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e-mail: gecekitapligi@gmail.com

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Chapter 1

AYVALIK VIRGIN OLIVE OILS: GEOGRAPHIC ORIGIN EFFECT ON VOLATILE CONSTITUENTS

Didar UCUNCUOGLU[1], Dilek SIVRI OZAY[2]

1 Dr. Öğr. Gör. , Cankiri Karatekin University, Faculty of Engineering, Department of Food Engineering, a.emir.57@gmail.com
2 Prof. Dr. , Hacettepe University, Faculty of Engineering, Department of Food Engineering,

1. Introduction

Sensory quality (colour and flavour) plays a promising role in the acceptability of foodstuffs for consumers. Particularly, flavour is a complex sensation consisting primarily of smell and taste, but it is complemented by tactile and kinaesthetic sensations. At the same time, flavour is vital in the control of food recognition, selection, and acceptance.

Virgin olive oil has special characteristics among the edible oils and important in the basic Mediterranean diet. It is extracted from the drupe fruit of the olive tree without a chemical refining process. Besides, it contains some minor compounds such as polyphenols and volatiles that give rise to a fragrant and delicate flavour desired by consumers. Phenolic compounds are mainly responsible for virgin olive oil taste; but, the presence of different or specific volatile/semi-volatile compounds gives rise to the exclusive aroma of virgin olive oil. That's why virgin olive oil commands mostly high prices on the market. A comprehensive knowledge of the generation chemistry of sensorial profile of virgin olive oil is therefore desirable.

The overall quality of olive oil is influenced by a great number of factors, in particular, the nature of the genetic cultivar and geographic origin. Hence, the European Community Council of Regulation published standards on olive oil production, such as Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI), concerning labelling giving the origin for virgin olive oils to avoid consumers being misled about their true characteristics and origin.

The quality classification of olive oil categories is mainly based on chemical parameters like free acidity as oleic acid percentage, peroxide value as meq active oxygen/kg oil or specific absorbance at 232, 266, 270 and 274 nm. However, discriminate olive oil premium quality we need advanced analysis. Some of these analyses are based on subjective methods or computer based. Many analytical procedures have been developed over recent years for explaining sensory profile objectively such as mass spectroscopy. Sensory analysis is of great importance inside the world of olive oil. According to the International Olive Council (IOC) declaration, positive and negative sensory attributes can probably be detected in virgin olive oil. Limited researches have established the relationships between volatile flavour compounds and how of these are effect sensory profiles of olive oil.

High qualified fresh extra virgin olive oils have an aroma profile mainly composed of volatile compounds (C6 and C5 aldehydes, alcohols, esters, ketones etc.) produced by biogenic pathways, for example, lipoxygenase (LOX) enzymatic pathway involving hydroperoxide lyase, alcohol acyltransferase, hydroperoxide lyase, alcohol dehydrogenase, acyl hydrolase that are heavily responsible for virgin olive oil basic green and fruity flavour.

Poor qualified or bad-processed olive oil usually shows much more complex profile like C3, C4, C7-C11 compounds. These compounds are responsible for virgin olive oil off-flavours and give rise to rancid, mustiness–humidity, winey-vinegary, fusty sensory defects. One of the main causes of sensory defects in virgin olive oil is the storage of olive fruits in piles before oil extraction; olives transpire during storage so that the temperature of the pile increases which favourite for the microorganisms. Hence, the microflora produces undesirable changes in the chemical composition of the volatiles.

Turkey is the third olive producer of the world. "Ayvalık" (Edremit Yağlık) is the eminent olive cultivar (*cv.*) which utilized for oil production in Turkey. Ayvalık cv. is a quarter of the olive trees in Aegean Region. However, this cultivar is more widespread in North Aegean Region; it was started to grown in other parts of Anatolia such as Antalya, Mersin, and Adana recently. Therefore, several researchers focused on "Ayvalık" oils quality and purity parameters. Classifying geographic origins of "Ayvalık" VOOs topic was examined before several researchers based on fatty acid profile and phenolic profiles. To the best of current knowledge, there was no research about geographical discrimination based on volatile profile and quality parameters of "Ayvalık" VOOs in Turkey. The main goal of this study was to contribute to the creation of a comprehensive "Ayvalık" VOOs database via examining chemical composition of VOOs harvested from 14 different growing areas in Northern Aegean region during three consecutive crop seasons. The volatile profiles of virgin olive oils are able to characterize it in relation to variety, degree of maturity, extraction system, and geographic origin. In the present study, gas chromotography coupled with mass spectrometric detector (GC-MS) and headspace solid-phase microextraction (HS-SPME) sampler was employed to define the volatile profile of extra virgin olive oils harvested from 14 different geographical areas of west Anatolia. There are as yet no data on the volatile composition of oils from these areas. It was also investigated that the effect of geographic origin on oils' chemical composition (quality parameters, fatty acid and volatile profile, oxidative stability).

2. Materials and Methods

The olive samples obtained from Ayvalik cultivars, were harvested from different locations of Turkey, namely Balikesir (Edremit, Gomec, Ayvalik, Havran, Burhaniye), Canakkale (Ezine, Ayvacik, Merkez), Izmir (Dikili, Bornova, Bergama) and Manisa (Kirkagac, Saruhanli, Akhisar) provinces, at early stages of maturation (maximum maturity index was 2.5), were collected during three consecutive harvest year (2013-2015) by hand-picking. The olive samples were immediately transported to the laboratory in the mesh-bags after harvest and the olive oils were extracted by a laboratory scale physical extraction unit (HAUS Centrifuge Technologies, Aydin, Turkey) including a crusher, a malaxer and a centrifuge without any delay. Malaxation process was performed for 30 min at 25°C. A vertical centrifuge (3500xg, 2 min) was used for solid-liquid phase separation. Samples were passed through cotton filter and stored at +4°C till analysis. Free acidity (as % oleic acid), peroxide value (as meq active O_2/kg oil), K_{232} and K_{270} values were calculated according to EEC regulations. L, a* and b* values was measured with Minolta Spectrophotometer (CM-3600d, Japan) as lightness, red-green and blue-yellow, respectively. Oxidative stability was measured with the Rancimat 743 (Metrohm, Basel, Switzerland) apparatus. Stability was expressed as induction (hour) time (AOCS Cd 12–57). ANOVA and Duncan statistical analysis was performed with SPSS 23 (IBM Statistics Inc. Chicago, IL). Fatty acid profile was determined according to IOOC method. Fatty acids methyl esters (FAMEs) were analysed by gas chromatography (GC; Thermo Scientific, Trace™ Ultra Gas Chromatograph, Waltham, MA, USA) equipped with a 100 m long capillary column (0.25 mm id, 0.20 µm film thickness) and a flame ionization detector (FID). All measurements were triplicated. The identification of individual fatty acids (%) was calculated by FAMEs mix standards peak area. Volatile compounds were determined using DVB/CAR/PDMS three phase fiber with SPME holder manual sampler and GC-MS (Thermo Scientific GC, DSQ II Series Single Quadruple GC/MS). The identification of volatile compounds was performed by comparing their retention time with NIST/WILEY library and mass isotope distributions. For qualitative characterization of volatiles as ppm, 4-methyl-2-pentanol internal standard was used. Statistical analysis was performed by SPSS (version 23, IBM SPSS Statistics Inc. Chicago, IL) statistical software and using One-way ANOVA method. Differences among all groups were determined by Duncan test at 95% confidence level.

3. Results

Free acidity, peroxide value, K_{232} and K_{270} absorbance, and fatty acid composition must be analysed for qualified the olive oil class such as "extra virgin" or "virgin" according to IOC. Overall chemical profile was given in **Table 1.**

3.1. Balikesir originated virgin olive oils

Free acidity (%) was calculated as 0.6, 1.0 and 0.5 among samples at three consecutive crop seasons. Peroxide value was determined as 15, 14 and 8 meq active O_2/kg oil, respectively. K_{232} value was measured as 2.3, 2.3 and 2.1; however, K_{270} value was calculated as 0.26, 0.38 and 0.16, respectively. L* was measured as 34.71, 32.70 and 31.36; a* was measured as 0.56, 1.30 and 0.86; b* was measured as 10.02, 8.68 and 14.62, respectively. Induction period was determined as 7.52, 7.49 and 6.52 hour, respectively. ΣSAFA content (%) was found as 20.06, 16.12 and 20.06 at three consecutive crop seasons. ΣMUFA content (%) was found as 62.30, 68.14 and 65.91, and, ΣPUFA (%) was found 17.55, 15.72 and 14.03, respectively.

3.2. Canakkale originated virgin olive oils

Free acidity (%) was meanly calculated as 0.4, 0.7 and 0.5 among samples at three consecutive crop seasons. Peroxide value was determined as 13, 11 and 8 meq active O_2/kg oil, respectively. K_{232} value was measured 1.95 in all harvest years; however, K_{270} value was calculated as 0.23, 0.20 and 0.14, respectively. L* was measured as 35.55, 32.70 and 31.08; a* was measured as 1.10, 1.12 and 0.79; b* was measured as 6.88, 10.92 and 6.18, respectively. Induction period was determined as 7.54, 6.20 and 7.95 hour, respectively. ΣSAFA content (%) was detected as 20.18, 15.85 and 20.15; ΣMUFA content (%) was detected as 62.69, 69.26and 64.97; ΣPUFA (%) content was detected 17.07, 14.86 and 14.87 during three consecutive crop seasons on average.

3.3. Izmir originated virgin olive oils

Free acidity (%) was calculated as 0.4, 0.8 and 0.5 among samples at three consecutive crop seasons. Peroxide value was determined as 9, 12 and 8 meq active O_2/kg oil, respectively. K_{232} value was measured as 2.4, 2.4 and 1.8; however, K_{270} value was calculated as 0.26, 0.20 and 0.12, respectively. L* was measured as 32.58, 36.34 and 30.65; a* was measured as 1.53, 0.16 and 1.04; b* was measured as 6.95, 11.18 and 6.54, respectively. Induction period was determined as 11.35, 4.11 and 7.07 hour, respectively. ΣSAFA content (%) was determined as 20.74, 18.11 and 17.17; ΣMUFA (%) content was detected as 61.65, 66.78 and 70.76; ΣPUFA content (%) was detected as 17.57, 14.75 and 12.05 during three consecutive crop seasons.

3.4. Manisa originated virgin olive oils

Free acidity (%) was calculated as 0.4, 0.3 and 0.6 among samples at three consecutive crop seasons. Peroxide value was determined as 8, 13 and 6 meq active O_2/kg oil, respectively. K_{232} value was measured as 2.2, 2.7 and 2.0; however, K_{270} value was calculated as 0.26, 0.45 and 0.13, respectively. L* was measured as 33.48, 35.60 and 31.48; a* was measured as 0.44, 1.21 and 0.92; b* was measured as 8.46, 11.48 and 7.30, respectively. Induction period was determined as 8.29, 9.05 and 6.79 hour, respectively. ΣSAFA content (%) was determined as 20.02, 18.55 and 16.60; ΣMUFA content (%) was detected as 62.67, 66.22 and 71.34, and, ΣPUFA content (%) was detected as 17.21, 15.22 and 12.05 during three consecutive crop seasons on average.

3.5. Determining Flavour Components

SPME-GC-MS technique was used for detecting volatile flavour compounds of virgin olive oils, by the way, 128 compounds were isolated at first crop season, 93 compounds were isolated at second crop season, and 166 compounds were isolated at third crop season.

Desired aroma compounds, which were mentioned at introduction part, gave positive notes such as green, cut-grass, fruity, flower, sweet, bitter almond, unripe or unripe banana, tomato and apple to virgin olive oils. These smell and tastes were caused by *E*-2-pentenal, *E*-2-hexenal, *Z*-3-hexenal, hexanal, 1-penten-3-one, hexyl acetate, *Z*-3-hexenylacetate, hexanol, 2-penten-1-ol, 1-penten-3-ol, *Z*-3-hexenol and *E*-2-hexenol volatile C5 and C6 compounds. These compounds all generate from LOX pathway. There was a significant difference ($p<0.01$) was detected between harvest seasons based on these LOX derivate components. So, flavour results were given at below based on harvest time.

At first crop season, many of detected volatile aroma components were generated from LOX pathway, in particular, C5 and C6 aldehydes (80.27%), ketones (91.32%), esters (25.00%) and alcohols (50.90%) in Balikesir sub-locations. It was found that C5 and C6 aldehydes were 63.24%, ketones were 90.21% and alcohols were 46.13% in Canakkale sub-locations. C5 and C6 aldehydes (90.33%), ketones (95.74%) and alcohols (42.14%) were also detected in Izmir sub-locations. C5 and C6 aldehydes (75.48%), ketones (80.65%) and alcohols (11.18%) were also detected in Manisa sub-locations. At second harvest season, C5 and C6 aldehydes was measured as 85.04%, ketones was measured as 25.35%, esters was measured as 66.67% and alcohols was measured as 71.60% in Balikesir. C5 and C6 aldehydes were measured as 79.21% and alcohols were measured as 71.02% in Canakkale. C5 and C6 aldehydes were measured as 82.94%, ketones were measured as 68.57% and alcohols were measured as 46.23% in İzmir. C5 and C6 aldehydes were measured as 82.30%, esters were measured as 100.00% and alcohols were measured as 32.61% in Manisa. At third harvest season, C5 and C6 aldehydes, ketones, esters and alcohols were detected as 73.93%, 23.06%, 26.46% and 53.43%, respectively, in Balikesir. C5 and C6 aldehydes, ketones, esters and alcohols were detected as 64.91%, 62.15%, 14.14% and 62.48%, respectively, in Canakkale. C5 and C6 aldehydes, ketones, esters and alcohols were detected as 76.83%, 57.24%, 7.46% and 54.51%, respectively, in Izmir. And finally, C5 and C6 aldehydes, ketones, esters and alcohols were detected as 86.54%, 75.01%, 12.81% and 75.99%, respectively, in Manisa.

Except those LOX derivate, it was isolated many chemical groups from studied samples as shown **Table 2**, **Table 3** and **Table 4**. These compounds can mostly generate during crushing and malaxation processes by enzymatic fragmentation of big organic compounds to small ones depending on genetic structure of Ayvalik cultivar and its geographic origin. It was also observed that basic statistically difference ($p<0.01$) was found between hydrocarbons such as terpenoids, for example, $C_{15}H_{24}$ hydrocarbons (copaene, zingiberene, curcumin, sesquiphelandrene, bergamotene, caryophyllene, funebrene, himachalene, valencene, muurolene, farnesene, cadidene).

