water increases with the precipitation (Yaramaz, 1992). The hardness of water depends on the amount of calcium and magnesium salts (Barlas et al., 1996). When Table 1. was examined, it is seen that the hardness value follows a parallel course with the Ca^{++} and Mg^{++} values. As a matter of fact, hardness was also maximum in July, when Ca++ and Mg++ were detected the most.

The hardness value, which we found on average as 31.25, is close to the values found by Şen and Toprak (1996) as 25-37.25 FrS for Kırk Gözeler, which has spring water characteristics. When the waters are classified according to their hardness, waters varying between 21.5-32.5 FrS are classified as medium hard waters (Yaramaz, 1992). Accordingly, the material is in the water medium hard water class.

3.1.5. Total Alkalinity

Total alkalinity values in water analyzed monthly are given in Table 1. When the alkalinity is analyzed by months, it was determined that the lowest with 115 mg/l in July, the highest with 298 mg/l and the average 239.25 mg/l in March.

Alkalinity is the ability to neutralize acidity in water (Akyurt, 1993). As seen in Table 1., the average alkalinity values we found are similar to the alkalinity value found by Turkmen (1997) as 226 ± 31.75 mg/l for the Karasu river, and the total alkalinity level in fish farming varies between 20*30 mg/l. (Boyd and Lichtkoppler, 1980).

3.1.6. Organic Matter

The organic matter values measured from the samples taken from the material water are given in Table 1. The organic matter level was determined as 0.56 mg/l (March-1997)-2.24 mg/l (April-1997) and the average was 1.29 mg/l.

Organic substances are compounds formed by carbon primarily with hydrogen and oxygen, second degree with nitrogen and phosphorus, sulfur and similar elements. Organic substances dissolved in surface waters consist of unnatural compounds of natural origin, both animal and vegetable origin, on the one hand, and untreated domestic and industrial waters on the other hand (Uslu and Türkman, 1987). The values determined according to the months for the amount of organic matter vary slightly, and it is thought that this is due to the rains.

As can be seen from Table 1., the average value of the substance determined for the Karasu Stream. It is lower than the organic matter value found by Yıldırım (1997) as 3.12 ± 0.46 mg/l on average for Oltu Stream and 3.96±0.01 mg/1 on average for Karasu Stream (Türkmen, 1997). It is thought that this is due to the fact that the environment is spring water and it is not polluted.

3.1.7. Conductivity

The conductivity values of water are given in Table1. The conductivity varied between 580 µmhos/cm (July-97) – 1300 µmhos/cm. (March-97). The mean value was found to be 895 µmhos/cm.

The electrical conductivity of a water is the sum of the amount of salt and soluble substances in the water, and there is a linear relationship between total hardness and conductivity (Şen and Toprak, 1996). This relationship can be seen from Table 1.

As can be seen from Table 1, the values we found are higher than the conductivity values found by Barlas et al., (1996) as 754 µmhos/cm and 522 umhos/cm for Akçapınar and Çay Stream, respectively. It is thought that this situation is due to the corrosive character of the soils of the region (Canbolat, 1990).

3.2. Population Structure of Roach (*Rutilus rutilus*)

3.2.1. Age and Sex Composition

Age determinations of 160 fish were made from scales. Proportional distribution of age groups by sex in the examined samples is given in Table 2 and Figure 3. As can be seen from Table 2, the age of the fish varied between III+ to VII+.

Table 2. *Age Composition of Rutilus rutilus Population*

	Male +Female		Male		Female		
Age Group	N	% N	N	% N	N	% N	P=0.05
3+	38	23.75	15	25.00	23	23	p>0.05
4+	102	63.75	38	63.33	64	64	P<0.05
5+	13	8.13	3	5.00	10	10	P<0.05
6+	5	3.13	2	3.33	3	3	P>0.05
7+	2	1.25	2	3.33	0	0	-----
Total	160	100	60	100.00	100	23	P<0.05

0+, I+ and II+ age group individuals could not be caught since tension nets were used as the hunting method. IV+ in caught fish age group was dominant in the population with a rate of 63.75%. Other age group in the sampled population were as follows III+ with 23.75%, and age group V+ with 8.12%. The difference between the numbers of male and female individuals in the same age group were significant ($p<0.05$) for IV+, V+, but insignificant ($p>0.05$) for III+ and VI+ age groups. For all sampled population the number of total male and female was also significant ($p<0.05$). Fish older than VII+ could not be caught, and the results are similar to those of Rincon and Lobon Cervia (1989). Of the 160 fish caught during the study, 60 (37.5%) were males and 100 (62.5%) were females (Table 2).

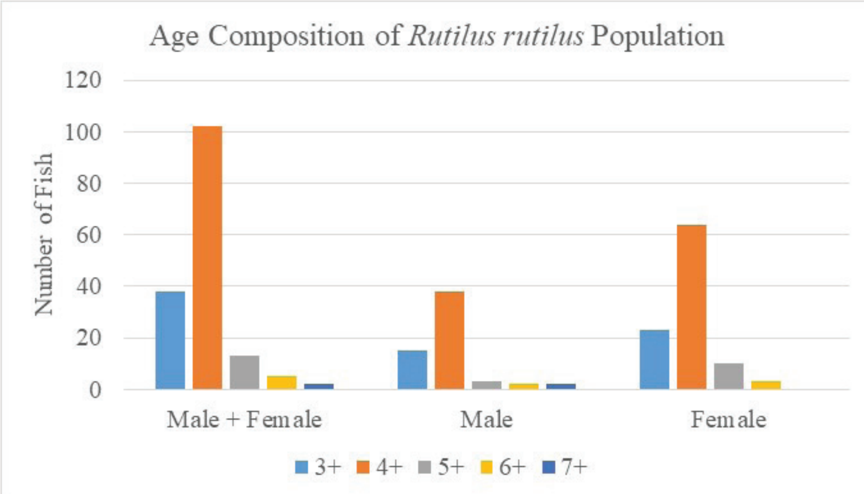

Figure 3. *Age Composition of Rutilus rutilus Population*

3.2.2. Length Composition

The fork length (FL) of 160 *Rutilus rutilus* caught during the research varied between 9.5-19.7 cm. The values of the height groups in the population are presented in Figure 4. In terms of length composition, the 11.1-12 cm group ranks first with 31.87%, and the 18.1-20 cm group ranks last with 1.25%.

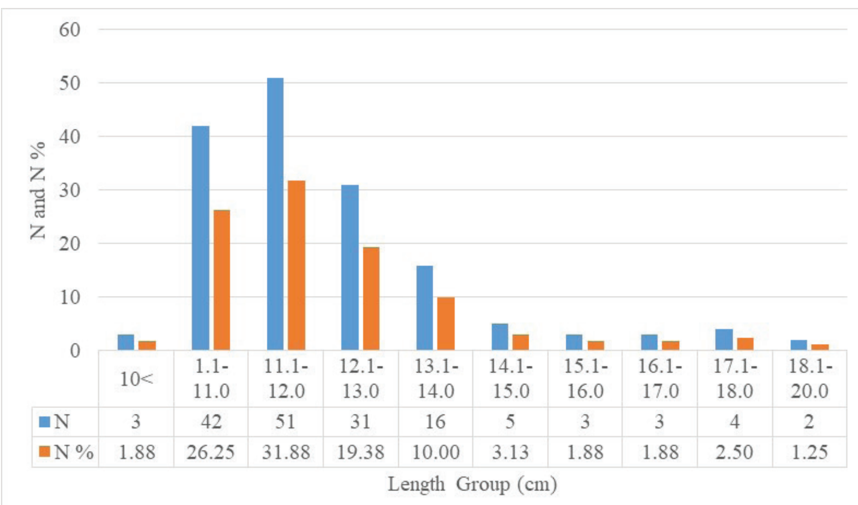

Figure 4. *Length composition diagram of Rutilus rutilus.*

3.2.3. Weight Composition

In the 160 samples examined, the total weight varied between 11.94-145.97 g and in terms of weight composition, the 20-30 g group ranked first with a 51.23 % share ranked in the first place. The weight groups of 0-15 g and 100-150 g were the last both with 1.25 percent (Figure 5).