Table 1. *Free acidity, peroxide value, K_{232} & K_{270}, colour indices, induction period and fatty acid profile of VOOs*

Parameter	BALIKESIR			CANAKKALE			IZMIR			MANISA		
	2013	**2014**	**2015**	**2013**	**2014**	**2015**	**2013**	**2014**	**2015**	**2013**	**2014**	**2015**
Free acidity (%)	0.6	1.0	0.5	0.4	0.7	0.5	0.4	0.8	0.5	0.4	0.3	0.6
Peroxide value	15	14	8	13	11	8	9	12	8	8	13	6
K_{232}	2.3	2.3	2.1	1.95	1.95	1.95	2.4	2.4	1.8	2.2	2.7	2.0
K_{270}	0.26	0.38	0.16	0.23	0.20	0.14	0.26	0.20	0.12	0.26	0.45	0.13
a*	0.56	1.30	0.86	1.10	1.12	0.79	1.53	0.16	1.04	0.44	1.21	0.92
b*	10.02	8.68	14.62	6.88	10.92	6.18	6.95	11.18	6.54	8.46	11.48	7.30
L	34.71	32.70	31.36	35.55	32.70	31.08	32.58	36.34	30.65	33.48	35.60	31.48
Induction period (hour)	7.52	7.49	6.52	7.54	6.20	7.95	11.35	4.11	7.07	8.29	9.05	6.79
ΣSAFA content (%)	20.06	16.12	20.06	20.18	15.85	20.15	20.74	18.11	17.17	20.02	18.55	16.60
ΣMUFA content (%)	62.30	68.14	65.91	62.69	69.26	64.97	61.65	66.78	70.76	62.67	66.22	71.34
ΣPUFA content (%)	17.55	15.72	14.03	17.07	14.86	14.87	17.57	14.75	12.05	17.21	15.22	12.05

Table 2. *Flavour Profile of Virgin Olive Oils (2013, %)*

Volatile group	BE	BG	BA	BH	BB	CE	CA	ID	MA
Aldehydes	47.50	52.90	48.49	40.16	28.08	25.46	27.08	55.04	29.42
Ketones	4.29	6.61	5.42	4.86	3.73	2.77	2.29	3.31	4.38
Esters	0.32	*nd*	0.50	0.23	0.00	0.37	2.44	1.48	0.71
Alcohols	22.16	12.01	8.94	12.27	26.42	13.84	10.46	10.50	21.92
Organic acids	5.56	6.34	5.54	2.31	3.32	3.51	12.03	1.69	5.52
Terpenoids	1.35	1.48	3.53	4.17	4.56	7.38	5.44	2.40	1.98
Aromatic hydrocarbons (benzenes)	0.32	0.54	0.50	3.82	14.66	2.21	3.87	0.85	6.51
Aromatic hydrocarbons (furans and pyrans)	1.99	4.05	3.53	1.62	1.24	2.21	6.88	3.17	0.99
Other hydrocarbons	16.52	16.06	23.55	30.56	17.98	42.25	29.51	21.56	28.57

nd: not detected

Table 3. *Flavour Profile of Virgin Olive Oils (2014, %)*

Volatile group	BE	BG	BA	BH	BB	CE	CM	ID	MA
Aldehydes	7.23	10.71	7.14	5.11	20.90	4.08	7.50	4.76	9.10
Ketones	1.58	0.67	0.34	4.15	*nd*	2.30	0.43	0.57	*nd*
Esters	0.05	0.10	0.06	0.17	0.23	0.04	0.02	0.39	0.05
Alcohols	10.28	13.83	12.13	48.76	4.08	13.29	8.05	21.35	1.15
Organic acids	0.29	0.42	8.92	0.00	0.08	0.03	0.70	0.33	0.53
Terpenoids	1.92	2.40	3.30	0.13	0.45	0.57	0.32	0,34	1.68
Aromatic hydrocarbons (benzenes)	5.43	6.23	29.77	25.45	6.81	1.64	2.56	8.16	0.20
Aromatic hydrocarbons (furans and pyrans)	0.22	*nd*	0.22	*nd*	0.08	0.06	0.09	*nd*	*nd*
Other hydrocarbons	72.99	65.65	38.13	16.24	67.38	77.99	80.32	64.10	87.30

nd: not detected

Table 4. *Flavour Profile of Virgin Olive Oils (2015, %)*

Volatile group	BE	BG	BA	BH	BB	CE	CA	IBO	IB	ID	MA	MS	MK
Aldehydes	30.46	26.49	37.95	26.54	20.87	64.04	42.93	21.20	35.77	23.06	54.17	47.45	42.65
Ketones	6.23	3.42	3.54	19.43	3.79	4.27	2.34	2.61	3.02	1.72	3.69	5.31	4.85
Esters	1.76	3.76	1.91	0.52	2.32	1.65	2.56	1.37	2.04	0.89	4.58	6.04	6.49
Alcohols	12.58	15.43	20.09	19.11	15.11	11.45	17.53	2.24	5.80	4.74	7.31	8.22	5.18
Organic acids	3.76	3.10	5.36	6.12	4.25	4.83	5.05	0.28	4.52	3.98	0.20	*nd*	0.74
Terpenoids	22.32	29.57	10.27	16.37	38.71	4.50	20.54	38.14	32.48	4.78	14.75	12.45	21.53
Aromatic hydrocarbons (benzenes)	1.34	1.60	0.91	1.63	1.82	3.53	1.48	1.10	4.45	4.59	4.03	5.24	5.67
Aromatic hydrocarbons (furans and pyrans)	*nd*	*nd*	*nd*	*nd*	0.27	1.15	0.62	*nd*	0.01	*nd*	1.02	0.87	1.48
Other hydrocarbons	21.55	16.62	19.97	10.29	12.87	4.59	6.95	33.06	11.90	56,24	10.25	14.41	11.42

nd: not detected

As a summary, the virgin olive oils are extracted from tree of *Olea europaea* L. using only physical processes. Growing area of olives, and its climatic and agronomic properties, genetic factors (cultivar), harvest time, harvesting methods and technological processes such as extraction, packing and storage conditions have critical influence on the virgin olive oils chemical composition. Olive oil consumption is still rising around the world. Moreover, the "geographic indications", which are considered as an assurance of quality and enhance the product value, are becoming increasingly widespread in olive oils. Thus, newly proved and practical analytical methods are needed that can be used to distinguish geographically labelled similar products from other regions. In this project, "growing area or geographic origin" effect was investigated on early harvest "Ayvalik" extra virgin olive oils some chemical features, particularly volatile consistent related fatty acids and functional groups which was detected spectroscopic and chromatographic methods. "Ayvalik" is the prominent olive cultivar around North Aegean Region in Turkey. It is cultivated such an extensive area in this region; however, it was observed that there were limited researches about geographical characterizations of "Ayvalik" olive oils. For this purpose, "Ayvalik" olives were harvested from different geographic locations of Balikesir, Canakkale, İzmir and Manisa provinces in 2012-2013, 2013-2014 and 2014-2015 crop seasons by hand-picking. The olives were carried to laboratory immediately for extracting virgin olive oils. After, low temperature (20^{o}C) and short time (30 min) malaxing, oil samples separated by vertical decanter. Then, oils filtered through a cotton filter and volatile profile (SPME-GC-MS), fatty acid composition (GC-FID) and oxidative stability (Rancimat test) were determined. Other quality parameters such as, free fatty acidity, peroxide and UV absorption (K_{232} and K_{270}), colour values as L, a* and b* were also measured. The results demonstrated that olive oil samples were classified as "extra virgin" olive oil and virgin olive oil according to Turkish Food Codex standard in terms of free acidity, peroxide, UV absorption (K_{232} and K_{270}) values and fatty acid composition. The samples were found very rich in terms of positive sensory attributes (green, floral and fruity notes) generated by LOX pathway enzymatically.

4. Conclusion

Lipolysis and oxidation are the processes leading to the most serious deterioration of olive oil and processes affect the composition and the sensory characteristics of the oil. Main volatile compounds usually found in high sensory quality virgin olive oil are produced through biogenic pathways of the olive fruit, such as the LOX cascade, and fatty acid or amino acid metabolism. These processes give rise to the wide variety of volatile compounds that constitute the profile of high quality virgin olive oils. It was viewed that main and dominant flavour compounds were C6 aldehydes and C6 alcohols for investigated geographic areas. There was a significant difference ($p<0.01$) was detected between harvest seasons based on these LOX derivate components. On the other hand, the results of the present study show that SPME-GC-MS analysis have a good potential for differentiation of olive oils based on geographical origin even in cases where such origins are in proximity. Geographical indications are an important value-creation tool for agricultural foodstuffs. Identifying a product with a geographical origin opens up potentially significant opportunities for producers. Recognition of a geographic indication generates added value and can create useful synergies with the geographical area with which the product is identified. It could be concluded that outcomes obtained from the thesis for Ayvalik cultivar will make a significant contribution to the dissemination and control of geographic indication in our country on the basis of objective criteria.

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Chapter 2

ASSESSMENT OF THE METHODS TO DETERMINE THE RESISTANCE TO COMMON PESTS (SESAMIA. NONAGRIOIDES LEFEBVRE AND OSTRINIA. NUBILALIS HÜBNER) IN CORN (ZEA MAYS L.) PLANTS

Erkan ÖZATA[1], Ali Beyhan UÇAK[2],Timucin TAS[3], Erdal ERBIL[4]

1 Dr., Blacksea Agricultural Research Institute, erkan.ozata@tarimorman.gov.tr
2 Siirt University, Faculty of Agriculture, Department of Biosystems Engineering, Siirt /Turkey
3 GAP Agricultural Research Institute,
4 GAP Agricultural Research Institute,

1. INTRODUCTION

Corn (*Zea mays* L.) is an important culture crop used in both human and animal nutrition. Corn plantation area in Turkey is 591544 hectares, total production is 5700000 tons, and the average yield is 9635 kg ha^{-1} (TÜİK, 2018). The yield of agricultural crops are mostly the main targets of the agronomists and plant breeders; therefore breeders are mostly concentrated to develop cultivars with high-yielding performances. Biotic stressors caused by climate change impact resulted in significant losses in agricultural production. Therefore, researchers started conducting studies to prevent further negative impacts of biotic stressors (Kozlowski and Pallardy, 1997).

There are many types of pests that have adverse effect on the corn production in Turkey, as in the world. European corn borer (*Ostrinia. nubilalis Hübner*) and pink corn borer (*Sesamia. nonagrioides Lefebvre*) are the two most important damagingpests of the corn plants (Meihls et al., 2012). The pink corn borer causes damage to all parts of corn plants except the root zone causes significant kernell yield losses (Samayoa et al., 2015; Jiménez-Galindo et al., 2017). Crop losses at harvest period was reported reaching 70% in fields where no insecticide applied and infestation observed up to 95% (Turkay et al., 2011a). Pink corn borer and European corn borer has been reported causing yield losses from 0 to 30% at moderate infestations and as high as 70 to 80% at severe infestations (Meissle, 2010; Mencarelli et al., 2013).

Chemical management of pink corn borer and European corn borer larvae is very difficult because they show endophytic feeding behavior (Gonza´lez-Cabrera et al., 2006). Therefore, insecticides should be applied before pink corn borer larvae tunneling into the stalk (Rice and Davis, 2010). Despite endophytic feeding behavior, farmers in the Çukurova region of Turkey generally prefers chemical management against European corn borer and pink corn borer. Several licensed insecticides containing about 20 effective substances are used in chemical management (Anonymous, 2002). In eastern Mediterranean region of Turkey, insecticide is used 1 or 2 times for the first crop corn, whereas 3 or 4 preventive insecticide applications is recommended against European corn borer and pink corn borer for the second crop corn (Simsek and Gullu, 1992; Anonymous, 2004). The ratio of the first crop corn in corn cultivation of the Mediterranean region was 42.5% and the second crop corn cultivation was 57.5%. The ratio has changed in recent years, and the first crop corn cultivation reached 64.3% in 2010, while the second crop decreased to 35.8% (Anonymous, 2010). The most important factor in decreasing the cultivation and production of the second crop corn is the prohibition of spraying insecticides by plane, and instead starting spraying with ground instruments.

The European corn borer is common in many countries, including Europe, United States, North Africa and part of Asia (Kim et al., 2009). However, the pink corn borer is a common pest in countries bordering the Mediterranean such as Spain, Portugal, France, Italy, Greece and Turkey (Stavrakis, 1967; Anglade 1972; Melamed-Madjar and Tam, 1980; Larue, 1984; Kayapınar and Kornosor, 1998; Zeren et al., 1988; Simsek and Gullu, 1992; Cordero et al., 1998), therefore, defined as "Mediterranean Corn Borer" in the literature (Castanera, 1986). In the eastern Mediterranean region, the European corn borer produces 3-4 generations per year, and the pink corn borer produces 4-5 generations per year (Zeren et al., 1988; Kayapınar and Kornosor, 1998). Previous studies reported that pink corn borer constitutes 38.95% of the two pest populations in the Eastern Mediterranean region and European corn borer constitutes 61.15% (Kayapınar and Kornosor, 1992). Simsek and Gullu (1996) reported that plants which were not sprayed insecticide in the Eastern Mediterranean were infested with European corn borer and pink corn borer up to 90-100%. The researchers found that adult population densities of European corn borer and pink corn borer were very close to each other (50%) in Icel province, however the pink corn borer population in Çukurova was higher than the European corn borer population. Cerit et al. (2006) indicated that the ratio of pink corn borer to European corn borer changes depending on the number of infested plants (the pink corn borer was 70% and corn borer was 30%) and the ratio of living larvae + pupa per plant (pink corn borer was 87% and European corn borer was 13%). The data confirms that rapid increase of pink corn borer ratio in the pest population. One of the reasons for the change in ratio is the mass production of natural egg parasitoid (*Trichogramma evanescens* West. Hym. Trichogrammatidae) of corn borer (*O. nubilalis* Hübner) by the Biological Control Research Station Directorate and widespread use of this parasitoid by farmers. The specific egg parasitoid (*Platytelenomus busseolae,* Gahan Hym. Scelionidae) of pink corn borer (*S. nonagrioides* Lefebvre) has not been produced artificially yet (Sertkaya et al., 1999).

In corn farming, there are other methods in pest management other than the chemical control, and the most important and cost effective one of these is to use a resistant cultivar. Considering the adverse effects of conventional insectices, the most effective way to control corn borer and pink corn borer is breeding of hybrid corn varieties resistant to these pests. Different methods are employed in the breeding of hybrid maize varieties resistant to the major pests. Koc and Tusuz (1995) conducted a study in Antalya province of Turkey to determine the most suitable plant growth period for artificial infection in developing resistant varieties against corn borer (*Ostrinia nubilalis* Hübn.) and pink corn borer (*S. nonagrioides*

Lef.). *Ostrinia nubilalis*, which gives 2-3 generations in a year, was reported preferring plants with a maximum of 7 week-old to lay eggs in the second crop corn cultivation, therefore the plant growth period (6-8) for the artificial infection should be carried out the week before peak tasseling and during flowering period. The researchers indicated that the most suitable period of artificial infection in the second crop cultivation against Sesamia spp., which produces 3 to 4 generations in a year, is between the top tasseling and pre-flowering period (when the plant is 10 to 12 leaves) which corresponds to the 6-9 week plant growth period, which is preferred by adults for stalk resistance. The criteria used in the assessment of resistance against insects in corn plants are defined based on their resistance mechanisms and their use in natural-artificial infection conditions. The amount of damage on a plant, the size of the lesions and cavities, and the number of holes caused by the larva to exit were reported important in indirect evaluations of the corn plants (Ortega et al., 1980).

The use of criteria such as larval exit holes, number and length of tunnels in the stalk, number of holes in 100 internodes, and number of larvae were recommended for the evaluation of stalk resistance against insects in maize plants (Awadallah et al., 1983; Showler et al. 2013; Mwimali et al. 2015; Bergvinson et al., 1987; Hunag et al., 2002; Li et al., 2017;Turkay et al. 2011c). Awadallah (1983) evaluated the resistance to *O. nubilalis* according to the ratio of "number of holes/100 internodes" and number of larvae. Damage index was rated as very resistant, number of holes is less than 20; resistant, number of holes is between 20 and 35; moderately resistant, number of holes is between 35 and 50; sensitive, number of holes is between 51 and 74; very sensitive, number of holes between 75 and 100, and extremely sensitive, number of holes is more than 100. The ratio of tunnel length within a stalk to the plant length or accepting a 2.5 cm length tunnel as 1 tunnel was used as the criteria for the insect resistance of maize plants (Guthrie, 1979). Turkay et al. (2011c) compared the resistance assessment methods used in the world and revealed their advantages and disadvantages in breeding studies. The resistance assessment methods were listed as number of holes method, tunnel length method, Larva + pupa number per plant method, number of plants surviving method.

Phenotypic assessments to investigate European corn borer and pink corn borer resistance revealed that corn has a common resistance mechanism against both pests. Various studies indicated the existence of some QTL regions in some corn populations that provide resistance to European corn borer and pink corn borer (Cardinal and Lee, 2005; Ordas et al., 2009;). The studies shown that QTL regions related to both European corn borer and pink corn borer are located very close to each other (Cardinal and Lee, 2005). The closeness of these two QTL regions can be considered an indication of the same resistance mechanism against two pests. However, further studies are needed to determine whether the resistance mechanism is controlled from the same QTL regions. The majority of genetic analysis studies focused on the B73 maize line (Ordas et al., 2009; Schnable et al., 2009; Ganal et al., 2011; Samayoa et al., 2015). Therefore, identification of the QTL regions that provide resistance to different gene sources and/or different corn lines is needed to better understand the genetic basis of QTL regions that cause resistance to these two pests. The variation in resistance to both Eurpoean corn borer and pink corn borer for especially in the collections of local European corn populations have been determined and the resistance was attributed to the additive and dominant gene effects (Krakowsky et al. 2004; Cardinal and Lee, 2005). Therefore, identifying the gene and/or the gene regions, which provide resistance, on the chromosome is very important. Although several studies have been carried out to determine the quantitative regions that provide pink corn borer resistance in corn, studies on identifying the gene regions on the chromosome have not been conducted (Jampatong et al., 2002; Cardinal and Lee, 2005). Since transgenic corn is not cultivated in our country, breeding European corn borer and pink corn borer resistant varieties that are harmful in corn are of great importance. Therefore, the aim of this study was to determine the appropriate method for the researchers conducting studies on resistance to corn pests or breeding. Hereby, the methods used in breeding hybrid corn varieties resistant to the common pests in corn plants were examined in this study, and the problems encountered in terms of the suitability of the methods were revealed and evaluated with the qualitative analysis technique. In this study, the problems encountered in the implementation of methods to determine the resilience mechanism were examined considering the strengths and weaknesses, and opportunities and threats were identified for the success of breeding studies in development of the new hybrids resistant to the common pests.

2. MATERIAL AND METHOD

The data was compiled from the primary and secondary data sources. The information obtained through the mutual interviews with the representatives of the Provincial Directorate of Agriculture and Forestry and corn producers in the Mediterranean and Southeastern Anatolia regions constituted the primary data of the study. All printed research, books, statistics and literature review on corn plant and corn production, marketing and economy were collected. In addition, data obtained from various government agencies (Turkey Statistical Institute, Ministry of Food, Agriculture and Livestock, Corn producers) constituted the secondary data source of the study.

In addition, the methods used in breeding hybrid maize varieties resistant to the common pests in the corn plant were examined in the literature review. The methods were given below;

1. Number of Holes Method: This can be used as the number of holes 100 internodes^{-1} and the number of holes per plant. Field studies using the number of holes were reported easy to conduct compared to the tunnel length method, however, the results were not as accurate as the tunnel length method.

2. Tunnel Length Method: This method is used in 3 different ways: tunnel length per plant, tunnel length plant length^{-1} and number of tunnels per plant. The tunnel length method was reported to be precise and accurate; thus a better selection criteria (Butron et al., 2014), but requires extensive field work.

3. Number of Larvae+Pupae per Plant Method: This method was reported easier to apply only in studies under artificial infection conditions where there is no natural population, or if the study is carried out under the influence of the natural population where a single generation is effective during the growing season of the corn plants. The plant cutting and counting process should be repeated in a certain period if the method is applied in an environment that the natural pest population produce more than one generations. This requires growing more plants. When working with a large number of lines or hybrids, more plants should be grown; thus, more seeds of line or hybrid have to be produced to grow this plant. Selfing and crossing are imperative to obtain a large amount of seeds. More labor would be needed since the cutting and counting process are repeated at certain intervals.

4. The Number of Surviving Plants: This method is easy to apply in the field, though it is used only by experienced researchers and only for pre-selection.

5. Scale 1-9: This method is easy to apply in the field, though it is used only by experienced researchers and only for pre-selection. On the other hand, some researchers have used the following methods which are;

a) The Number of Holes/100 internodi: In the resistance studies, 25 plants are cut from the two rows of each variety, the leaves of the cut plants are collected together with the sheaths, the number of internodes per plant and the exit holes of the pests are determined separately for the corn cob and top of the corn cob (Awadallah, 1983Turkay et al., 2011c).

b) The Length of Tunnel (gallery) per Plant: Twenty five plants, which the number of holes on them counted, are split from the middle, and the tunnels created by the pest are determined by measuring with ruler as under the corn cob and above the corn cob (Bergvinson et al., 1987; Hunag et al., 2002; Li et al., 2017).

c) The Number of Living Larva + Pupae: It is calculated by counting the living larvae and pupae in 25 plants cut in the middle (Anonymous, 2012).

Consequently, the methods used in breeding hybrid corn varieties resistant to the common pests in corn plants were examined, and the problems encountered in terms of the suitability of the methods were revealed and evaluated with the qualitative analysis technique.

3. RESULTS AND DISCUSSION

Corn (Zea mays L.) is an important cash crop used in both human and animal nutrition. The corn introduced to Turkey through Syria in the early 16th century and has been adapted to different ecological regions of the country. The coverage of corn cultivation area in the world is 161.821.251 ha, total production is 844.358.253 tons and the average yield is 5210 kg ha^{-1} (FAO 2019). The cultivation area of corn in Turkey is 594,000 ha, total production is 4,310,000 tons and the average yield is 7260 kg ha^{-1} (TURKSTAT, 2019). The Eastern Mediterranean Region, which includes Adana, Mersin, Osmaniye, Kahramanmaraş and Hatay provinces, is the most intensively corn grown region of the country. The total corn cultivation area in the Eastern Mediterranean region is 258,173 ha, total production is 2.318.974 tons and the average yield is 10 tons ha-1. The average yield per unit area in the Eastern Mediterranean region is about 2 times higher than the world average and about 3/2 times higher than the country average (TURKSTAT, 2019).

The first crop corn cultivation area in the Mediterranean region was 42.5% of the corn cultivation area in 2006, while 57.5% of the corn production was carried out as the second crop; the ratio has changed recently and the first crop corn cultivation increased up to 64.3% of in 2019 while the second crop cultivation area decreased to 35.8% (Anonymous, 2019). Similar to the elsewhere in world, many types of pests adversely affect the corn production in Turkey. European corn borer (*O. nubilalis* Hübner) and pink corn borer (*S. nonagrioides* Lefebvre) are the two most important pests. The recent decrease in the cultivation area of the second crop corn cultivation in the Mediterranean region can be attributed to the increasing the pink corn borer and European corn borer pest population in the region and the difficulties in in management of the pests. In addition, the sensitivity of cultivars grown in the region to the common corn pests also limits the second crop corn cultivation. Three times insecticide spraying against pink corn borer and European corn borer provided only 60% protection in the second crop corn (Turkay et al. 2011a). European corn borer is a common chronic pest in many countries, including the Europe, United States and Turkey (Kim et al., 2009). The pink corn borer is especially a common pest in Mediterranean countries such as Spain, Portugal, France, Italy, Greece, and Turkey (Kayapınar and Kornoşor, 1998). The European corn borer is reported producing 3-4 generations a year, while pink corn borer produces 4-5 generations in Çukurova region of Turkey (Zeren et al., 1988; Kayapınar and Kornoşor, 1998). Şimşek and Güllü (1996) reported in their study conducted in Çukurova region during 1995 and 1996 growing seasons that the infestation of European corn borer and pink corn borer in non-sprayed plants may reach up to 90 to100%. Cerit et al (2006) reported that considering the number of infested plants in Çukurova, 70% of the infestation was pink corn borer and 30% was European corn borer. The researchers indicated that considering the ratio of living larvae + pupa per plant, 87% of infestation was pink corn borer and 13% was European corn borer. The results revealed that the pest populations in Çukurova constitute from 1/3 European corn borer and 2/3 pink corn borer. European corn borer feeds by the maize stem pith; thus causes significant kernel yield losses (Samayoa et al., 2015; Jiménez-Galindo et al., 2017). The losses in corn yield caused by pink corn borer at the beginning of the season was reported between 0 and 10% in Greece, while the loss at the end of the season reached 100% (Tsitsipis, 1988). Chemical control of common corn pests is quite difficult because the larvae of corn stalk borer and European corn borer tunnel throughout the plant stem from the first instar (Gonzalez-Cabrera et al., 2006). However, farmers in Çukurova region still use chemical control agents against European corn borer and corn stalk borer. A large number of licensed insecticides containing about 20 effective substances are used in the borer management (Anonymous, 2002). The second product corn in Cukurova region is sprayed 3 to 4 times to control the European corn borer and pink corn borer (Anonymous, 2004). The success rate to control borer damage in 3 spraying was reported only 60% (Turkay et al., 2011a). However, if the insecticide cannot be sprayed just in time, the larvae of European corn borer and pink corn borer enter the plant and thus chemical control would not effective (Gonza´lez-Cabrera et al., 2006). Therefore, most of the insecticides used cause environmental pollution as well as economic losses and disturb the natural balance. The aforementioned information emphasizes the importance of breeding and cultivation of high-yielding corn varieties resistant to European corn borer and pink corn borer. Turkay et al (2011d) reported the breeding of Turkay variety, which is pink corn borer and European corn borer resistant, by crossing the European corn borer and pink corn borer resistant lines existing in the Eastern Mediterranean Agricultural Research Institute. However, researchers indicated that the yield of Turkay variety was not high to compete with the first crop corn varieties cultivated in the region. In another study, Turkay et al. (2011b) reported that the variability within the European corn borer and pink corn borer resistant lines that exist in the Eastern Mediterranean Agricultural Research Institute is narrow. Therefore, in order to develop high-yielding and resistance varieties, the researchers indicated the necessity of cross-breeding between lines with high ability to transfer resistance to F1 hybrids and sensitive lines with high ability to transfer high yielding character to F1 hybrids.

Some studies have been carried out to reveal the heritability of pink corn borer resistance in corn plants (Ordas et al., 2011). Turkay et al. (2011c) stated that narrow heritability ratio of pink corn borer resistance for the number of holes/100 internodes was 53% and for the tunnel length/plant height was 57%. The resistance, even if some of the resistance lines were used as the mother or father in hybridization, could be transferred to the F1 hybrid regardless of whether the line is resistance or sensitive. The resistance to Sesemia spp. in a narrow sense heritability was reported as 60% for tunnel length/plant by Tüsüz and Koç (1995) who stated that the additive gene effect was the most important factor controlling the resistance as shown by the diallel analysis, the gene frequency that provides the resistance can be increased by repetitive selection or backcrossing method, and the presence of dominant gene effect in addition to the additive gene effect can also be ensured by the presence of a single resistant parent in the hybrid. Scot et al. (1966) found that the high resistance of the B-52 line can also transferred to the generations. In addition, Scot et al. (1964) stated that resistance is a quantitative character, as in yield and lodging, and resistance can be increased by accumulation of additive genes, and the heritability of resistance is higher than that in yield and lodging.

Different resistance assessment methods have been applied in breeding of European corn borer and pink corn borer resistant variety. For example; Koç and Tüsüz (1995) investigated the most suitable artificial inoculation period in west Mediterranean region of Turkey against European corn borer (*Ostrinia nubilalis* Hübner.) and pink corn borer (*S. nonagrioides* Lefler.). The researchers stated that *Ostrinia nubilalis*, which produces 2-3 generations in a year in the Western Mediterranean region, prefer plants with a maximum of 7 week-old to lay eggs in the second crop cultivation, therefore, the artificial inoculation period was determined as between before top tasseling and flowering period which corresponds to 6-8 weeks of the plant growth. Artificial inoculation in second crop cultivation against *Sesamia spp*, which gives 3 to 4 generations in one year, can be performed between before the top tassel formation and flowering period, which is the 6-9 week old plant growth period (10-12 leaves period) preferred by adults for egg laying due to the stalk resistance.

The criteria used in corn insect resistance assessment was classified according to their resistance mechanisms and their use in natural-artificial infestation conditions (Ortega et al., 1980). Indirect assessment techniques on corn plants were reported as the amount of damage in the plant, the size of the lesions and cavities, the number of holes used to exit of larva, etclarva exit holes (Showler et al. 2013; Mwimali et al. 2015), number and length of tunnels in a stem (Bergvinson et al., 1987; Hunag et al., 2002; Li et al., 2017), number of holes in 100 internodes (Turkay et al. 2011c) and number of larvae Awadallah (1983) were used as the criteria for the assessment of corn resistance against corn borers.

The resistance to *O. nubilalis* have been evaluated according to the number of holes/100 internodes and the number of larvae by Awadallah (1983). Corn plants were considered very resistant when number of holes was less than 20, resistant: number of holes between 20-35, moderate resistant: number of holes between 35-50, sensitive: number of holes between 51-74, very sensitive: number of holes between 75-100, highly sensitive: number of holes more than 100. In pest resistance studies in corn plants, the criteria used by Guthrie (1979) were the ratio of tunnel length in a stalk to plant length or the number of tunnels calculated by accepting 1 tunnel of the 2.5 cm long tunnel.