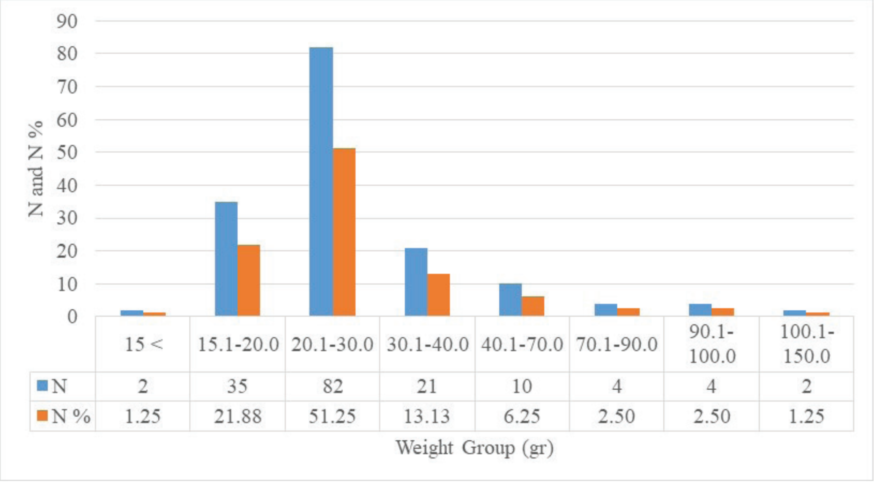

Figure 5. *Weight composition diagram of Rutilus rutilus.*

3.3 Weight-Length Relationship

The equations for the length-weight relationship calculated by the least squares method using the fork lengths (FL) and total weights of the *Rutilus rutilus* population are given in Table 3, and the graphs of the equations of these relationships are given in Figure 6.

Table 3. *Length-Weight Relationship Equations by Sex and Population for Rutilus rutilus from Karasu Stream*

Sex	Log a	b	r	Equation
Male	-1.728	3.109	0.851	$W=0.0188xFL^{3.109}$
Female	-1.178	3.332	0.975	$W=0.0066xFL^{3.332}$
Population	-1.036	3.205	0.961	$W=0.0092xFL^{3.203}$

The differences between the length-weight values (expected values) calculated using the equations and the values determined from the individuals in the population were subjected to the "X^2" fit test and it was observed that the equations obtained fit the population ($p>0.05$).

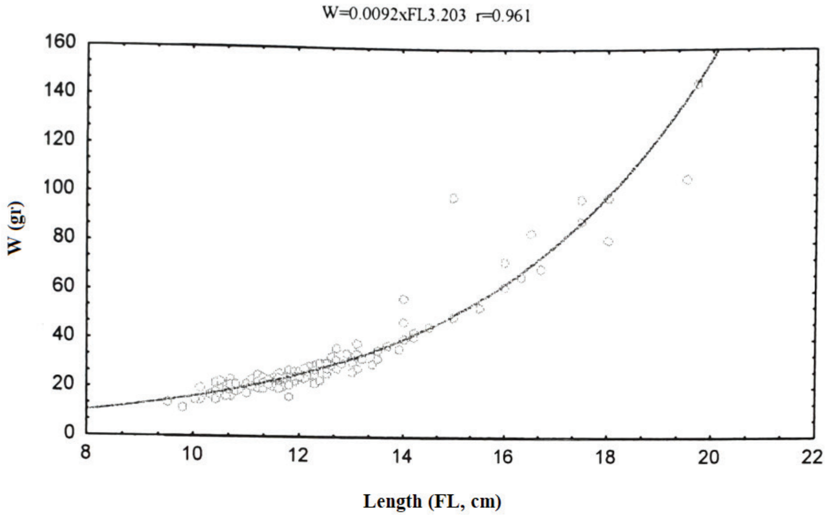

Figure 6. *Length-Weight Relationship Curve for the Rutilus rutilus Population*

The "b" value indicates the body shape of the fish according to the conditions. When the "b" value is > 3, the fish are in the form of a short blunt (Atay, 1989). At the same time, the value of "b" can give an idea about the nutritional capacity of the environment in which the fish live (Ricker, 1975). In this case, the "b" values found for the population are quite parallel to the "b" values found by Libosvarsky and Saeed (1983) and Rincon and Lobon Cervia (1989), and the resulting values show that the fish are well adapted to the environment.

The "r" value in the length-weight equations is the correlation coefficient that indicates the degree of relationship between the lengths and weights of the sexes (Altındağ, 1996). As can be seen in Table 3.7, the "r" values found for the population show parallelism with the "r" values found by Libosvarsky and Saeed (1983), and from these data, it was observed that both sex groups have similar physiognomy, Also, males and females of the same height have the same physiognomy. It could be said that they have a similar average weight.

3.4. Condition Factor

Condition factor (K) values calculated from the roach population are given in Table 4 according to age and sex. The mean Condition factor of the population was 1.54±0.02, and it was calculated as 1.50±0.03 for males and 1.57±0.02 for females. The difference between males and females according to age was significant in age group V, and it was higher in males

($p < 0.05$). It is thought that this may be due to the fact that the rate of male individuals who have reached sexual maturity in this age group is higher than the rate of female individuals.

Since the condition value means the ratio of length to a certain amount of weight, it can also be considered as a measure of the fish's adaptation to the habitat in which they live. Because length and weight are criteria that can show the effect of habitat on fish (Şevik, 1993). The condition factor varies according to age, gender and seasons in a population (Atay, 1989). Şevik (1993) found the Condition value of Capoeta trutta to be between 1.453 and 1.676. Çetinkaya (1992) found the average Conditioning coefficient of C. carpio to be 1.541 ±0.029. Condition factor values found for the Rutilus rutilus fish population, which is a member of the Cyprinidea family, showed parallelism with the condition factor values of the two Cyprinidae family species (Capoeta trutta and C. carpio) and the values found by Ekmekçi (1996) and Altındağ (1996).

Considering the condition factor values found in the population according to age, it is seen that there is an increase depending on age. This situation gives us the impression that the population adapts to the habitat it lives in. The research was carried out during the breeding season. So, the reason for the low at age for VII was thought to be due to the fact that the individuals belonging to this age group have ejaculated their eggs or sperm.

Table 4. *Condition Factor by Sex and Age for Roach*

	Male + Female		Male		Female	
Age	N	$\bar{K} \pm Se$	N	$\bar{K} \pm Se$	N	$\bar{K} \pm Se$
3+	38	1.56±0.03	15	1.49±0.03	23	1.56±0.01
4+	102	1.53±0.02	38	1.45±0.04	64	1.34±0.03
5+	13	1.55±0.12	3	1.86±0.55	10	1.45±0.04
6+	5	1.75±0.13	2	1.64±0.20	3	1.82±0.19
7+	2	1.27±0.14	2	1.27±0.14	0	
Total	160	1.54±0.02	60	1.50±0.03	100	1.57±0.02

3.5. Carcass Yield and Proportional Head Weight

The carcass and head weights of the caught fish were determined and their ratios to the total weight are given in Table 5. The distribution of meat yields by gender is presented in Table 6. The proportional head weight was found to be 15.45% on average, it was higher in the first years and gradually decreased in the advancing ages. This is an expected result, and head weight decreases proportionally with age in all living things (Nikolsky and Birkett, 1963).

Table 5. *Carcass Weight and Head to Total Weight Relativity in Roach Population*

Age Group	Carcass (%)	Head (%)
3+	62.47	16.67
4+	60.99	16.63
5+	59.39	15.69
6+	66.05	14.51
7+	69.90	13.73
Mean	60.89	15.45

Proportional carcass weight was calculated on average as 60.89, 65.17 and 58.45 for overall, male and female, respectively (Table 6). The differences between the sexes were found to be significant in favor of males in the III, IV and V age groups (P<0.05).

Table 6. *Carcass Weight by Age Groups for Sampled Population and Both Sex.*

Age	Male + Female		Male		Female		P=0.05
	N	$\bar{C} \pm Se$	N	$\bar{C} \pm Se$	N	$\bar{C} \pm Se$	
3+	38	62.47±3.78	15	64.91±2.03	23	57.82±0.84	p<0.05
4+	102	60.69±0.98	38	64.83±1.02	64	58.31±1.20	p<0.05
5+	13	59.39±1.45	3	64.86±2.20	10	57.75±1.43	p<0.05
6+	5	66.05±3.16	2	71.75±0.54	3	62.25±3.90	p>0.05
7+	2	69.90±1.81	2	69.90±1.18	0		p>0.05
Mean	160	60.89±0.57	60	65.17±0.59	100	58.45±0.72	p<0.05

One of the most important evaluations of the economic feature of slaughtering fish is the determination of meat binding and yield (Akyurt et al., 1985). The findings obtained in this study show closeness to the values (Yıldırım, 1997) for Capoeta tinca living in Oltu Stream, which are generally found to be 664.75, 9664.74 and 664.86% in males and females, respectively, while Şevik (1993) and Karataş (1995)' s *Ch. regium* and *Capoeta trutta* were lower than the values they calculated (71.105 and 70%). When the values in Table 6 are examined, the proportional increase of carcass weight according to age was due to the fact that the weight growth is higher in older fish, and this is an expected result.