The resistance assessment methods used in the world have been compared and the advantages and disadvantages of the methods in breeding were revealed (Turkay et al. 2011c). The resistance assessment methods were summarized as follow; 1. Number of Holes method; the method is used in 2 different ways: number of holes/100 internodes and number of holes/plant. Field studies can be carried out more easily with this method compared to the tunnel length method, but the results are not as accurate as those obtained by the tunnel length method. 2. Tunnel Length Method; the method is used in 3 different ways: tunnel length / plant, tunnel length / plant length and number of tunnel / plant. The results obtained by this method were considered precise and clear, but the method requires extensive field work. 3. Number of Larvae+Pupae / Plant Method: 3. Number of Larvae + Pupa / Plant Method: This method is easy to apply only in studies under artificial infection conditions where there is no natural population, or if the study is carried out under the influence of the natural population where a single generation is effective during the growing season of the corn plants. The plant cutting and counting process need to be repeated in a certain interval if the method is applied in an environment that the natural pest population produce more than one generations in a year. Under this conditions more plants have to be grown. When working with a large number of lines or hybrids, more plants have to be grown; thus, more seeds of line or hybrid have to be produced to grow these plants. Therefore, selfing and crossing are imperative to obtain a large amount of seeds. More labor is needed since the cutting and counting process are repeated at certain intervals. 4. The Number of Surviving Plants: This method is easy to apply in the field, however it is used only by experienced researchers and only for pre-selection. 5. Scale 1-9: This method is easy to apply in the field, though it is used only by experienced researchers and only for pre-selection.

Ucak et al. (2017) conducted a field experiment in the Southeastern Anatolia region during 2015 and 2016 growing seasons to determine the effects of different irrigation levels (I100, I70, I35) on European corn borer populations (*S. nonagrioides* Lef.) by using chemical analyzes in corn genotypes (31D24, ADASA16, P1429). The effect of irrigation treatments on genotypes was reported statistically significant ($P<0.01$) and significant differences were recorded between the corn genotypes. The highest average number of holes/100 internodes were recorded in the full irrigation x variety interaction (I100x31D24), while the lowest value was determined in the extreme limited irrigation x variety interaction (I100xP1429). However, the highest average yield (2657.67 kg ha^{-1}) was obtained in low living larvae + pupae number, tunnel length, and high oil ratio (%) was determined in full irrigation x variety interaction (I100X31D24). The lowest yield (2597.63 kg ha^{-1}) was determined in the constrained irrigation x variety interaction (I100x31D24) with high living larvae + pupae number, tunnel length, and low oil ratio (%). The results revealed that the use of tunnel length and oil ratio as a screening parameter rather than 100 internodes/holes x100 in corn resistance studies will provide more precise results. In European corn borer resistance studies for corn genotypes or lines, the researchers suggested to test genotypes under no water stress and extreme water stress conditions, and to determine those with similar performance as resistant by evaluating the tunnel length, number of living larvae and oil ratio.

Phenotypic assessments conducted to determine corn resistance to European corn borer and pink corn borer showed a common resistance mechanism of corn plants against both pests. The QTL regions, ensure resistance to European corn borer and pink corn borer, have been identified in some corn mapping populations (Ordas et al., 2011; Li et al., 2016; Jiménez-Galindo et al., 2017). Studies pointed out that aforementioned QTL regions are close to each other (Cardinal and Lee, 2005; Li et al., 2016), which was related to the same resistance mechanism of corn plants against two pests. Despite the information stated, studies to explain the resistance mechanism relate to the QTL regions are needed to ensure whether both regions are linked to the resistance mechanism. The B73 maize line has been the main corn variety investigated for genetic analysis studies (Ordas et al., 2011; Ganal et al., 2011; Samayoa et al., 2015). However, identification of QTL region in different gene sources or different corn lines/varieties may help to explore the resistance mechanism against European corn borer and pink corn borer. The studies indicated a variation in resistance to borer for local European corn populations; thus, the resistance against European corn borer and pink corn borer in local corn populations of Europe was linked to the additive and dominant gene effects (Ordas et al., 2011). Therefore, the gene and/or the gene regions which ensure the resistance should be identified on the chromosome. The quantitative regions which are important for the resistance to pink corn borer in corn plants have been documented in many studies (Cardinal et al.2001; Cardinal and Lee, 2005; Ordas et al., 2011), however, such studies have not been conducted in our country.

Transgenic corn which produces *Bacillus thutingiensis (Bt)* toxins, cultivation is not very common in most countries of the world (González-Cabrera et al., 2006; Meissle et al., 2011), therefore, breeding European corn borer and pink corn borer resistant varieties are of great importance for a cleaner environment and sustainable agriculture.

4. CONCLUSION

European corn borer and pink corn borer are the two common pests observed in corn cultivation. European corn borer is an invasive pest in many countries of Europe, part of North America, North Africa and part of Asia (Kim et al., 2009), while pink corn borer is encountered only in countries bordering the Mediterranean Sea. Corn producers apply protective insecticide 1-2 times in the first crop to prevent and/or reduce the damage and 3-4 times in the second product, but the protection rate remains only around 60%. However, if insecticide application cannot be carried out just in time, European corn borer and pink corn borer larvae enter inside the corn plants and chemical control becomes impossible. Numerous spraying causes both economic losses and disrupts natural balance by causing environmental pollution. Therefore, determining the most suitable method to assess the European corn borer and pink corn borer resistance will be useful for the breeding of resistant and high yielding corn hybrids. However, the use of tunnel length and oil ratio as a screening parameter will provide more precise information compared to 100 internodes/holes numberx100 in resistance assessment studies. The common pests prefer the full irrigation (I100) conditions and the number of pests in highly-constrained irrigation (I35) is at the lowest level. However, the preference of pest even under full irrigation changes depending the type of genotypes. The pest does not prefer genotypes with high oil content, and the high oil rate has a repellent effect. In addition, the genotypes with the highest number of holes had the highest yield, whereas the genotypes with the longest tunnel length had the lowest yield.

Corn genotypes or the lines should be tested under water stress-free and extreme water-stress conditions against borer resistance and genotypes or lines with similar performances should be identified as resistant.

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Chapter 3

ENERGY USE EFFICIENCY IN ORGANIC OLIVE (OLEA EUROPAEA L.) PRODUCTION

Mehmet Fırat BARAN[1], Osman GÖKDOĞAN[2]

1 Siirt University Agriculture Faculty Biosystem Engineering Department, mfb197272@gmail.com

2 Isparta University of Applied Sciences Agricultural Machinery and Technologies Engineering Department

Introduction

Olive (*Olea europaea* L.) is a member of Oleacea family. Olea cultivar and its motherland is Upper Mesopotamia, covering South-eastern Anatolian Region too and South Asia Minor (Heywood, 1978). Olive can be consumed directly or it can be used to produce oil. Olive oil is natural fruit oil produced through physical methods only and contains unique antioxidant matters (phenolic compounds, tocopherol and other aromatic matters), high levels of fatty acid (oleic acid) and high oxidative stability (Öztürk et al., 2009). Organic olive is commonly produced in Mediterranean countries. The important olive producing countries are Spain, Italy, Greece, Tunisia, Turkey, Morocco and Syria (Özkaya et al., 2015).

Energy usage is one of the key signs for advancing more sustainable agricultural practices. Wider use of renewable energy sources, increase in energy supply and efficiency of use can do a valuable support to meeting sustainable energy development goals (Streimikiene et al., 2007; Kızılaslan, 2009). Efficient usage of energies helps to obtain increased production and productivity and contributes to the economy, profitability and competitiveness of agriculture sustainability in rural life (Singh et al., 2002; Kızılaslan, 2009).

Energy use efficiency was computed in some researches on organic olive (Gökdoğan and Erdoğan, 2018), organic apricot (Gündoğmuş, 2006), organic black carrot (Çelik et al., 2010), organic strawberry (Baran et al., 2017), organic wolfberry (Oğuz et al., 2019), sweet cherry (Demircan et al., 2006), cherry (Kızılaslan, 2009), kiwifruit (Mohammadi et al., 2010), quince (Gündoğmuş, 2013), groundnut (Baran et al., 2018; Saltuk, 2019), citrus (Yılmaz ve Aydın, 2020), etc.

In this research was purposed to compute an energy use efficiency of organic olive production in Adıyaman province in Turkey. In order to compute the energy use efficiency of organic olive production, trials and measurements were done in organic olive farm in the Adıyaman province. Human labour energy, machinery energy, diesel fuel energy, farmyard manure energy and organic chemicals energy were computed as energy inputs. The organic olive yield were computed as output energy. Energy use efficiency, specific energy, energy productivity and net energy in organic olive production were computed.

Material and Method

Southern section of the Adıyaman province is hot and dry during summer months and rainy and cold during winter months. Adıyaman is located at 37° 45’ north latitude and 38° 16’ eastern longitude. Adıyaman’s altitude from sea level is 672 m. The daily difference between highest temperature and lowest temperature is about 10 °C (Anonym 2016a). Soil structure of the Adıyaman province is ¾ clayed-loamy (Anonym 2016b). The research was done on fields that has 0.5 hectare in 9 hectares, located in Adıyaman province.

It was done randomized complete-block design with three replicates in this research. For computing energy input-output, the researches done on determining the coefficients of energy equivalents of inputs-outputs were used (Table 1). Organic olive input-output values were determined and the computations were given in Table 2. Energy use efficiency computations in organic olive production were given in Table 3.

Fuel consumptive of each parcel was computed as 1 ha^{-1}. Full tank method was used for measurement the amount of fuel (Göktürk, 1999; El Saleh, 2000; Sonmete, 2006). Experiments in parcel were measured with using the effective labour time (t_{ef}) (Özcan, 1986; Güzel, 1986; Sonmete, 2006). The time spent during agricultural operations in the parcel was measured by means of chronometer (Sonmete, 2006). Energy equivalents of efficiency used in agricultural production were given in Table 1. Energy use efficiency, specific energy, energy productivity and net energy were computed with using the following formulas (Mandal et al., 2002; Mohammadi et al., 2008; Mohammadi et al., 2010).

Energy use efficiency = Energy output (MJ ha^{-1}) / Energy input (MJ ha^{-1}) (1)

Specific energy = Energy input (MJ ha^{-1}) / Product output (kg ha^{-1}) (2)

Energy productivity = Product output (kg ha^{-1}) / Energy input (MJ ha^{-1}) (3)

Net energy = Energy output (MJ ha^{-1}) - Energy input (MJ ha^{-1}) (4)

Table 1. Energy equivalents of inputs and outputs in organic olive production

Inputs	**Unit**	**Energy equivalent (MJ unit^{-1})**	**References**
Human labour	h	1.96	Mani et al., 2007; Karaağaç et al., 2011
Machinery	h	64.80	Singh, 2002; Kızılaslan, 2009
Farmyard manure	kg	0.30	Singh, 2002
Organic chemicals	kg	77.20	Guzman and Alonso, 2008; Bilalis et al., 2013
Diesel fuel	l	56.31	Singh, 2002; Demircan et al., 2006
Output	**Unit**	**Energy equivalent (MJ unit^{-1})**	**References**
Yield	kg	11.80	Özkan et al., 2004

Results and Discussion

In the farm producing organic olive, an average of 5100 kg ha^{-1} organic olive was yielded during the 2017-2018 production season. The energy use efficiency in organic olive production was given in Table 2. According to Table 2, energy inputs in organic olive production were computed as 6168.65 MJ ha^{-1}, energy output was computed as 60180 MJ ha^{-1}. Energy inputs consist of machinery energy by 3666.96 MJ ha^{-1} (59.45%), diesel fuel energy by 1187.20 MJ ha^{-1} (19.25%), human labour energy by 827.19 MJ ha^{-1} (13.41%), farmyard manure energy by 275 MJ ha^{-1} (4.46%) and organic chemicals energy by 212.30 MJ ha^{-1} (3.44%), respectively.

Other in previous researches; Gökdoğan and Erdoğan (2018) computed that the diesel fuel energy had the biggest share by 50.31% (organic olive), Gündoğmuş. (2006) computed that the diesel fuel energy had the biggest share by 44.99% (organic apricot), Çelik et al. (2010) computed that the diesel fuel energy had the biggest share by 35.26% (organic black carrot), Baran et al. (2017) computed that the organic fertilizers energy had the biggest share by 26.32% (organic strawberry), Oğuz et al. (2019) computed that the human labour energy had the biggest share by 39.26% (organic wolfberry), etc.

Energy use efficiency, specific energy, energy productivity and net energy in organic olive production were computed as 9.76, 1.21 MJ kg^{-1}, 0.83 kg MJ^{-1} and 54011.35 MJ ha^{-1}, respectively (Table 3). In previous researches; Gökdoğan and Erdoğan (2018) computed energy use efficiency as 2.72 (organic olive), Gündoğmuş (2006) computed energy use efficiency as 2.22 (organic apricot), Çelik et al. (2010) computed energy use efficiency as 1.90 (organic black carrot), Baran et al. (2017) computed energy use efficiency as 0.25 (organic strawberry), Oğuz et al. (2019) computed energy use efficiency as 1.40 (organic wolfberry), etc.

Table2. Energy use efficiency in organic olive production

Inputs	**Unit (br)**	**Energy equivalent (MJ br^{-1})**	**Input used per hectare (unit ha^{-1})**	**Energy value (MJ ha^{-1})**	**Ratio (%)**
Human labour	h	1.96	422.03	827.19	13.41
Tillage	h	1.96	8.56	16.77	0.27
Pruning	h	1.96	66	129.36	2.10
Hoeing	h	1.96	91.67	179.67	2.91
Fertilization	h	1.96	24.20	47.43	0.77
Spraying	h	1.96	1.83	3.59	0.06
Harvesting	h	1.96	134.44	263.51	4.27
Transporting	h	1.96	22	43.12	0.70
Order applications	h	1.96	73.33	143.73	2.33
Machinery	h	64.80	56.59	3666.96	59.45
Tillage	h	64.80	8.56	554.40	8.99
Fertilization	h	64.80	24.20	1568.16	25.42
Spraying	h	64.80	1.83	118.80	1.93
Transporting	h	64.80	22	1425.60	23.11
Farmyard manure	kg	0.30	916.67	275	4.46
Organic chemicals	kg	77.20	2.75	212.30	3.44
Diesel fuel	l	56.31	21.08	1187.20	19.25
Total				6168.65	100.00
Outputs	**Unit (br)**	**Energy equivalent (MJ br^{-1})**	**Output per hectare (unit ha^{-1})**	**Energy value (MJ ha^{-1})**	**Ratio (%)**
Yield	kg	11.80	5100	60180	100.00
Total				60180	100.00

Table3. Energy computations in organic olive production

Computations	**Unit**	**Values**
Energy use efficiency		9.76
Specific energy	MJ kg^{-1}	1.21
Energy productivity	kg MJ^{-1}	0.83
Net energy	MJ ha^{-1}	54011.35

Conclusions

Following conclusions were summarized in organic olive production.

Organic olive production consumed a total energy of 6168.65 MJ ha^{-1}, which was the highest due to machinery energy (59.45%). The energy input of diesel fuel energy (19.25%) and human labour energy (13.41%) were the second and third share with in the total energy inputs.

Demircan et al. (2006) reported that, "proper tractor selection and management of machinery to reduce direct use of diesel fuel (Işık and Sabancı, 1991) have needed to save non-renewable energy sources without impairing the yield or profitability, to develop the energy use efficiency of sweet cherry production". For reduce of inputs (machinery and diesel fuel) of organic olive production, these advices may apply for organic olive production.

Energy use efficiency, specific energy, energy productivity and net energy were computed as 9.76, 1.21 MJ kg^{-1}, 0.83 kg MJ^{-1} and 54011.35 MJ ha^{-1}. In this research, the energy use efficiency of organic olive production in the Adıyaman province was computed. According to the evaluated results, organic olive production is an economic production in terms of energy usage (9.76).

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Chapter 4

UNMANNED SURFACE VEHICLES (USVS) IN ENVIRONMENTAL MONITORING RESEARCH: AN OVERVIEW

Semih KALE[1]

1 Çanakkale Onsekiz Mart University, Faculty of Marine Sciences and Technology, semihkale@comu.edu.tr

Water is the most important natural resource for people to live, and due to its limited nature, it must be used and shared in a sustainable way. Sustainability is possible only through the continuous monitoring of water resources (Akın and Akın, 2007). Water resources are used in many areas such as drinking water, agricultural irrigation, industry, fishing, and tourism. The most important factor in determining the use of a water source is the quality of the water, except for the amount of water it has. The physical, chemical, and biological properties of the water source are called water quality (Yalçın and Gürü, 2010). It has been understood that the existing water resources must be protected in a sustainable way in order to meet the increasing water demand. However, environmental problems arise due to reasons such as an extremely increasing population, industrialization, and urbanization. Water pollution is at the top of these environmental problems. Water pollution is the changes that occur because of human effects in water resources, partially limiting or completely preventing the use of water in line with its purpose, and causing the deterioration of ecological balance (Kocataş, 1994).

Nowadays, water resources are polluted due to many factors. Therefore, water resources must be used and protected in a sustainable way. The determination of surface water quality is of great importance in the development and management of water resources. The amount of available water varies depending on the quality of the water. Considering the intended use of water, pollution of the water source will damage the entire ecosystem associated with that source. It is very important to choose the appropriate parameters to determine the quality of the water source and to understand for what purpose this source can be used. The parameters to be selected in water quality monitoring, surveillance, and control vary depending on the type and purpose of the use of that water source. The quality of water resources should be determined by measuring the parameters within the framework of national and international standards (WHO, 1963; EPA, 2004; Anonymous, 2004; WHO, 2018) and within these standards. It is important to measure the physicochemical parameters (e.g., water temperature, light transmittance, suspended solids, dissolved oxygen, total phosphorus, and total nitrogen) and biological parameters for the studies in the lakes. For this reason, it is necessary to determine the most appropriate stations, measurement times, and frequencies for the measurements to be carried out in order to monitor the water quality and determine the water quality. In order to manage the water resources in the best way, it is important to carry out the monitoring works successfully and systematically.

Limnological research and monitoring studies carried out using traditional methods require a lot of labour, time, and material resources. These challenging works can be carried out in a shorter time with lower costs and with minimum labour, owing to hybrid controlled (autonomous and manual control) USVs to be developed. In addition, data those are very difficult to obtain spatially and temporally with manpower can be easily obtained in such situations as bad weather conditions that may make it difficult to carry out studies, day and night studies, the location of the working area, transport impossibilities.

In artificial lakes and ponds, the structures (tree, house, minaret, etc.) that appear with changes in water level depending on the season make it difficult to take measurements and take water samples. Such difficulties and obstacles encountered can be easily overcome with USV. However, the physicochemical properties of the study areas, taking measurements in these areas and continuing the studies based on human power can pose vital dangers for human health. Yucel and Baba (2012) carried out measurements in five different acid mineral lakes and reported the pH value of the waters as 1.99 and the highest 4.35 in the measurements recorded between 2009 and 2012. In addition, the researchers stated that the pH value varied between 2.85 and 5.75 in the rivers in the region. Sudden changes in pH values may have negative effects on water quality. Although pH value varies between 0-14, it expresses a neutral ambient condition when it is 7. The fact that the pH values measured in this study are so low poses great dangers for human health and aquatic ecosystems. Working in areas with similar characteristics poses a great danger to human health. Through USV in such areas, great conveniences can be provided and measurements can be made without compromising human health.

Turkey is considered a water-rich country in terms of the number of freshwater resources. However, contrary to popular belief, it is not a water-rich country. In fact, it is among the countries with the water shortage in terms of the amount of water per capita (Hisar et al., 2015). If the compulsory precautions are not taken, it may become a country with water scarcity in the future. Several investigations have been carried out to understand the potential effects of climate change and forecast the future of water resources in Turkey (Kale et al., 2016a, 2016b, 2018; Ejder et al., 2016a, 2016b; Kale and Sönmez,2018a, 2018b, 2019a, 2019b, 2019c; Arslan et al., 2020; Sönmez and Kale, 2020). Nevertheless, long-term and integrated water management should be implemented instead of evaluating water resources by making separate plans for basins, local or regional, with the studies carried out. In order to leave high quality and large amounts of water to future generations, artificial or natural water resources must be well evaluated, protected and managed. Especially in recent years, the unconscious consumption of water, which is one of the most important issues in many academic environments, the nature-nonfriendly interventions of the enterprises opened, the global climate change and the decrease in water quality and quantity caused by a number of negative effects broadly affect the world. Therefore, in Turkey, the Directorate General of Water Management was established on July 6, 2011, for ensuring both coordination with other institutions intended to take the necessary measures for the hydrological basin in Turkey. In this context, within the scope of the "Draft Regulation on Ground and Ground-Water Monitoring" (March 1, 2013), the present state of all surface and groundwater in terms of quantity, quality and hydro-morphological factors throughout the country, monitoring the waters with an approach based on ecosystem integrity, standardization in monitoring and infrastructure works have been accelerated to determine the procedures and principles for ensuring coordination between monitoring institutions and organizations.

Considering the water resources as a whole on the basin basis (water, soil, forest and vegetation, etc.) and creating environmental awareness considering that they are also ecosystems apart from their socio-economic values, is very important for the future of water resources and the organisms living in those resources (Brierley and Harper, 1999). The regulation prepared by the Ministry of Forestry and Water Affairs emphasized that sustainable development and improvement of water resources should be carried out for protecting the water resources used for purposes such as drinking water, nutrient supply, discharge and agricultural irrigation in terms of quantity, physical, chemical and ecological quality and preparation of watershed management plans.

It is necessary to ensure the continuity of subject-related investigations and to monitor them for available water resources. In order to implement successfully water management, it is necessary to carry out studies using state-of-the-art tools and equipment and to create databases of water resources. USV will provide continuity in the works to be carried out and will create great facilities for stakeholders and decision-makers in the protection and management practices related to these water resources.

USVs have been used in applications such as data collection studies that can assist in environmental monitoring and marine production policies, surveillance of territorial waters, protection of offshore systems, and support for oil and fuel activities in the Arctic regions. The use of USV contributes to lowering personnel costs, increasing personnel safety, covering wider areas of work areas, and carrying out much more environmentally friendly activities.

When studies on USV at the national and international level in the literature are examined, a master plan for USV has been published by the US Navy for the first time in the world (US Navy, 2007). In this plan, USV is defined as a vehicle that can displace immobile water and operate with close contact with the water surface, and perform unmanned operations with varying degrees of autonomy (independence). Studies on USV have started in the last 25 years. USVs, which have started to become widespread in various fields over time, are being developed for their purposes in many environmental research fields such as environmental monitoring and sampling, coastal protection, bathymetric research (Caccia et al., 2008a). In recent years, unmanned surface vehicles continue to be developed for the military, environmental and robotic research applications (Caccia et al., 2008b).

Yaakob et al. (2012) developed an unmanned surface vehicle that can collect data in real-time and can be controlled remotely, but they did not give this vehicle any name. The developed USV was used in environmental monitoring studies, monitoring of oil spill in the seas, fisheries inventory research, observing the environmental conditions of the reefs and collecting water quality data.

When the developments in Europe are examined, the vehicle named “Measuring Dolphin” was designed and developed within the Rostock University of Germany. This vehicle can be used in shallow water with depth, discharge etc. It has been used to verify the location information of the measuring devices, route guidance and move these devices to the places to be measured (Majohr and Buch, 2006).

The vehicles named “ROAZ” and “ROAZ 2” developed at the Autonomous Systems Laboratory (ISEP-LSA) within the Engineering Institute of Porto (Portugal) were primarily used within the scope of researches for oceanographic data collection and automation (Martins et al., 2007). The autonomously controlled vehicle named “Springer” was also developed by the research group called Marine and Industrial Dynamic Analysis (MIDAS) within the University of Plymouth (UK) and was used to monitor and monitor water pollution (Naeem et al., 2006; Naeem et al., 2007).

Vehicles named “Delfim” and “Caravela” with autonomous control are used as an auxiliary communication tool for the autonomous underwater vehicle (AUV) in the Dynamic Systems and Ocean Robotics Laboratory (DSOR) within the Institute of Robotics and Systems (ISR-IST) in Lisbon (Portugal). It was developed as part of the ASIMOV project supported by the European Union (EU). With the help of the developed tool, it is aimed to support fast acoustic communication with AUV. The vehicle was also used as a stand-alone unit to collect bathymetric maps and marine data (Pascoal et al., 2006).

The autonomously controlled vehicle named “Charlie” was designed and developed in the Marine Technology laboratories of the Automation Intelligent Systems Institute (ISSIA) within the Italian National Research

Council (CNR) in Genoa (Italy). Charlie was used to collecting samples from the microlayers of the sea surface (Caccia et al., 2005). Later on, it continued to be developed for robotics research on autonomous ships. The tool named ALANIS was also used to collect water samples and to study sea layers (Caccia et al., 2009).

Vehicles named Kaasboll USV, Viknes USV, Mariner USV have been developed and used in research by Maritime Robotics at the Norwegian University of Science and Technology (Breivik, 2010).

Manley (1997) and Manley et al. (2000) developed USVs "ARTEMIS" (fishing trawler), "ACES" (Autonomous Coastal Research System), and "AutoCat" for education and civilian applications within the Massachusetts Institute of Technology (MIT) of the USA. Curcio et al. (2005) also developed autonomous ships, including vehicles such as "SCOUT" (Surface Tool for Oceanographic and Submarine Research). These unmanned surface vehicles allow autonomous control and collection of hydrographical data, as well as GPS-based navigation. Thus, data can be collected from the right points by entering coordinate information.

"EDEDRON" was the first Polish USV developed by researchers from the Naval Academy in Gdynia and Gdansk University of Technology in Poland (Kitowski, 2011, 2012). EDEDRON was developed for the protection of national sea services (Kalinowski and Malecki, 2017).

Unmanned surface vehicles have been developed and used in many different fields and for various purposes. Apart from environmental research and monitoring, many tools have been developed and used in the military and defence industry. Vehicles called "Stingray" and "Silver Marlin" manufactured by Elbit Systems in Israel and "Protector" produced by Rafael Advanced Defence Systems have been developed for use in the protection of ports and terrorist attacks. In Canada, the unmanned surface vehicles named "Barracuda USV-T" and "Hammerhead USV-T" have been developed and used for underwater threats and mining as well as for marine defence purposes. In Sweden, unmanned surface vehicles named "SAM" and "Piraya", developed by Kockums, were also used in mining operations. "Blackfish" and "Sentry" vehicles developed by a multinational company called Qinetiq in Britain are designed to be used for harbour protection and petroleum operations. The USA has an important place in the development of unmanned surface vehicles for defence purposes. In the USA with well-established USV programs, vehicles named "SSC San Diego", "Draco ASW", "Textron CUSV" and "Piranha" were developed and used in defence research and studies (Larson et al., 2006, 2007).

Recently, Pennington et al. (2016) developed an autonomous underwater vehicle titled "Gulper". The AUV Gulper was operated for sampling seawater and basic oceanographic sample collecting. Demetillo and Taboada (2019) used USV for monitoring real-time water quality. Carlson et al. (2019) developed a USV named "Arctic Research Centre Autonomous Boat (ARCAB)". ARCAB operated autonomously in winter-time conditions in Greenland and measured bathymetry and ocean currents in rocky and shallow areas that would make the use of manned vessels too risky. Raber and Schill (2019) developed a small autonomously controlled USV for mapping and monitoring coral reefs with a relatively low-cost. The USV was named Reef Rover and used to collect data. Mogstad et al. (2019) used a USV for mapping shallow-water habitats. Sousa et al. (2019) used USV for real-time monitoring in aquaculture environments and they integrated the internet of things (IoT) for the acquisition of environmental data.

In Turkey, the Global Tech Inc. produced "GLOBİDA" which is the first unmanned surface vehicle for Turkey. GLOBİDA was developed with the work supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK). GLOBİDA, target platform for offshore protection, smuggling, customs, lifesaving, over-the-water training shooting, sabotaging, maritime traffic control, taking measures against sea hazards, combating drugs, and use as a weapon in war, intelligence, reconnaissance, and surveillance can be used for purposes. In addition, it is expected to be used in environmental pollution control and analysis studies (Gözcelioğlu, 2010). In addition, BİLTİR (Computer-Aided Design, Manufacturing, and Robotics Centre) at Middle East Technical University in Turkey works for developing unmanned surface vehicles (Anonymous, 2014). Furthermore, ASELSAN (Military Electronics Industry Inc.) also produced the unmanned surface vehicle named "LEVENT". LEVENT can be used in various missions such as reconnaissance, surveillance and intelligence, coastal patrol, search and rescue, emergency response, creating a target platform, providing logistic support and communication relay (ASELSAN, 2013).

In many parts of the world, unmanned surface vehicles have been developed and used in various fields and for various purposes. USVs continue to be developed for the military, environmental, and robotic research applications in recent years (Caccia et al., 2008b). Israel and the USA have an important place in terms of USVs developed for military and defence purposes. In addition, Canada, Sweden, Britain, Norway and Italy are countries that have made progress on ISA. In Turkey, there are two USVs those named GLOBİDA (Gözcelioğlu, 2010) and Levent (ASELSAN, 2013) developed for military and defence purposes. Apart from military and defence purposes, there are also USVs developed for civil applications and training activities. Manley (1997), Manley et al. (2000), Curcio et al. (2005) developed USV to be used in training and civil applications.

USVs have been developed in accordance with the study objectives in many environmental research fields such as environmental monitoring and sampling, coastal protection, bathymetric research (Caccia et al., 2008a). Yaakob et al. (2012) have used USVs which can collect real-time data and can be controlled remotely, in environmental monitoring studies, in the monitoring of the oil spill in the sea, in fisheries stock research, in the monitoring of the environmental conditions of the reefs and in the collection of water quality data. Majohr and Buch (2006) have used USV for verifying the location information of the devices making measurements and route guidance in shallow waters with depth, discharge, etc. Martins et al. (2007) used USVs for oceanographic data collection. Naeem et al. (2006) and Naeem et al. (2007) used the USV in monitoring water pollution. Pascoal et al. (2006) used the USV for autonomous underwater vehicles to provide fast acoustic communication, as well as to collect marine data and create bathymetric maps. Caccia et al. (2005) used the USV to collect samples from the microlayers of the sea surface. Caccia et al. (2009) used USV to collect water samples. Breivik (2010) stated that USVs developed in Norway are used in many different studies. In this way, it is suggested that USVs can be used actively in such studies, considering the contribution it will make to the data collection in a very short time compared to the conditions in normal land conditions and the determination of the water quality and pollution of the created maps with USV.