4. Conclusion

Population characteristics of *Rutilus rutilus* living in the Karasu Stream located in Iğdır Plain and some physico-chemical properties of this water were studied between March, 1997 and July, 1997.

Since all the water samples were taken about the spring, the water temperatures were not affected by the ambient temperature values (9.5-32.0 °C) and the mean temperature of the water was determined as 16.8

°C. Water pH ranged between 6.96 and 7.73 with an average of 7.35. French Water Hardness values ranged between 25.0 and 46.1 (31.25 on average). Ca, Mg, CaCO3, organic matter and conductivity in water were; 63 mg/l, 25.32 mg/l, 239.25 mg/l, 1.50 mg/l and 895 µmhos/cm respectively.

The distribution of age in population varied between III+ and VII+, the number of age group IV+ was observed to be higher than that of other age groups. The population was made of 37.5 % males and 62.5 % females and the differences between sexes were statistically significant ($p<0.05$). The mean fork length and the mean body weight of examined 160 individuals were 13.42 cm and 43.4 g respectively. The differences between sexes according to ages groups for fork length were not statistically significant ($p>0.05$), weight was statistically significant in the age group of III+ ($p<0.05$). The Length-Weight relationship of population was calculated by least squares method and the logarithmic equation was found as LogW= 1.036+3.203xLogFL (Fork Length). The mean condition factor of population was found as 1.54, and differences between sexes were statistically significant on the behalf of the males at the age of VI+ ($p<0.05$). Meat yield of individual was determined as 57.17 % in males and 58.45 % in females, and the differences between sexes were statistically significant ($p<0.05$). The relative head weight for population was determined as 15.45 %.

Below are some suggestions that may be useful to those who want to deal with the subject in the future:

Since the water temperature of the study area does not fall below 15 °C in any season, naturally it does not seem suitable for the trout to live (as it does not allow egg hatching). However, successful trout farming can be done by culture from the fingerling stage onwards. However, in order to reach more definite judgments, water samples should be taken and examined for at least one year. The fact that the research area is located in a sensitive area is one of the most important reasons that prevent obtaining more extensive information about the roach population. Therefore, researchers who want to study this fish population in the future should go for a larger number of samplings in a larger time, taking into account the fishing method. When the Rutilus rutilus species was evaluated in terms of meat yield, it was found to be at a normal level among other species belonging to the Cyprinidae family. However, the values found for % carcass weights are the meat yields with awn, and for the accurate determination of the economic value of the roach, the yield of boneless meat should be determined. During the study, *L. lapidus* and *Carassius carassius* species were also caught, in addition to the common roach, and it is recommended to study these two species living in this region in the future.

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Chapter 6

MARINE BIOMATERIALS AND THEIR APPLICATIONS

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1. INTRODUCTION

In today's world, the problems brought by advancing technology such as population growth, diseases, global warming, and pollution have led to the search for new and different materials that are sustainable, easy to process, nature-friendly, and quickly obtainable both in the industrial field and in the field of science(Wan et al., 2021). Studies conducted for centuries have revealed that the raw materials that support the industry obtained from terrestrial systems (Mahendiran et al., 2021; Insuasti-Cruz et al., 2022). However, the increasing and renewed needs, the lifestyle that has been moved to the advanced technologies platform that the existing raw materials do not respond to, and jumping in size have searched for new raw materials essential (Wan et al., 2021). In this context, marine organisms; has the potential to respond to agriculture, pharmacy, medicine, environment, space, biomedical, and newly developing advanced technologies. Because it is predicted that biomaterials comply with the newly sought blue bio-economy criteria such as structure, function, diversity, and sustainability (Nekvapil et al., 2019; Binnewerg et al., 2020; Araujo et al., 2021).

At the beginning of the problems waiting for the solution within the framework of the integrated approach of the European Union to bio-economy; environment and climate change, pressure on natural resources, and sustainable management of renewable resources(Araujo et al., 2021). At the global level, problems such as maintaining competitiveness in the economy and science, creating economic growth and employment, reducing dependence on energy security and fossil fuels, and food security come to the fore(Bell et al., 2018).

With this review, in developing a strategy within the scope of the bio-economy, in particular, the blue bio-economy; 1. Smart growth (knowledge and innovation-based economic growth), 2. Sustainable growth (greener, more resource efficient and more competitive economy), 3. The potential of marine biomaterials were evaluated by taking into account criteria suitable for the strategy such as inclusive growth (the economy providing high employment and social peace) (EC, 2010).

2. BIOMATERIALS AND MARINE BIOMATERIALS

Biomaterials are natural or synthetically prepared materials that can heal or replace an organ, tissue, or functional part of the human body(Park andLakes, 2007). Biomaterials science is the intersection of medicine, biology, chemistry, physics, and materials science and deals with the interaction of substances with biological metabolism(Ratner et al., 2004; Carvalho et al., 2021). One of the most interesting areas of modern science, the biomaterials market certainly has a significant opportunity for innovators. However, extensive research is required to develop new and innovative products at competitive prices(Basu, 2017. In parallel with the developing technologies, the problems waiting to be solved cannot be fully solved with the existing materials (Balagangadharan et al., 2019). Marine biomaterials, which have been suggested as a potential use in many industrial areas, have traditional uses such as medicine, pharmacy, and medicine, especially in recent years. In addition to these, in recent years, there has been a tendency to shift to biomedical fields that include advanced technologies such as genetics, Nano medicine, biomechanics, biomimetic, biotechnology, controlled drug release and delivery, biomolecular machines, textiles, biomedical imaging, space technologies(Ehrlich et al., 2013; Jana et al., 2020; Nayak et al., 2022).

Marine biomaterials have a wide applicability potential in many industrial areas due to their non-cytotoxic properties, biodegradability, and biocompatibility (Binnewerg et al., 2020; Nayak et al., 2022). Because of the stereochemical properties of marine biomaterials, they can be modified and antioxidant, anticoagulant (Nayak et al., 2022), anticancer (Oliveira et al., 2020), antimicrobial, anti-allergic, anti-adhesive (Jana et al., 2020), anti- Having biological properties such as angiogenic and anti-inflammatory is one of the reasons why it is preferred for different industrial areas (Kim, 2013). Especially in functional product development processes, its structure, bioactivity, and physical properties offer a high usage area, especially in the biomedical field. The first use of marine biomaterials began with the extraction of holothurin from marine organisms in 1967, which was used experimentally as an anti-tumor agent in in vivo cancer models. (Wan et al., 2021; Sharifian et al., 2022). This process has spurred intensive research on marine biomaterials as four major discoveries. In the first phase, studies include coral bone graft substitutes, in the second phase polysaccharide-based polymers, in the third phase the use of collagens in tissue regeneration. Finally, marine-derived composites constitute the fourth stage of development of marine-derived biomaterials. At this stage, advanced approaches such as nanotechnology and three-dimensional (3D) printing are used. (Wan et al., 2021).

3. CLASSIFICATION OF BIOMATERIALS

Biomaterials divided into two groups natural and synthetic according to their origin. Ceramics are handled in four groups metals, polymers, and composites (Parida et al., 2012; Biswal et al., 2020). It can be used to create functional biomaterials that can be developed with biochemical, biophysical, or biomechanical signals as needed (Srivastava et al., 2015;Ehrlich et al., 2019). In this study, biomaterials of marine origin discussed (Figure 1).