Studies for determination and monitoring of the water resources quality in Turkey are carried out by universities, ministries, and other organizations that interact with local governments and water resources. However, these studies require a lot of workforces, material resources, and time. With developing technology, such technological products can be produced at lower costs. Due to the increase in technology, the cost of production decreases compared to previous times, it is now easier to manufacture these tools. Although there are examples in the world, there are unmanned surface vehicles named “Levent” and “GLOBİDA” which are used only for military purposes in Turkey. This gap needs to be filled urgently, and it is important that USVs to be developed are used in environmental monitoring, instant monitoring of lake/sea parameters.

With the help of physicochemical water parameters (pH, temperature, conductivity, oxidation-reduction potential (ORP), amount of dissolved oxygen) measured using USV, it will be possible to measure the quality of water at any time and place. Studies can be carried out without endangering human health by using less labour, time, and material resources. In this way, the relevant private or legal persons, institutions, and organizations will be able to access the data and information that are extremely important for the interventions and measures to be taken within the scope of the management of the said areas. For subsequent studies, more investigations should also be conducted on the use of USV by providing autonomous control, controlling using GPRS and WI-FI communication protocols, and ensuring data transfer, and collecting surface water samples by placing water sample collection modules.

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Chapter 5

THE VALUE OF SOME LEGUMES CONSUMED AS ROUGHAGE IN ŞANLIURFA IN ANIMAL NUTRITION

Ayşe ÇALIK[1]

1 Dr.Öğrt.Üyesi, Department of Field Crops, Faculty of Agriculture, Harran University, aysgns@yahoo.com

INTRODUCTION

It they are used for nutrition for legumes, humans and animals in feed crops. Among these, legumes such as alfalfa, korgula, vetch, hornbeam and triangular fodder are the most important. Legumes have high protein content and are very rich in minerals and vitamins. It is used as a source of protein in developing and producing legumes in countries where high levels of production are made. Legumes have a high nutritional value and are also highly useful for animals. In general, legume grass is not easy to cartagorize, abundant leaf and soft body feature shows[1]. Feed crops fed to animals as silage at the same time allows them to complete their nutrition through grazing. Rhizobium bacteria found in the roots of legume feed plants enrich the soil by binding free nitrogen to the soil. In agricultural areas where grain cultivation is done too much on top of each other, they enable the soil to be taken off. Legume fodder plants play a major role in making the soil productive, but they provide the soil to be enriched in terms of nutrients and organic matter. Legume fodder plants are important for soil improvement and conservation and are in the state of pioneering plants of the newly opened areas of Agriculture. Legumes are richer in feed crops than other coarse foods in terms of minerals and vitamins, especially protein.

In terms of forage crop production, our country has not yet reached the desired level in crop and animal production. When we look at the roughage production situation, it is seen that animal husbandry of our country is highly dependent on pasture. Elimination of animal feed deficit from natural pastures results in excessive destruction of pastures. However, the poor vegetation in our region, as well as the warm climate, is due to the fact that the soil structure of large areas is stony and bedrock covers the areas in large part. Completion of the work in order to ensure that surface storage facilities and groundwater reservoirs are maintained at the highest level with maximum feeding, proper water collection application, methods according to land use types and effective water use methods should be developed [2].

In şanlıurfa, given the situation of the field cultivated forage crops, it is observed that grain stems and barley are generally fed as feed to animals. In addition, some problems in vegetable and animal production due to the roughage deficit problem occurs. In the present state of the province of Şanlıurfa, the cultivation of feed plants is not done much. Legumes in the feed plant group have an important role in animal feeding and improvement of soil structure. Despite this, the production of legume fodder crops is not sufficient in our total agricultural areas.

As one of the main elements of sustainable agricultural production is the cultivation of fodder crops, it has become necessary to increase the production of fodder crops in field agriculture, to produce quality fodder for animals and to prevent early and overgrazing of grasses and meadows [3]. It is known that legumes grown as a mixture with cereals and have been used in our country since the last year.

Wheat and legume forage crops can be grown pure in agriculture for fodder crops, and higher yields and quality crops can be obtained by growing these crops in a mixture. Yesil Yesil was found to have a statistically significant effect on the yield of green grass and the values of green grass ranged between 1763.8-2947.5 kg/da [3]. It was determined that different doses of nitrogen and phosphorus applied to the mixture affected the fresh grass yield of animal grass at a statistically significant level and that the fresh grass values ranged between 1763.8-2947.5 kg / da [3].

When determining the amount of seed used in mixed planting, it is recommended to be generally 1/3 wheat type and 2/3 legume type. The most important of these is that the yield of mixed crops is higher than the lean planting of legumes[4]. This problem is less visible if the legumes that cause swelling problem in animals are grown in mixture. Often seen in legume fodder plants lying down problem is prevented by growing in mixture with wheat. Legumes are used as dry herbs and silages, and are widely used in feed rations since grains are rich in protein content, energy value, minerals and vitamins. In this study, the importance of some leguminous feed plants such as vetch, Burçak, alfalfa and peas in animal nutrition, quality of feed and protein ratio were investigated in terms of quality and delicious feed obtained from leguminous feed plants in the region.

In this study, legumes grown in the region such as vetch, burçak, alfalfa and feed peas were investigated. Crude protein rates of these legumes, dry, green grass yields, acid detergent insoluble fiber (ADF) rates, neutral detergent insoluble fiber (NDF) rates, digestible dry matter (SMM) rates and relative Feed values (NYD) were investigated. Crude protein ratios were calculated according to method in calculations [4]. The ADF and NDF ratios were made according to [5]. Other calculations are also used in the following formulas[6]. To calculate the relative feed value, first digestible dry matter (SKM) was made using ADF.

SKM= 88.9-(0.779 x ADF)

KMT= 120/NDF

NYD= (SKM x KMT) / 1.29

Sanliurfa, under the influence of the Mediterranean climate. Precipitation is increasing from south to North and from West to East. The region is situated in the semi-dry climate zone. Summers are hot and dry, winters are warm and rainy. Climate characteristics are the most important determinant of products to be grown in a region. Many years of Sanliurfa province (1960-2015) some climate values are given in Table 1 [7].

Şanlıurfa province has partially salty, salty alkaline areas. Water erosion is observed in an important part of the territory. The soil analysis sample belonging to Şanlıurfa province bears the characteristics of Harran plain soils. Harran plain lands are composed of flat, low-lying, mid-deep and deep soils with coluvial main material entering the series. Soils are very calcified and clay textured and soil pH is between 7.3-7.4, organic matter on the surface is 1.1% and depth is reduced to 0.8% in the structure shows[8].

In areas of agricultural production under dry conditions, organic fertilization has increased plant growth and yield. Organic fertilization was done in dry conditions, the plant only benefited from winter rains. Organic fertilizer preserved moisture in the soil [9]. Chemical properties of soils are given in Table2.

Long years in Sanliurfa (1960-2015) average climate values

Parameters	April	May	June	July	August	Septem.	October	Novmb.
Average vapor pressure (hPa))	10.4	11.9	12.5	13.9	14.3	12.3	10.6	9.9
Average temperature (^{o}C)	16.2	22.3	28.2	31.9	31.2	26.8	20.2	12.7
Average humidity (%)	56.2	44.9	32.8	30.1	33.1	35.8	46.4	59.9
Average overcast	4.1	2.9	1.0	0.4	0.5	0.8	2.5	3.6
Total Precipitation (mm)	46.8	28.1	3.6	0.6	0.8	3.3	27.4	46.0
Average wind speed (m s^{-1})	1.9	2.0	2.5	2.6	2.3	2.0	1.5	1.4
Average open surface evaporation (mm)	107.4	177.3	268.0	322.1	286.6	201.4	115.8	23.7
Average total Sun duration (sa-da)	7.43	10.01	12.16	12.25	11.27	10.03	7.46	5.51

Year	2016			2017		
Months	Minimum-heat ^{O}C	Maximum heat ^{O}C	Average heat^{O}C	Minimum-heat ^{O}C	Maximum-heat ^{O}C	average heat ^{O}C
January	-6.2	13.7	4.6	-5.2	15.5	5.5
february	2.1	25.5	11.4	-5.4	21.5	7.5
mach	2.7	24.5	13.6	4.2	24.9	12.7
april	7.4	32.7	20.5	5.8	30.4	16.5
may	10.7	35.0	23.2	12.3	37.4	22.9
June	18.9	42.0	29.8	17.5	41.8	29.9
July	20.9	43.0	33.0	22.4	43.5	34.2
august	21.2	43.0	33.4	21.4	44.8	32.1
september	14.7	39.0	26.5	18.3	42.1	29.7
october	12.3	33.9	22.2	11.3	30.9	20.6
november	3.0	24.4	12.7	2,5	24.5	13,4
december	-2.2	13.7	5.5	2,3	30.9	10,3

Deep	Saturated with water (%)	Sieve. Forward. (dsm-1)	Lime CO3 (%)	pH	Phosphorus (kg da1)	Potassium (kg da^{-1})	Organic matter (%)
0-30	90	0.67	7.90	7.85	3.74	241.80	2.33
30-60	107	0.59	9.50	7.94	0.53	98.40	1.31
60-90	104	0.86	9.80	7.62	0.65	108.60	1.49

Soil survey of Şanlıurfa province

In Fresh and Dry Grass Yields

It is estimated that the amount of dry grass produced in the meadows and pastures in şanlıurfa, which is the province with the highest animal presence in southeastern Anatolia region, is more than any other province in southeastern Anatolia region. Vetch types of plants grown in the region are usually fine-handled, abundant leaf, green and dry coarse feed to animals by giving the animals love to eat rich foods rich in herbs, one-year legume fodder plants. It is a legume feed plant that can be grown all over the world with temperate climate and is not resistant to cold and dry. If the Vetch legume feed plant is harvested late, the flowering will end up painful and more milk in cows will spoil the taste of milk and produce milk soreness. If planted with oats in the form of a mixture, the bitterness disappears.

One of the legume forage plants, Burçak is botanically connected to the Vetch genus, and is a single annual forage plant, usually grown for one of them. Ruminant is similar to vetch in terms of feed value, but it meets half of the need for roughage and is very nutritious both green and dry grass and yesilesi. The area of use as roughage is less and less is given to dairy cows.

Alfalfa (Medicago sativa), a legume of many years, is a feed plant with high herb yield and grass quality. As the age of animals as yediştirildiğinde cause swelling is dried, no problems encountered. Alfalfa flowering is harvested when 1/10 and the first form is used in silage construction. An average of three or four times a year, the Clover is harvested every 6-8 weeks.

It is rich in flavour, protein, mineral content and vitamins. Because of low cellulose level of alfalfa feed plant, it is useful to be supplied with dry coarse feed. Fresh, dry and silage is given in the form of grazing can be grown for purposes as well.

Feed Pea is a single-year legume feed plant grown for green and dry grass production, grazing or green Fertilizer.

It is used successfully in feeding all farm animals, although it is mainly grown for grass and one. The protein content (20% - 30%) in the grain can be mixed with coarse feed after breaking. Animals should be given in mixture with cereals as there is a dangerofinflating.

Common Vetch (Vicia Sativa L.) in the study on the effect of harvest time on crop yield and quality of genotypes, green grass yields were found to be between 1212.1-4386.0 kg/da and dry grass yields were found to be between 213.7-709.6 kg/da [9].

In a different study, it was determined that different nitrogen and phosphorus doses applied to the mixture in Şanlıurfa conditions were statistically significantly affected by the yield of fresh and dry herbs per decare and that the yield of fresh herbs ranged between 1763,8-2947,5 kg/da and the yield of dried herbs ranged between 722,81-1478,8 kg/da. The highest fresh grass yield was 3064.3 kg / da from N_9p_6 and dry grass yield of 1545.3 kg/da. [10]. In the study conducted with different alfalfa cultivars, green grass yield was determined at 7540-8552 kg/da and dry matter yield at 1925-2185 kg/da[11].

In the study on the determination of crop yields and some yield elements of feed peas cultivars, green grass yield was found to be 907-1109 kg and dry grass yield was found to be 221-281 kg/da[12]. The wet grass yield obtained in the Vetch type was 659 kg/da and dry grass yield was 175.7 kg/da[13]. Green grass yield obtained from Horoscope was 410 kg/da and dry grass yield was 95.3 kg/da[14]. In this study, the average yield of green grass was 3257-9286 kg/da, and the yield of dry grass was 787-2135 kg/da[15]. In the determination of yield and yield elements of some feed peas genotypes in winter planting in the region, green grass yield was examined at 853.6-2442 kg/da,dry grass yield at 264-580, 8 kg/da[16].

As a result of the research, some legumes such as vetch, alfalfa and feed peas in our region green and dry crop yields in our region, 1000-4000 kg/da and 200-700 kg/da, 7000-8000 kg/da and 2000-2500 kg/da, 900-1200 kg/da and 200-300 kg/da respectively are suitable to be obtained.

Crude protein ratio (%)

Crude protein means the total amount of protein contained in a feed substance. The most obvious indicator of Feed values of roughage is the ratio of crude protein and at least 6% of the animal's rations should be found in raw protein[17]. Crude feed quality increases as the increase in crude protein content is observed in studies performed. As a result of the studies carried out in different genotypes and different ecologies in the Vetch, it is also reported by many researchers that the crude protein rates ranged from 9.08% to 22.30%.[17][18][19][20][21][22][23][24][25][26]. In the study of different Clover cultivars, they found a value of 20.97% in crude protein content[27].

In this study, it was found that the ratio of crude protein to feed peas was 19.83% [28]. V. V. used in the study of vetch type in the region Peregrin L. it was observed that the ratio of crude protein to crude protein was 25.06% [29]. In another study conducted in Şanlıurfa province, the highest crude protein ratio of vetch plant was obtained from N9P3 with 27.26% fertilizer application parcels, while the lowest ratio was obtained from N0P0 control parcels with 16.55% [30]. In the study of Burçak feed plant, crude protein content was analyzed as 12.1% [11]. In the study of alfalfa feed plant, the crude protein content was 17.7% [31].

In the study of the determination of yield and yield components of some feed peas genotypes in winter cultivation, crude protein ratios were investigated as 10.3%-20.1% [13].

As a result of the research, raw protein ratios of some legumes such as vetch, alfalfa and feed peas in our region are suitable to be obtained in 9-20%, 17-20% and 11-20% respectively.

Values of feed plants grown in the region

Vegetation	G reen grass yield	Dry yield	Crude prt. ratio (%)	ADF ratio	NDF ratio	Digestible Dry Matt. Cotent(%)	Relative Feed Value	Dry Matter Consumption (%)
Vetch	659kg/da	175.7kg/da	%25.06	%31.30	%41.93	%64.52	143.13	%2.86
Burçak	410kg/da-	95.3kg/da	%12.1	%25.6	%31.0	%69.0	206.8	%3.9
Clover	3257-9286 kg/da	787-2135kg/da	%17.7	%30.5	%44.1	%65.1	137.5	%2.7
Peas forage	853.6-2442 kg/da	264-580.8 kg/da	%10.3-20.1	%21.7-36.4	%33.2-43.4	%60.6- 72	136.6-202.1	%2.7- 3.6

ADF and NDF ratio (%)

It is obtained by removing Hemi-cellulose content from the NDF content of the ground and dried feed. Gives information about the quality of the oath. The digestibility and energy value of Feed containing high ADF (acid detergent insoluble fiber) is low[31]. The plant structure and cell wall material of feed is composed of nitrogen and acid insoluble ash connected to the cell wall, hemicellulose, lignin and lysine. The structures that make up the NDF cannot be broken down by ruminant digestive enzymes[32]. Since the NDF (non-soluble fiber in neutral detergent) value is directly effective in animal feed intake, the animal feed intake increases as this value drops[5]. As a result of the studies carried out in different genotypes and different ecologies, vetch also indicated that ADF values were 18.6-41.8%, NDF values were changed between 34.97-66.7% by many researchers.[22][26][21][24]. In the study of different Clover cultivars, the ADF ratio was 25.47% and the NDF ratio was 28.66% [27]. In the study performed with feed peas, the ADF ratio was 37.74% and the ADF ratio was 44.83% [28]. V used in the study belonging to the type of vetch made in our region. Peregrin L. the ADF ratio was 31.30% and the NDF ratio was 41.93% [29]. In the study performed in Burçak plant, the ADF ratio was 25.6% and the NDF ratio was 31.0% [13]. In the study of alfalfa feed plant, the ADF ratio was 30.5% and the NDF ratio was 31.0% [30]. In this study, the ADF ratio was 21.7 - 36.4% and the NB ratio was 33.2 -43.4% in the determination of yield and yield elements in winter planting of some feed peas genotypes[15].

As a result of the research, some leguminous feed plants such as vetch, alfalfa and feed peas in our region, ADF and NDF rates, respectively, 19-30% and 35-45%, 26-30% and 29-31%, 20-36% and 30-43% respectively are suitable to be obtained.

Digestible Dry Matter Content(%)

Digestible dry matter (SKM) is an estimate of the total digestibility of the oath and is calculated using the percentage of insoluble fiber in acid detergent (% ADF) [38]. In quality studies on Vicia species, the digestible dry matter 52.1-72. 8 percent [33][34][24][35][36] they found that the rate of digestible dry matter in horçak plant was between 53.5% and 73.8% in the ecological conditions of Bingöl[37](çaçan et al. 2015). The digestible dry matter ratio was expressed as 69.06% in different Clover cultivars[27]. In this study, the digestible dry matter ratio was expressed as a value of 59.50% [28]. V. V. used in the study of vetch type in the region Peregrin L. in the study, the digestible dry matter was found to be 64.52% whereas the digestible dry matter was found to be 69.0% [13]. In the study of alfalfa feed plant, the digestible dry matter ratio was found to be 65.1% [30]. In the determination of yield and yield components of some feed peas genotypes in winter planting, digestible dry matter ratios were expressed as a value of 60.6-72% [15].

As a result of the research, the digestible dry matter ratios of some legumes such as vetch, alfalfa and feed peas in our region are suitable to be obtained between 53-65%, 65-69% and 59-70% respectively.

Dry Matter Consumption (%)

Dry matter means 100% waterless portion of feed ingredients. Although it is a very important criterion in ration regulation, high dry matter consumption refers to a high amount of energy and nutrient intake. In the calculation of dry matter consumption (KMT) based on estimating the amount of food consumed by an animal as %of body weight, the percentage of insoluble fiber (% NDF) in neutral detergent is used[38]. In quality studies on Vicia species, dry matter consumption is 2.6-3.1%.[34][24][36], the dry matter consumption rate in different Clover Clones was 4.28% [27].

In this study, dry matter consumption rates were found to be 2.35-3.08% [39]. V. used in the study of vetch type in the region Peregrin L. the rate of dry matter consumption in the cultivars was 2.86% [29]. The rate of dry matter consumption was found to be 3.9% in the study of Burçak feed plant[13]. The rate of dry matter consumption was found to be 2.7% in the alfalfa feed plant[30]. However, dry matter consumption rates were expressed as 2.7-3.6% in the determination of yield and yield items of some feed peas genotypes in winter planting[15].

As a result of the research, dry matter consumption values of some legumes such as vetch, alfalfa and feed peas in our region are suitable to be obtained at 2-3%, 2-4% and 2.5-3.5%, respectively.

Relative Feed Value

The relative feed value (NDA), which is included in the different quality indexes for the determination of quality coarse feed, is based on the ADF and NDF content and the estimate of the energy value of the animals with the potential to consume these feeds. The relative feed value is of great importance in determining the quality and marketing of feed. The relative feed Value Index is based on 100 indices calculated from the ADF (41%) and NDF (53%) content of the Alfalfa dry grass (yko) in the whole flower. The lower the value, the lower the feed quality, and the higher the feed quality[40]. It has been reported that the relative feed value in vetch genotypes ranged from 141-172 kg/da [24]. In the study conducted in different Clover cultivars, they reported that the relative feed value ranged from 231.43 kg/da[27]. The relative feed value was found to be 124.7 kg/da in the study of feed peas[28]. In the studies carried out in the region, V used in the study belonging to the type of vetch. Peregrin L. the relative feed value was found to be 143.13 kg/da[29]. In the study conducted with Burçak feed plant, the relative feed value was found to be between 206.8 kg/da[13]. In the study of alfalfa feed plant, the relative feed value was found to be 137.5 kg/da[30]. In the study of the determination of yield and yield components in winter planting of some feed peas genotypes, it was stated that the relative feed value ratios were between 136.6-202.1 kg/da[15].

As a result of the research, the relative Feed values of some legumes such as vetch, alfalfa and feed peas in our region are suitable to be obtained at 143-170 kg/da, 136-236 kg/da and 125-200 kg/da respectively.

CONCLUSIONS

According to the ecological conditions of the region, determination of Feed values by considering the value of vetch, Busch, alfalfa, feed peas in Animal Nutrition, Green/dry grass yields, crude protein rates, ADF and NDF rates, digestible dry matter rates, dry matter consumption and relative Feed values were investigated. As a result of the studies carried out in the region, the values of some legumes such as firecrackers, bushels, alfalfa, feed peas, green grass yields; 659 kg/da, 410kg/da, 3257-9286 kg/da, 853.6-2442 kg/da, dry grass yields; 175.7 kg/da, 95.3 kg/da, and 787-2135 kg/da, 264-580.8 kg/da, raw protein rates; %25.06, %25.06, %17.7, 10.3-20.1 ADF rates; %31.30, %25.6, %30.5, %21.7-36.4, NDF rates; %41.93, %31.0, %44.1, 33.2-43.4 digestible dry matter ratios: %64.52, %69.0, %65.1, %60.6-72, dry matter consumption rates; %2.86, %3.9, %2.7, %2.7-3.6 relative Feed values; 143.13 kg/da, 206.8 kg/da, 206.8 kg/da, 136.6-202.1 kg/da. As a result of the research, the yield values of some legumes such as vetch, alfalfa and feed peas in our region, respectively.;

green and dry grass yields,1000-4000 kg/da and 200-700 kg/da, 7000-8000 kg/da and 2000-2500 kg/da, 900-1200 kg/da and 200-300 kg/da, crude protein rates between 9-20%, 17-20% and 11-20%, ADF and NDF rates 19-30% and 35-45%, 26-30% and 29-31%, 20-36% and 30-43%, digestible dry consumption rates; 2-3%,2-4 and 2.5%-3.5 and relative Feed values; 143-170 kg/da 136-236 kg/da and 125-200 kg/da values are appropriate to be obtained.

Legumes are a source of quality feed plants for animals. In our country, in line with the support of feed crops in recent years, the ratio of feed crops in the field cultivation 2-3% to 7.40% in spite of the increase in the Southeastern Anatolia region remained at 1.57% [2]. Animal production by decreasing the cost of farming in the field of feed plant cultivation by increasing the desired level of animal products must be obtained from animals. Cotton Plant support given to feed plant as a result of the support is more than the growers prefer to plant cotton instead of feed plant. Cotton cultivation in our region is very common because of the agricultural lands are left Nadal. During this period where agricultural areas are left empty, it should be ensured that legumes such as vetch, bushes, single-year clovers, mürdüğü, feed peas should be grown in the form of mixture with cereals, taking into account the presence of animals in the region into consideration. They suggested that the main crop in irrigated areas of Southeastern Anatolia, where the dry agricultural system is applied, usually grain Nadas, grain-edible grain legumes and partially grain-summer products were planted. [41] the main crop in irrigated areas and feed crops were grown in nastas in dry areas. Vetch species can be planted in irrigated agricultural areas as a winter intermediate product in cotton-cotton or wheat-cotton plantation. In our region, it is recommended that varieties of one-year vetch plant suitable for the region with annual feed crops such as alfalfa for the production of fodder crops should be taken into the field with Summer main products and that alfalfa should be grown in irrigated areas and in Nadas areas by increasing the sowing areas of one-year legumes.

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Chapter 6

FACTORS AFFECTING ESSENTIAL OIL CONTENT AND COMPONENTS IN MEDICINAL AND AROMATIC PLANTS

Belgin COŞGE ŞENKAL[1]

1 Prof. Dr. ,Yozgat Bozok University, Faculty of Agriculture, Field Crop Department, belgin.senkal@yobu.edu.tr

INTRODUCTION

Medicinal and aromatic plants; carries bioactive substances (secondary metabolites) such as alkaloids, terpenoids or phenolics with pharmacological activity in one, several or all of its organs such as leaves, stems, bark, flowers, fruits, seeds, roots, rhizomes, onions, and tubers, and therefore drug, perfume, cosmetics, spices, dyes etc. refers to plants used for purposes (Baydar, 2019; Figueiredo et al., 2008).

The peculiar smells of aromatic plants are caused by terpenoids, which are expressed as essential oil or etheric oil. Especially monoterpenes and partially sesquiterpenes are the most important odor molecules of essential oils secreted in aromatic plants. Aromatic plants that are rich in essential oils are called essential oil plants. Aromatic plants generally contain 0.1-5.0% essential oil, except for some plants such as oil rose and clove. Essential oils obtained from aromatic plants by distillation methods are also very valuable medicines, flavors, cosmetics and perfume raw materials (Baydar, 2019; Anulika et al., 2016).

Medicinal and aromatic plants are produced by gathering or cultivating intensively from nature as the most important secondary metabolite sources. Medicinal and aromatic plants are plants cultivated due to the bioactive substances they contain. Bioactive substances, on the other hand, vary significantly depending on the organs of the plant, the life cycle of the plant and the harvest / harvest / harvest time of the plant. For this reason, medical and aromatic plant producers must first of all know the source of bioactive substances and collect, harvest, harvest and harvest at the time and time when it is richest in active substances (Baydar, 2019).

The aim of this study was to evaluate the factors affecting the amount and composition of essential oil obtained from medicinal and aromatic plants within the scope of research results and literature data.

MATERIAL AND METHOD

In this study, the results of the literature and different research results conducted in previous years were used.

In all research, essential oils were obtained using Clevenger device. The samples of plant were dried in the shade at room temperature. Average 50 or 100 g of these parts ground was extracted using a Clevenger type apparatus for 3 h in 750 mL water. Essential oil values (%, v/w) were calculated by volume over dry mater. The obtained essential oils were taken into dark colored flasks and stocked at 4^{o}C in a refrigerator until they were analyzed.

The chemical composition of essential oils was determined gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) analyses (Figure 1).

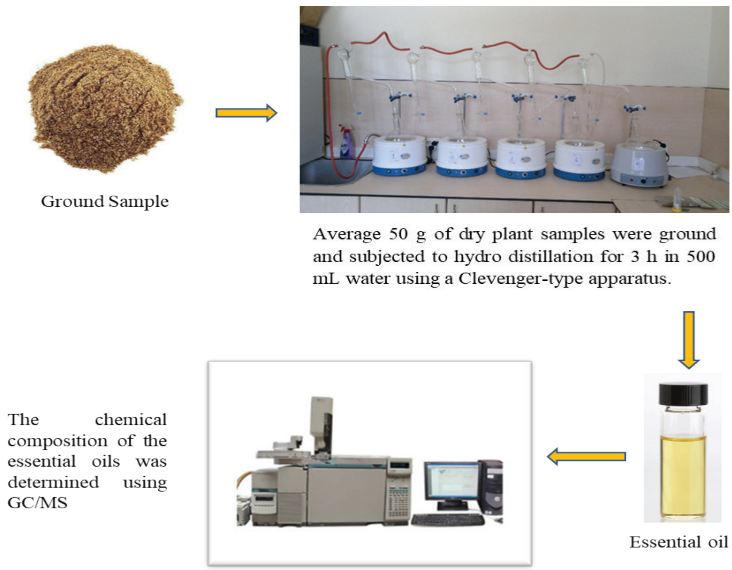


Figure 1. *Analysis process in obtaining data*

RESULT AND DISCUSSION

Secondary metabolites

Secondary metabolites are organic molecules that are not involved in the normal growth and development of an organism (Mazid et al., 2011). Plant secondary metabolites can be divided into four major classes as terpenes, phenolics, compounds, alkaloids and sulfur-containing compounds (Anulika et al. 2016). Secondary metabolites (essential oils, alkaloids, glycosides, steroids, saponins, resins, etc.) are very valuable phytochemicals not only for the plants they are synthesized, but also for other creatures fed with these plants.

Essential oils

Essential oils, also known as volatile oils or ethereal oils, are natural metabolic secretions of plants, are obtained from various organs of plants such as leaves, petals, flowers, stems, seeds, and roots etc. (Hariri et al 2008). They are generally colorless or light-yellow colored, volatile, strong smelling and oily mixtures that are liquid at room temperature, sometimes freeze, easily crystallize. These oils are called “essential oil” because they can evaporate even at room temperature when they are left exposed, and "essential oil" because they fly like ether (Yaylı, 2013; Dhifi et al., 2016; Rassem et al. 2016). Essential oils are aromatic substances found in the special cells or glands of some plants that they use to protect themselves from predators and pest, but also to attract pollinators. (Hariri et al. 2018).

Essential oils are a complex mixture of organic substances (Hariri et al 2008). A large number of compounds (over 300) have been identified that make up essential oils ((Dhifi et al., 2016; Butnariu & Sarac 2018). In the composition of essential oils, there are terpenic or non-terpenic components. These are hydrocarbons and their oxygenated derivatives. Some components may contain nitrogen or sulfur. It is available in alcohol, acid, ester, epoxide, aldehyde, ketone, amine, sulfite and in their compositions. Terpenes are structures formed by connecting isoprene units to each other. Many of the monoterpenes, sesquiterpenes and diterpenes are included in the composition of essential oils. In addition, alcohols, hydrocarbons, phenols, aldehydes, esters and ketones are some of the main components of essential oil (Younis et al. 2008; Baser, 2009 Dhifi et al., 2016, Tanu & Harpreet, 2016).