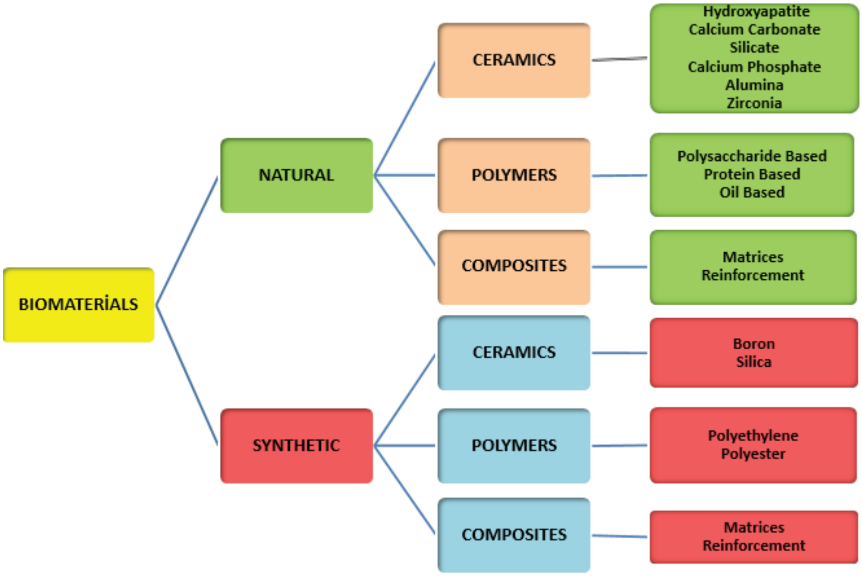

Figure 1. Classification of Biomaterials by Origin

3.1. Natural Biomaterials

Technological developments and marine materials with rich biodiversity are natural resources that offer important opportunities for the development of new medicinal products. Natural biomaterials have certain structures and properties compared to synthetic materials (Oliveira et al., 2020; Nayak et al., 2022). It has many different and functional uses depending on its rich biochemical structures (Srivastava et al., Ehrlich et al., 2019). Natural biomaterials divided into four groups: ceramics, polymers, metals,and composites.

3.1. A. Ceramics

Recently, marine products, such as ceramics, whose structure is similar to bone, are used in medicine and engineering due to their surface chemistry, bioactivity, and unique bone-binding properties. Because these biomaterials are important raw materials for bone replacement (Silva et al., 2012; Diaz-Rodriguez et al., 2019). The bone matrix structure consists of hydroxyapatite Nano crystals and collagen fibers. Therefore, synthetic Nano-hydroxyapatite (nHA) mimics the inorganic phase of bone tissue and creates a natural environment for the bone cell osteoblast (Pallela et al., 2012; Mondaland and Dey, 2016). Some biomimetic ceramics can also be used as therapeutic molecules, providing glass antibacterial activity. Some examples of ceramic materials found in marine environments include calcium phosphate, hydroxyapatite, and bioactive glasses. Hydroxyapatite (HA), tricalcium phosphate (TCP), and bio glass ceramics are widely used in bone tissue repair applications (Granito et al., 2017; Lalzawmliana et al., 2019). Due to their thermal stability, mechanical strength, biocompatibility, and similarity to bone tissues thanks to the inorganic components in their content, ceramics are biomaterials with increasing application areas in bone and dental surgery, generally within the scope of tissue engineering (Silva et al., 2012; Diaz-Rodriguez et al., 2019). Ceramics can be classified as non-absorbable/inert (Alumina, zirconia, silicon nitrides, and carbons) and absorbable/non-inert (calcium phosphates and calcium aluminates) (Silva et al., 2012; Vallet-Regi, 2001)

Bioceramics can be obtained from five main sources in the marine environment. These are Corals, Sponges, sea urchins, Mollusk shells, fish bones, and algae (Silva et al., 2012; Mondaland and Dey, 2016; Diaz-Rodriguez et al., 2019).

Corals, which are invertebrate sea creatures; Because of their biocompatibility and skeleton, they have been used in humans since the 1970s for bone grafting, spinal fusion (Damien et al., 2004; Yahia et al., 2021), maxillofacial surgery (Nandi et al., 2015), dental surgery (Supova, 2014) and other orthopedic applications. Corals can form mechanical bonds due to their large porosity, thus allowing the implant to grow into the blood vessels to supply blood to the bone. Despite having these important features, one of its main disadvantages is that it destroys coral reefs, which represent an important ecosystem for the conservation of marine life and biodiversity (Supova, 2014)

Sponges and sea urchins; In vitro and in vivo studies have shown that they can be a new source of bioactive ceramics for tissue engineering and medicine (Barros et al., 2014). Mollusks; Molluscan shells such as snails, which are abundant in the marine environment, have unique properties in obtaining biomaterials. Snail shells are one of the important sources of hydroxyapatite due to the CaCO3 structure they contain (Miranda-Hernandez et al., 2018).

Fish bones; the chemical composition of fish bone varies with the season, size, and age of the fish. However, it mainly consists of calcium phosphates (HA, β-tricalcium phosphate), non-collagenous protein, type I collagen, and water (Toppe et al., 2007). Bones are composed of 30% organic compounds and 70% inorganic substances by weight (Aydin et al., 2021). Fishbone is shown as an alternative biomaterial source for Hydroxyapatite (HA), which has good biological activities, and is non-toxic (Terzioğlu et al., 2018; Maidaniuc et al., 2020). Unlike commercially expensive synthetic hydroxyapatites, fish bones are natural and inexpensive ceramic resources derived from fish waste (Ozawa and Suzuki, 2002). Hydroxy appetites, which have chemical properties similar to the mineral composition of bones, are one of the most popular ceramic materials used in biochemical research and medical applications related to orthopedics, bone implants, dental care, and plastic surgery (Nam et al., 2019). Industrial use of fish bones in this way will also contribute significantly to reducing pollution (Ozawa and Suzuki, 2002; Aydin et al., 2021). In addition, fish bones are a natural source of P and Ca. It is a natural source of HA, which can partially convert to β-tricalcium phosphate (β-TCP) when calcined above 600°C (Ozawa and Suzuki, 2002; Aydin et al., 2021).

Algae; the potential for synthesizing red macroalgae as a more environmentally compatible hydroxyapatite (HA) product when processed under low-pressure conditions has been demonstrated (Walsh et al., (2008) For example, using different techniques to develop calcium-phosphate particles of Coralline officials red algae in bone filling and tissue engineering scaffolds applications. (Oliveira et al., 2007) Algae provide important opportunities in tissue engineering by forming composite materials as well as being used alone. The addition of *Sargassum vulgare* algae powders into poly-lactic acid shows superior cell interaction with human osteoblasts. Thus, it has been suggested that it has appropriate potential in biomedical applications such as bone tissue engineering, especially in dentistry and orthopedics (Reichstein et al., 2021).

3.1. B. Polymers

a. Protein-based polymers

Proteins, biologically produced, are the most important biopolymers of life with their unique functionality and constitute about half of the dry weight of living cells. Proteins; It can be found in different forms such as collagen, gelatin, elastin, and actin. Marine protein-based polymers attract the attention of both researchers and various sectors with their newly discovered uses for many industrial disciplines and show promise for advanced technologies (Khrunyk et al., 2020). Due to the absence of possible human pathogens in marine biomaterials, some of them (i.e. collagen, gelatin, and keratin) have become an alternative source of long-established biopolymers in medicine and cosmetics (Khrunyk et al., 2020).

Collagens are among the most studied proteins because of their important functions in mammals, including humans (Ehrlich et al., 2018). Collagens can be obtained from different sources in the marine environment. Marine collagen is obtained by extraction from different sources such as fish or invertebrate marine animals such as sea sponges or jellyfish. Although the total weight of the fish varies according to the species, parts such as skin, bones, fins, head, intestines, and scales, which constitute approximately 75%, are discarded and cannot be evaluated. However, it is possible to achieve a significant increase in economic value by obtaining high-value-added materials such as collagen from these wastewater products. Collagens have different subtypes. Type I collagen is obtained from the bones, skin, and scales of fish. It is also obtained from the skin of cephalopods and jellyfish (Senaratne et al., 2006). Type II Collagens are obtained from the cartilage of sharks and jellyfish. Type IV Collagen can be obtained from sea sponges (Pallela et al., 2011; Silva et al., 2014).

The removal of all fats from the tissue during collagen production makes marine collagen odorless and tasteless, making its use attractive. In parallel with advanced technological developments, an increasing number of biomimetic composites based on marine-derived collagen are being developed and exhibit very promising properties. Also rich in hydroxyproline, an essential amino acid for skin, blood vessels, and other connective tissues, marine collagen is making it attractive for a variety of uses in cosmetics, functional food, and tissue engineering.

Keratins represent the largest subgroup among all intermediate filament proteins. It is the most common and the most important biopolymer that provides the outer covering for humans and animals (Sarma, 2022). These structural proteins are mechanically robust and chemically non-reactive because they are cross-linked by cysteine disulfide bonds (Ehrlich, 2014). In general, keratins exist in two different forms depending on the type of tissue. Soft tissues contain α-keratin, while hard tissues contain β-keratin (Khrunyk et al., 2020). Keratin has various functions such as waterproofing, excretion of wastes, regulation of temperature, and buffering to protect deep tissues against mechanical shocks in structures consisting of skin and appendages such as hair, nails, feathers, hooves, and scales (Ferraro et al., 2016).

Keratins are obtained from the shells of sea turtles, the feathers of seabirds, whales, and structures secreted by hagfish during stress (Ehrlich, 2014). Due to its poor solubility and difficult extraction methods, the use of keratin has so far been limited. However, to expand its usage areas, it has been focused on cells and their behavior on keratin-containing films. Keratin films have also been proposed for ocular surface reconstruction due to their good corneal biocompatibility and transparency (Ehrlich et al., 2018).

Gelatin is a multifunctional ingredient used as a gelling agent, stabilizer, thickener, emulsifier, and film former in foods, medicines, cosmetics, and photographic films (Boran and Regenstein, 2010). Gelatin can act as a cell carrier in repairing tissue damage. In addition, due to its gel-forming properties, sea gelatin, yogurt, ice cream, jam, cream cheese, marshmallows, etc. It is also used in the food industry as a stabilizer, texturizer, thickener, and foaming agent in products. Gelatin inhibits peroxidation and prevents food spoilage by acting as an outer protective film against dehydration, oxygen, and light. Sea gelatin is also widely used in the encapsulation of temperature-sensitive water-soluble vitamins (B group and C vitamins) and other nutrients (Ehrlich et al., 2018). Gelatin obtained from mammals such as pigs and bovine hides accounts for 46% of the world's gelatin supply. Bones (23%) and hooves (29%) follow these sources. The gelatin obtained from marine resources constitutes only 1%.

The fish processing industry produces a significant amount of by-products and waste when producing fish fillets because the product yield is only between 30-50%. Moreover, these wastes and by-products are very rich in gelatin protein. However, to date, the use of fish gelatin in the food industry is quite limited compared to mammalian gelatin. The main reason for the less use of fish gelatin is weaker gelling ability (Rather et al., 2022). The increase in the halal food and additives market in recent years has led researchers to search for alternative, new, halal gelatin sources. In this context, fish and poultry by-products offer significant potential for the gelatin market (Rakhmanova et al., 2018).

b. Polysaccharide-based polymers

It has been found that the seafood industry produces large volumes of waste products consisting of shrimp shells, fish bones, fins, skin, guts, and carcasses (Nag et al., 2022). The use of wastes from the fishing industry in the production or consumption process is not a common enough practice. Since a large percentage of these wastes are thrown directly into the environment without prior treatment, it causes a great waste of various nutrients and causes serious environmental problems (Nag et al., 2022). In fact, such wastes are sources of raw materials containing very useful large amounts of lipids, amino acids, proteins, polyunsaturated fatty acids, minerals, and carotenoids that can be used to manufacture bio-compounds. Chitin and chitosan have an important place among these potential raw material sources (Santos et al., 2020; Nag et al., 2022).

Chitin;

Although chitin is the second most abundant renewable polysaccharide in biomass after cellulose, it is the most abundant natural biopolymer among nitrogen-carrying polymers in nature (Özdemir, 2014; Hajji et al., 2014). Chitin can generally be obtained from the exoskeletons of terrestrial insects and aquatic crustaceans such as crabs, shrimps, and lobsters, marine diatoms, algae, and fungi (Roberts et al., 1992; Regionn et al., 2016). In addition to these, Squid is another important source of chitin. The β isomorph is the source of chitin, which shows higher solubility, higher reactivity, and higher affinity for solvents and swelling than α chitin found in other organisms (Hajji et al., 2014).

Despite the abundance of chitin, it is an underutilized resource. However, recent developments in chitin chemistry have shown that it has a high potential to be used in various fields as new functional material (Kumar et al., 2000; Nessa et al., 2010; Santos et al., 2020) (Figure 2).

Figure 2. Chitin obtained from crayfish (Pontastacus leptodactylus) shell

Chitosan;

Chitosan is one of the chitin derivative products that can be obtained by N-deacetylation (Novikov et al., 2020). The degree of deacetylation expresses what percentage of the acetyl groups in the chitin chain structure are reduced (Santos et al., 2020). Compared to the chitosan kit, it finds more widespread use due to its easier processing properties. It also has biological properties such as biocompatibility, biodegradability, and non-toxicity to living cells (Nessa et al., 2010). chitin and chitosan; It is widely used in the industrial field due to its unique features such as being a natural resource, biodegradable, bioactive and not causing environmental pollution, being compatible with both plant and animal tissues and not having any toxic effects, being a biologically functional compound, and being able to change its molecular structure. (Nessa et al., 2010; Santos et al., 2020).

Chitin and Chitosan are used in various fields. While chitin is mostly used in agriculture and pharmaceutics, chitosan is used in pharmacy (controlled drug release), food (stabilizer, gelling agent, binder), cosmetics (protection of skin moisture and oral health), agriculture (controlled release), tissue engineering (renewal of damaged tissues), antimicrobial agent. In addition, it makes it possible to use it as a functional feed additive in water treatment (removal of toxic metals, oils, and heavy metals) in aquaculture and in some biomedical applications (surgery suture, dental implant, and artificial skin) (Özdemir, 2014; Joseph et al., 2022; Liao et al., 2022) (Figure 3).

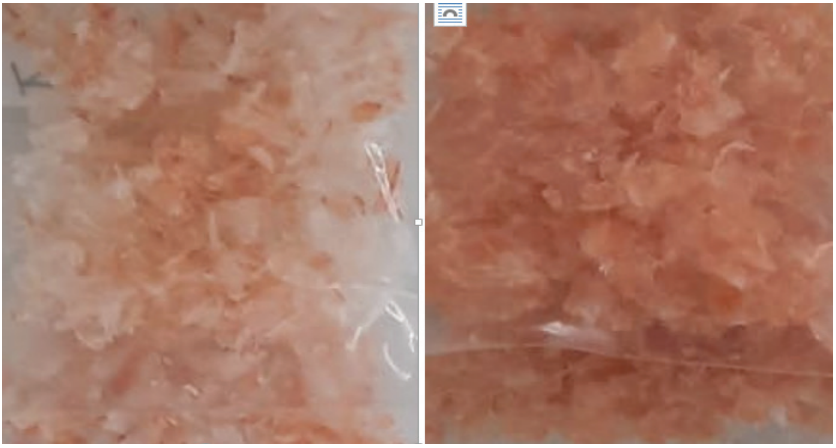

Figure. Chitosan obtained from different sources of crayfish (Pontastacus leptodactylus)

Algal-derived polysaccharides

Brown macroalga epolysaccharides;

Macroalgae are photosynthetic organisms that live in water and differ according to their cell wall composition (Dobrincic et al., 2020). Environmental factors such as sunlight, salinity, depth, water temperature, and nutrient availability are the main factors affecting the distribution, diversity, and chemical composition of macroalgae (Dobrincic et al., 2020). Macroalgae are divided into three groups according to their pigmentation and chemical composition: brown (Phaeophyceae), red (Rhodophyceae), and green (Chlorophyceae) (Dobrincic et al., 2020). The biological potential of algae is largely due to the polysaccharides it contains. The structure and composition of algal polysaccharides (APS) vary according to algae species.

In recent years, studies on polysaccharides such as laminarin, alginate, and fucoidan with high potential obtained from brown algae used in biological applications in functional foods, cosmetics, and pharmaceutical products have increased. Laminarin is mainly isolated from brown algae species Laminaria and Alaria, and it constitutes about 22-49% of algae dry matter depending on various factors. Since laminar shows anti-metastatic effects, it has been stated that it can potentially be used in the treatment of cancer (Sharma et al., 2021).

Alginates, Microcystis, Laminaria, and *Ascophyllum* sp. It is obtained from the cell walls of various brown algae living in colder seas such as it may also be present in the form of alginic acid, which constitutes approximately 40% of the dry matter of the algin biomass, and in the form of its salt (Dobrincic et al., 2020). Some alginates show higher viscosity according to their properties, while others show better gelling ability.

Studies have reported that alginates prevent the absorption of heavy metals in the body and are effective in lowering blood pressure and cholesterol. It has been suggested that alginates with higher molecular weights can be used in the treatment of diabetes. In addition, studies have shown that alginates have anticarcinogenic and antibacterial properties (Sharma et al., 2021). Because of all these properties, alginates are widely used as stabilizers, emulsifiers, or thickeners in the food industry, cosmetics, and pharmaceutical industries (Figure 4).

Figure 4. Alginate feom Cystoseira barbata (a) and Sargassum vulgare (b)

Fucoidan is a sulfated polysaccharide found in the fibril tissue of the cell wall and the intercellular space of brown algae (Senni et al., 2006). It is most abundant in the orders Laminariales and Fucales. Depending on the algae types, the dry matter of the algae ranges from about 5% to 10%, while the sulfate content ranges from 5% to 38% (Dobrincic et al., 2021). Fucoidan, one of the most researched algal polysaccharides, has been proven to have many positive effects such as antioxidant, anti-inflammatory, and antitumor effects (Fitton et al., 2015). The biological activities of Fucoidan vary depending on its physicochemical properties. Apart from these properties, it is being investigated as a heparin-like anticoagulant and antithrombotic agent, and as a functional additive in drug delivery systems and functional foods development due to its non-toxicity and biodegradability. Marine APS has the potential to be used in functional foods, cosmetics and pharmaceutical industries due to biological activities (Barbosa et al., 2019).

Green macroalgae polysaccharides

Ulvan;

In particular, algal biomass, which is abundant and underutilized in eutrophic coastal waters, constitutes a great potential resource for low-cost renewable polymers such as ulvan (Tang et al., 2021). Ulvan is obtained from the cell walls of the green marine algae Ulvales, Ulva, and *Enteromorpha* sp. (such as *U. lactuca*, *U. Rigida*, *U. armoricana*, and *E. linza*), as a water-soluble sulfated polysaccharide. Ulvan mainly consists of four monosaccharides including rhamnose, xylose, glucuronic acid, and iduronic acids (Tang et al., 2021) and exhibits various biological activities depending on its structure (Tziveleka et al., 2019).

In addition to being used alone, Ulvan can be designed for biomedical applications by forming composites with other materials (Tziveleka et al., 2019). With these unique structural properties, the wide spectrum of biological activities exhibited, and tunable physicochemical properties, there has recently been increased interest in ulvan as a promising material for applications in the food, pharmaceutical, chemical, and agricultural industries as a functional feed additive in aquaculture (Tziveleka et al. al., 2019; Harikrishnan et al., 2021; Tang et al., 2021).

The yield and specific composition of Ulvan polysaccharides, as with other algal polysaccharides, vary depending on the specific species, environmental factors, harvest season, and extraction method used (Tziveleka et al., 2019) (Figure 5).

Figure 5. Ulvan obtained from Ulva rigida

Red macroalgae polysaccharides

The red algae "Rhodophyta" is an important group of macroalgae containing approximately 7000 species, a rich source of structurally diverse bioactive compounds including protein, sulfated polysaccharides, pigments, polyunsaturated fatty acids, vitamins, minerals, and phenolic compounds of nutritional, medical, and industrial importance. (Ismail et al., 2020).The hydrocolloids galactans, carrageenans, and agars are polysaccharides, the main component of the red seaweed cell wall, with broad-spectrum therapeutic characters. They constitute approximately 40-50% of the dry weight (Ismail et al., 2020). Sulphated polysaccharides from red algae are environmentally friendly, and safe, and are commercially applied in the food and pharmaceutical industries as a useful ingredient as a thickening agent, stabilizer, emulsifier, tissue modifier, and dietary fiber. Of the red algae, Gracilaria spp., Pterocladia spp. Jania spp. and Corallina spp. Species with higher medicinal potential were studied intensively by researchers (Ismail et al., 2020).Although the high biodiversity in the marine environment offers a great opportunity as a drug source, drug sources have mostly been obtained from terrestrial organisms to date. (Ruocco et al., 2016).

Agar is a compound found in the cell wall of the red alga Rhodophyceae and forms their structures. The Agar Gelling part consists of a combination of two polysaccharides, agarose and non-gelling part agaropectin (Muthukumar et al., 2020). Red algae such as Gelidium, Gracilaria, Hypnea, and Gigartina are the main sources of agar (Rucco et al., 2016). Due to their easy availability and low cost, they can be easily converted into commercial products. They used as immune-enhancing nutraceuticals due to their rich biological properties (Muthukumar et al., 2020). Agar E406 used in the cosmetics, and food industry as a food additive and gelling agent, in the preparation of solid media for bacteria. In addition, it has widespread use in medicine and pharmacy (Rucco et al., 2016; Muthukumar et al., 2020).

Carrageenans are sulfated polysaccharides isolated from marine red algae linked by glycosidic bonds. The most commercially used carrageenans are κ-, ι-, and λ-carrageenans (Ghanbarzadeh et al., 2018). Carrageenan is one of the most researched sulfated polysaccharides in the cosmetic industry due to its physical and functional properties and antioxidant activity. In addition, its anti-aging and anticarcinogenic properties have been identified (Rucco et al., 2016; Ghanbarzadeh et al., 2018). Carrageenans constitute up to 50% of the dry weight in the species in the genus Kappaphycus, Hypnea, Eucheuma, Gigartina, and Chondrus from which it is extracted, Euchemacottoni and E. spinosum species are the most used for industrial production (Ghanbarzadeh et al., 2018).The gelling property of carrageenan has encouraged its use in many products such as skin lotions, toothpaste binders, and shaving foams (Rucco et al., 2016) (Figure 6).

Figure 6. Carrageen obtained from Corallina elongata

3.1. C. Composites

Multifunctional biomaterials obtained from seafood add innovations to modern materials science in many areas and offer many advantages in tissue engineering (Wan et al., 2021).

Composites are products obtained by combining two or more materials with different structures and properties to form a matrix phase and a reinforcement phase (Callister, 1991; Pellicer et al. 2017). The development of composite materials aims to produce materials with superior properties by combining the properties of the components under a single structure (Callister, 1991). Composite materials can be used not only in structural applications but also in electrical, thermal, and various other applications (Selvaraju and Ilaiyavel, 2011). Many composite materials consist of only two phases. It is called the matrix, one of which is continuous and surrounds the other phase, and represents the material that is often used as a component of polymers. Composite materials generally classified according to the type of reinforcement used. Composites are preferred because they contain materials that are stronger, lighter, and cheaper compared to conventional materials (Pellicer et al. 2017). In vitro studies have proven that scaffolds support biocompatibility and osteoblast differentiation at the cellular and molecular level, while in vivo studies have proven that scaffolds have an important role in promoting bone tissue regeneration (Choi et al., 2019).

The rich biodiversity of the marine ecosystem, material continuity, biocompatibility, and superior biomaterial properties in their mechanical behavior, forms, and application areas offer use in many fields that will form the future of modern materials science (Wan et al., 2021). Marine-derived biocomposites are materials with high potential for use in tissue engineering, dental surgeries, and drug delivery applications (Choi et al., 2019).

Especially in tissue engineering studies, the results obtained with the use of particle-reinforced composites to strengthen the mechanical properties of polymers such as polylactic acid (PLA) as a matrix are promising. When the research is examined, the use of marine algae in the development of composite materials has started to attract attention. Veziroğlu et al., (2021) studied a new composite patch on the effectiveness of "*Sargassum vulgare*" powders on osteoblast cells by mixing PLA. In this study, they reported that the prepared composites showed better cytocompatibility and higher proliferation properties than pure PLA. In addition, it can be used as both matrix and reinforcing filling material (cellulosic fibers) in the composite material studies of algae (Bulota and Budtova 2015). Here, especially in the composites developed for tissue engineering, the use of structural composites (such as Alginate, Fucoidan, Cellulose) and algae and algal polymers as matrices are among the important developments for obtaining functional biocomposites (Reichstein et al., 2021).

The high potential of marine-derived structures has shown that composites have the ability to promote osteogenic differentiation (Diogo et al., 2018). Different composite scaffolds were produced by freeze-drying and crosslinking mixtures of collagen obtained from shark (Prionaceglauca) skin and bioceramics obtained from shark (Isurusoxyrinchus) teeth (Diogo et al., 2018). Characterization of the resulting composite structures, it has been suggested that the developed composites can support the attachment and proliferation of osteoblast-like cells (Diogo et al., 2018). In another study, biomimetic mineralization of collagen shown to be an advantageous method to obtain resorbable collagen/hydroxy-apatite composites for application in bone regeneration (Hoyer et al., 2012). Hoyer et al., (2012) reported that the scaffolds exhibit interconnected porosity, are sufficiently stable under cyclic compression, and exhibit elastic mechanical properties. Human mesenchymal stem cells were able to adhere to the scaffolds, increased the number of cells during cultivation, and showed osteogenic differentiation in terms of alkaline phosphatase activity. These advantages have brought natural structural composites into focus as the demand for new, sophisticated, multifunctional materials has increased and they have undergone significant optimization through long processes of evolutionary selection and adaptation (Wan et al., 2021).

Composite materials have recently been created with more than two components. Three-component scaffold systems, specially prepared with natural materials of marine origin, are of great interest in bone tissue engineering applications today. Chitosan (Chi), hydroxyapatite (HAp) and sea sponge (*Ircinia fusca*) collagen (MSCol) derived from the bone of the bigeye tuna (*Thunnus obesus*) fish. A new scaffold containing (Chi-HAp-MSCol) was prepared using the freeze-drying and lyophilization method. Findings from the study indicate that the new Chi-HAp-MSCol composite scaffolds are promising biomaterials for matrix-based bone repair and bone augmentation (Pallela et al., 2012).

4. CONCLUSION

Although the current knowledge about marine materials and mechanisms is in its infancy, studies have shown that the seas are an enormous source of materials.Marine biomaterials are of particular interest as they may have novel properties as well as unique biochemical properties. In addition, the diversity of these materials and especially the potential of polysaccharides have been important raw materials in terms of forming complex structures with other polymeric materials, chemicals or salts. Advances in marine biomaterials research can be achieved mainly through strong interdisciplinary scientific partnerships and studies where they can be applied to practical fields. The structural properties of the materials used in these studies should be determined at the molecular and even nano level. In addition, while creating composite materials, studies to determine their interactions with each other should be increased. Therefore, more studies needed to evaluate both marine products and their wastes.

5. FUTURE PERSPECTIVE

Although the oceans and seas constitute approximately 70% of the world, the amount of biomaterials obtained from terrestrial sources is still quite high compared to marine sources. Every year, millions of tons of marine resources are obtained by hunting or aquaculture, some of them are consumed as human food, but the majority of them are transferred to the environment without being evaluated. While this situation poses a serious threat to the human environment, on the one hand, it also leads to the wastage of biomaterials with unique properties and high benefit. Awareness has arisen that the by-products of marine resources are no longer waste, but an alternative raw material source to synthetic analogues for many different sectors such as food, medicine, medicine, cosmetics, and biomedical. Because the pollution caused by microplastic wastes from synthetic plastic materials has led to a serious and global threat in the oceans. In addition, the market demand for marine biomaterials is increasing rapidly as they offer important opportunities to humanity in parallel with their rich biodiversity. Systemic use of marine biomaterials will reduce pollution, increase the use of natural resources, help create innovative products for high-profit commercial purposes, and contribute to reducing the use of synthetic polymers.

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Chapter 7

THE ROLE OF NITROGEN-FIXING BACTERIA IN SUSTAINABLE AGRICULTURE

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Introduction

Sustainable agriculture is an agricultural system that examines the impact of agricultural activities on each unit of the ecological cycle, based on protecting and managing natural resources. For this purpose, it aims to make agricultural production equally accessible to all people all over the world and to leave these opportunities to future generations. In order to achieve this sustainability, the planning and management of product variety, irrigation and the use of chemicals (fertilizers and pesticides) in agricultural production are key factors. The management of agricultural lands constitutes the highest proportion of sustainable agriculture. Agricultural land management must protect soil properties and soil biodiversity, taking into account adaptation to the effects of climate change (FAO, 2014).

Sustainable agriculture is gathered in line with three main purposes;

1. Environmental health
2. Economic profitability
3. Social equality.

These aims are focused on some agricultural methods that will ensure sustainability in agricultural production (Horrigan et al., 2002; Ryan et al., 2008; Kaspar et al., 2011; Galindo et al., 2020; Afshar et al., 2022).

- Crop rotation
- Cover crops
- No-till and low-till farming
- Soil management
- Diversity
- Nutrient management
- Integrated pest management
- Rotational grazing, etc.

The common point of agricultural activities is concentrated on soil organic matter. Soil organic matter is a feature that affects the physicochemical, mechanical, and biological properties of the soil, positively affecting soil health and blocking soil degradation (Aksakal et al., 2016; Sari et al., 2017; Kopittke et al., 2020). At the same time, many researchers stated that soil organic matter in agricultural areas decreased due to conventional agricultural practices (Guo and Gifford, 2002; Wei et al., 2014; Sanderman et al., 2017; Kopittke et al., 2017). Fossil fuels and soil organic matter contain about 5 times more carbon than the atmosphere and this accounts for 30% of the available carbon. At the same time, soil organic matter has a carbon-nitrogen ratio of 10/1 and contains a large part of the available nitrogen necessary for plants (Aiken et al., 1986).

Nitrogen in Sustainable Agriculture

Nitrogen (N) is a crucial component of soil fertility and productivity (Fang et al. 2018; Richard et al. 2018), but its uncontrolled and extravagant use can lead to environmental contamination and financial losses (Reddy et al., 2002). Incorrect or uncontrolled use of N causes serious environmental problems with the leakage of reactive N into surface and subsurface waters and the release of N (as N_2O) into the atmosphere (Glick, 2003; Galloway et al., 2003; Lassaletta et al., 2014; Lal, 2015). This situation is contrary to the philosophy and principles of the sustainable agriculture system, and it should be ensured that the nitrogen used chemically is converted in the most effective way in a controlled or where it is used (Li et. al. 2009; Lal, 2015).

Plants take nitrogen, which is vital for plants, as NO_3^- and NH_4^+ ions. (Britto and Kronzucker, 2013; Bloom, 2015; Cui et al., 2017).The nitrogen source of the plants is organic nitrogen (Tohumcu and Aydın, 2016; Bian et al., 2021), inorganic fertilizers (Fixen and West, 2002; Rothe et al., 2019; Stevens, 2019; Mahmud et al., 2020) and biological nitrogen fixation (Liu et al., 2019; Soumare et al., 2020) (Figure 1).

These nitrogen sources become suitable for plant use in the soil environment and/or are removed in many complex cycles. Many cycles occur, such as the formation of NO_3^- and NH_4^+ as a result of mineralization of organic matter; oxidation of NH_4^+ to NO_3^-, formation of N_2O and N_2 by NO_3^- denitrification; leaching of NO_3^- in the soil; removal of NH_3 by volatilization; uptake of nitrogen by plants; nitrogen into the soil by precipitation, transferring nitrogen to the soil by independently living microorganisms, fixing nitrogen in an organic way by microorganisms in the soil (Fowler et al. 2013; Rütting et al. 2018)..

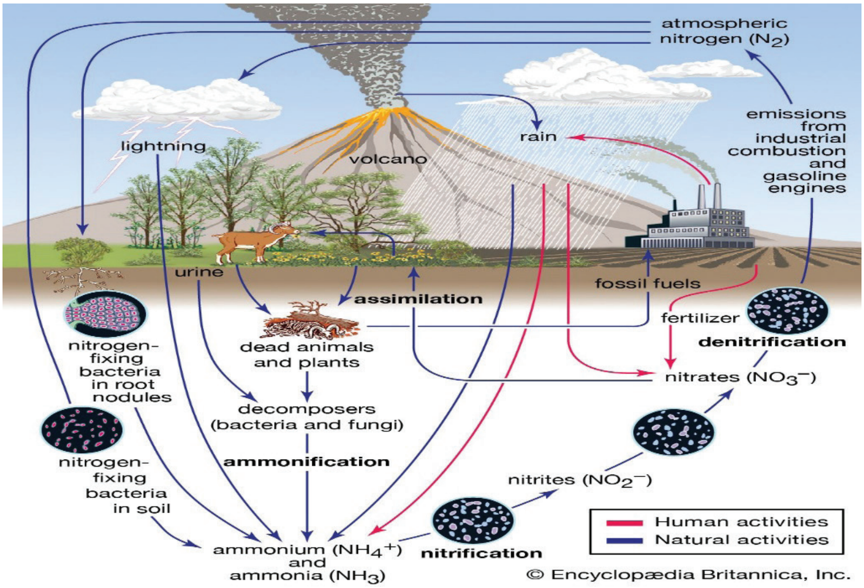

Figure 1. *Nitrogen Cycle (Anonymous 2022).*

These cycle processes are shaped as a function of soil properties, plants and microorganisms. 65% of the mineral nitrogen applied to the soil is lost in the soil and plant system by emission gas and erosion (runoff and leaching) (Rejesus and Hornbaker 1999). What is important in sustainable agriculture is the protection of mineral nitrogen applied to agricultural fields by human hands, by ensuring its effectiveness, apart from the natural cycle. First of all, it is suggested by many researchers to ensure the ergonomics of mineral nitrogen to be added to the soil system by making site-specific fertilization (Diacono et al. 2013; Li et al. 2019). This is exactly what is true in practice.

At the same time, the use of soil bacteria, which has positive effects on plant growth, as a source of biological fertilizer for sustainable, healthy agriculture is an important issue to be considered. With the widespread use of bacteria as a source of biological fertilizer, the consumption of chemical fertilizers can be reduced, the negative effects caused by the use of chemical fertilizers can be prevented, and a contribution to the reduction of production costs can be achieved. Experts evaluate the bacteria in the soil into two classes: beneficial and harmful. This classification was made according to factors such as bacterial functions, soil quality, plant health, plant growth, and yield. From this point of view, when used correctly, bacteria are effective in the healthy development of plants, increase in yield and control of harmful organisms.

Biological nitrogen fixation for sustainable agriculture

Biological nitrogen fixation emerges as the main source of nitrogen needed by field crops and as a key process on earth in the development of sustainable agriculture (Castro et al., 2016). In addition, the nitrogen provided by biological nitrogen fixation is more environmentally friendly than the nitrogen to be applied chemically, and it also prevents a great loss of expense. Therefore, it is a complementary element for sustainable agriculture (Ritika and Uptal, 2014; Rashid et al., 2015; Soumare et al., 2020). Davies-Barnard and Friedlingstein (2020) conducted a meta-analysis on biological nitrogen fixation on a global scale and stated that biological nitrogen fixation in terrestrial ecosystems ranged from 52–130 Tg N y^{-1} and an average of 88 Tg N y^{-1} in natural ecosystems.

Biological nitrogen-fixing bacteria are classified as symbiotic bacteria, associative symbiotic bacteria and free-living bacteria. (Rashid et al., 2016).

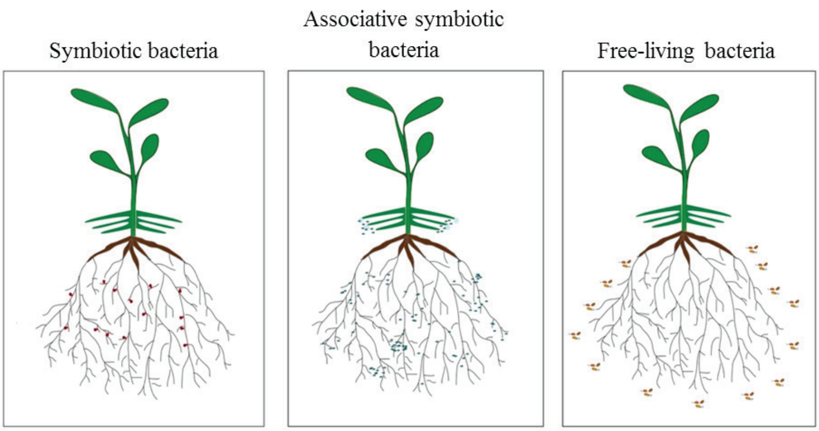

Figure 2. *Types of nitrogen-fixing bacteria (Pankievicz et al., 2019).*

When nitrogen-fixing symbiotic bacteria are mentioned, the first thing that comes to mind is *Rhizobium bacteria*, which live symbiotically with legumes (Bhattacharjee et al., 2008). These bacteria fix atmospheric nitrogen as well as promote the formation of nodules in plant roots (Liu and Murray, 2016; Htwe et al., 2019). Due to the symbiotic relationship of legumes with nitrogen-fixing bacteria, they meet the required nitrogen needs by binding atmospheric nitrogen to the soil (Rashid et al., 2015; Castro et al., 2016). It has been emphasized by many researchers that this relationship prevents excessive nitrogen use, nitrogen balance in the soil, greenhouse emissions (N_2O) and underground water leaching (Sawamoto et al., 2005; Lv et al., 2019; Qasim et al., 2021). Due to this feature of legumes, it has been stated that legumes should be included in different cultivation combinations such as rotation and mixed planting in sustainable agriculture (Li et al., 2018; Naseri, 2019; Shah et al., 2021).

Non-legume plants also contain nitrogen-fixing associative symbiotic bacteria (Dupin et al., 2020; Mahmud et al., 2020). The best example of N-fixing bacteria for non-legume plants is Cynobacterium *anabaena azollea*, which lives symbiotically with the *azolla* plant grown on the edge of the rice paddy fields. It is known that most of the nitrogen needs of rice fields have been met by these plants and bacteria since a thousand years ago (Wagner, 2011). Thanks to this bacterium, up to 600 kg N ha^{-} y^{-} of nitrogen can be fixed during the growing period (Postgate, 1982; Fattah, 2005). In addition, it has been discovered by research that there are many bacteria that are in symbiotic relationships with crop plants such as grain, corn, potato, forest areas and pasture plants and that make biological nitrogen fixation (McInroy and Kloepper, 1995; Yanni et al., 1997; Webster et al., 1997; Chaintreuil et al., 2000; Lupwayi et al., 2004; Castanheira et al., 2014; Richard et al., 2018).

Azotobacteria, which are free-living nitrogen-fixing bacteria, have the capacity to fix 25-40 kg ha^{-1} of nitrogen annually under aerobic conditions. In addition, bacteria such as *Chlorobium, Clostridium, Chromatium* and *Desulfovibrio* have been identified as nitrogen-fixing bacteria under anaerobic conditions. Azotobacter is used as fertilizer as it fixes atmospheric nitrogen (Rashid et al., 2016). At the same time, with the discovery of the existence of many microorganisms that support plant production, the subject of applying these microorganisms to different plants and areas by first isolating and then multiplying them has emerged. This gave rise to the term bio-fertilizer. In general, biofertilizers are defined as microbial preparations containing living cells of different microorganisms, which have the ability to convert the nutrients in the soil into suitable forms (Ritika and Utpal, 2014).

When applied to seed or soil, bio-fertilizers increase yield by 10-25% by improving nutrient availability without damaging the soil or the environment. Bio-fertilizers produce plant nutrients such as nitrogen and phosphorus in the soil or rhizosphere and make them accessible to plants As a result, bio-fertilizers have increasingly gained popularity as a result of the growing emphasis on maintaining soil health, reducing environmental pollution, and reducing the use of chemicals in agriculture, all of which will contribute to sustainable agriculture (Rashid et al. 2016). Bacteria such as *Azolla pinnata*, *Rhizobium spp., Azotobaster chroococcum, Azospirillum lipoferum, Acetobacter diazotrophicus, Derxia gummosa* are used in nitrogen-fixing bio-fertilizers (Ritika and Utpal 2014). Scientific research has shown that if these bacteria, which promote plant growth, are used as bio-fertilizers, they will contribute to an increase in plant production and yield (Garcia et al., 2015). Studies have shown that *Azotobacter* and

Azospirillum r*hizobacteria* cause significant increases in production. *Rhizobacteria* can be applied with seeds, or they can be applied to the soil surface or to the plant by foliar grafting methods. In addition, it has been observed that the use of biological and mineral fertilizers together with chemical fertilizers increases the effectiveness of chemical fertilizers (Cakmakci, 2005).

Conclusion

One of the most important production costs for agricultural production is fertilization. Nitrogen-containing fertilizers are the most commonly used fertilizers. Nitrogen plays an important role in the life of every living thing by being included in the structure of proteins. Nitrogen, which is found at the highest rate (78%) in the atmosphere, is also an element that is most frequently deficient in agricultural production. The way to use this resource in agricultural activities can be through biological nitrogen fixation. This is accomplished by nitrogen-fixing bacteria in the soil. The majority of nitrogen-fixing bacteria perform this process by establishing a symbiotic relationship with plants. However, in order for the nitrogen fixation to be carried out by the bacteria, there must be bacteria suitable for that plant in the environment. If there are no bacteria in the environment, it is necessary to transfer those bacteria to that area by grafting and applying it as a bio-fertilizer. Although these applications are not very common today, their importance is increasing day by day due to the increase in the world's protein needs and the environmental problems that arise during the production and use of mineral nitrogen fertilizers.

Adhering to the principles of sustainable agriculture, meeting the absolute necessary nitrogen for plant development and yield; Application of mineral fertilizers at site-specific doses, increasing the use of organic waste and fertilizers in agriculture, including legumes in plant rotation, using bio-fertilizers, using nitrogen-fixing bacteria are considered more environmentally friendly and sustainable.

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