Essential oil is used in perfumery, aromatherapy, cosmetics, incense, medicine, household cleaning products and for flavoring food and drink. They are valuable commodities in the fragrance and food industries (Rassem et al., 2016; Dhifi et al., 2016).

Factors Affecting Essential Oil Content and Components in Medicinal and Aromatic Plants

Secondary metabolites differ according to the genetic structure of the plant (genotypic and chemitypic variability), the organs of the plant (morphogenetic variability, the plant's life circuits (ontogenetic variability), as well as environmental factors such as climate, soil, altitude and topography. Factors affecting secondary metabolites from plants are summarized in Figure 2 below (Figueiredo et al., 2008; Bara 2009; Acıkgoz et al. 2017; Pasa et al. 2019).

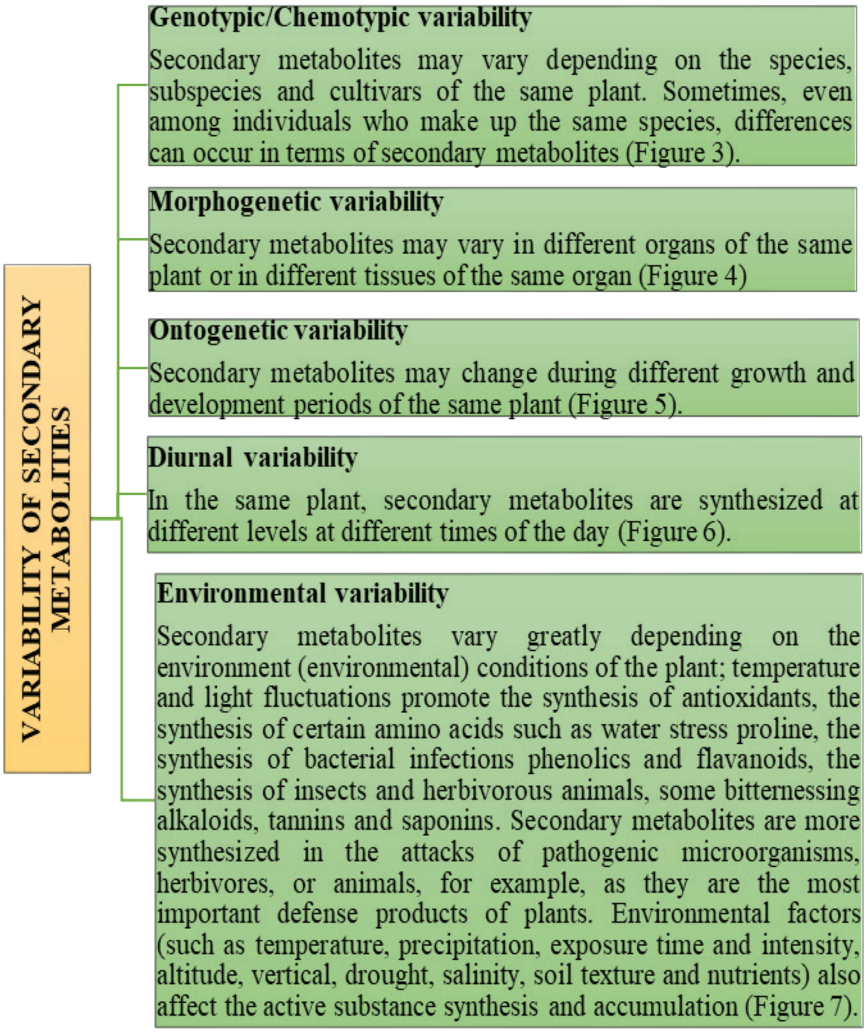


Figure 2. *Variability of secondary metabolites obtained from medicinal and aromatic plants*

1-Genotypic/Chemotypic variability

This study was conducted to investigate the essential oil content and chemical composition of sweet fennel (*Foeniculum vulgare* Mill. var. *dulce*) lines originating from Turkey. According to the findings from the study, both the content and chemical composition of the essential oils of the lines (LINE-7 and LINE-8) grown in Ankara ecological conditions have changed. While the essential oil rate of LINE-7 was 4.44%, this value was recorded as 1.90% in LINE-8. Similarly, the main components of the two lines were found proportionally different (Cosge et al., 2008). Analysis results of two lines are given in Figure 3.

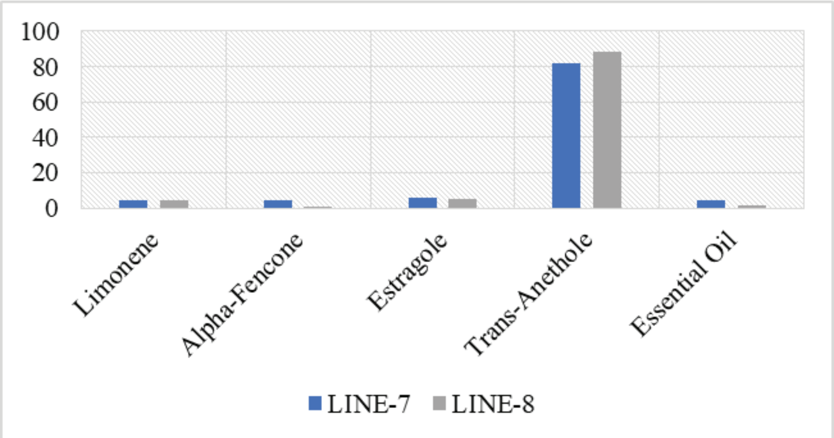


Figure 3. *Essential oil content and main components in two sweet fennel (Foeniculum vulgare Mill. var. dulce) lines*

2-Morphogenetic variability

The essential oils obtained from fruit, stem, leaf stalk and leaf of bitter fennel (*Foeniculum vulgare* Miller, Apiaceae) were analyzed using GC-MS. The essential oil content was determined as 7.25%, 0.375%, 0.857% and 0.75% in fruit, stalk, leaf stalk and leaf, respectively. *trans*-Anethole was the major component in the fruit (75.05 %), stem (64.09 %) and leaf stalk (75.64%) and the leaf oil which contained (α-phellandrene (38.23%) and (α-pinene (31.79%) as the main components (Figure 4). It has been observed that the chemical composition of the essential oils studied varied both quantitatively and qualitatively. It is noted that the component with the highest value in essential oils from fruit, stem and leaf stem is the trans-anethole. The leaf essential oil contained lower trans-anethole and higher α-phellandrene and α-pinene concentrations compared to the other essential oils studied (Cosge et al., 2009).

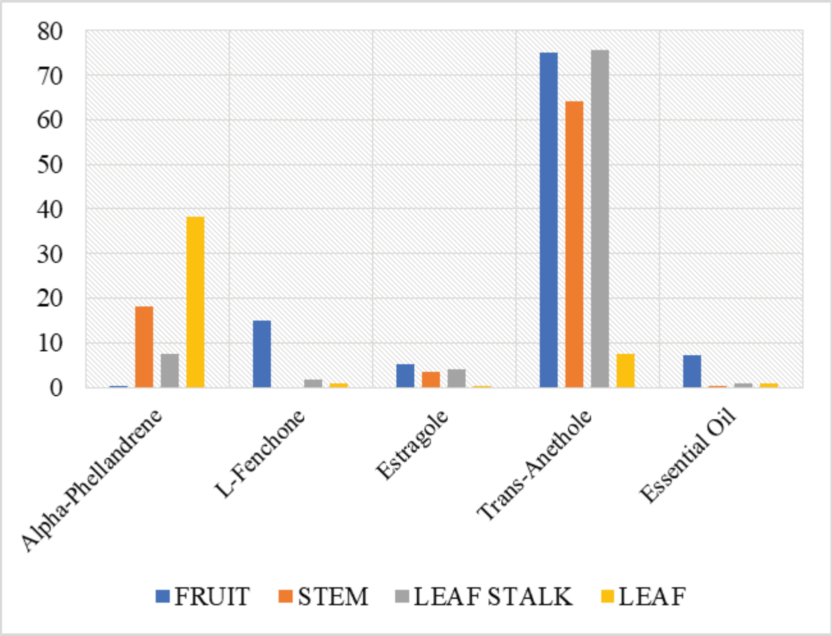
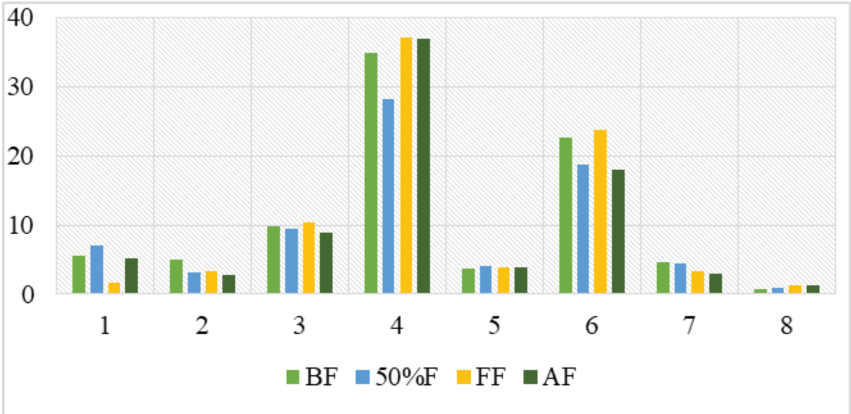


Figure 4. *Morphogenetic variability of essential oil content and main components in Foeniculum vulgare Miller*

3- Ontogenetic variability

The aerial parts of *Artemisia annua* grown in culture conditions were formed in four different development periods, before flowering, 50% flowering, full flowering and after flowering. The essential oil rate has shown an increasing change with form periods. The highest value was obtained from the period after flowering with 1.38%. Proportional values of the components of the essential oil also changed according to the development periods. For example, while artemisia ketone was 28.30% in 50% flowering period, it was determined as 37.15% in full flowering period (Figure 5). Both the amount of essential oil and the components of the essential oil obtained from *A. annua* were affected by the development periods and showed differences (Cosge et al., 2015).



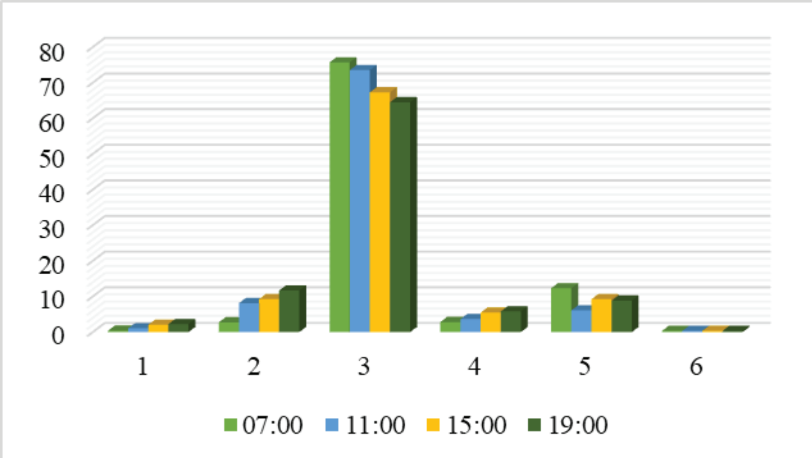
1-*Alpha-pinene,* **2**-*Camphene,* **3**-*1,8-cineole,* **4**-*Artemisia ketone,* **5**-*Artemisia alcohol,* **6**-*Camphor,* **7**-*Beta-selinene,* **8**-*Essential oil content*

BF: *Before Flowering,* **50%F**: *50% Flowering,* **FF**: *Full Flowering,* **AF**: *After Flowering*

Figure 5. *Essential oil content and composition of Artemisia annua L. at different development stages (%)*

4-Diurnal variability

In this study, coriander (*Coriandrum sativum*) cv. Arslan was used as a material. In the study carried out under the ecological conditions of Yozgat, the seeds were harvested in four different hours when the seeds were greenish brown. The essential oil rate of cv. Arslan was 0.31-0.33%, the highest essential oil rate was taken from the harvested plants at 19:00. The essential oil rates (0.31%) of the plants harvested between 07:00 and 11:00 were found the same. In essential oils obtained from seeds harvested at four different hours, linalool was identified as the main component (64.49-75.69%). This value was found higher in plants harvested at 07:00. Linalool value tended to decrease with delay of harvest time. Geraniol 12.31% (07:00), gamma-terpinene 11.67% (19:00) and camphor 5.81% (19:00) (Figure 6). In Gamma-terpinen, the highest value was taken from the harvested plants at 19:00 and the lowest value at 07:00. Similar situation is valid in camphor (Cinarlidere & Cosge Senkal, 2019).

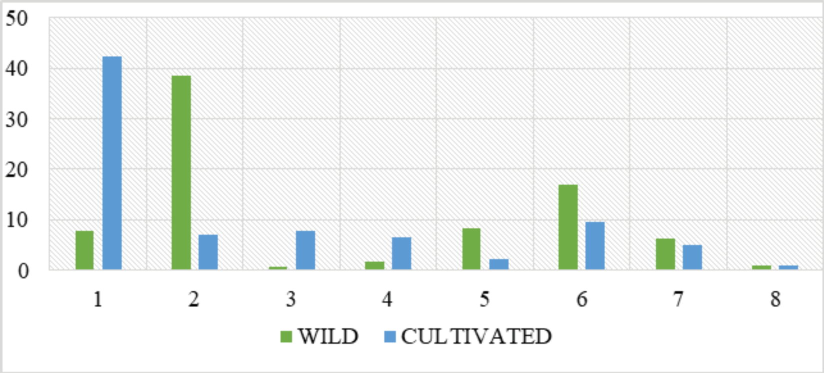


1-*Alpha-pinene,* **2**-*Gamma-terpinene,* **3**-*Linalool,* **4**-*Camphor,* **5**-*Geraniol,* **6**-*Essential oil content*

Figure 6. *Diurnal variability of essential oil content and main components in Coriandrum sativum L.*

5-Environmental variability

The aerial parts of *Salvia tomentosa* species, which are collected from natural environment and grown under culture conditions, were collected during the flowering period. Essential oil contents and chemical compositions of plant samples collected were examined. According to the findings; Natural area essential oil rate of *S. tomentosa* is 0.83%, culture condition essential oil rate is 0.98%, 21 components representing 97.79% of oil in natural field essential oil and 20 components that constitute 96.34% of oil in culture field essential oil were recorded. 38.39% of the natural field essential oil constituted beta-pinene. Other important components are beta-caryophyllene (16.81%), isoborneol (8.26%), alpha-pinene (7.68%) and alpha-humulene (6.37%). 42.41% of the essential oil obtained from the culture condition constituted alpha-pinene. 9.62% of this essential oil was beta-caryophyllene, 7.90% myrcene, 6.91% beta-pinene and 6.40% camphor (Figure 7). The essential oil rate and composition obtained from plants differed according to the environmental characteristics of the growing medium (Cosge Senkal et al., 2012).



1-*Alpha-pinene,* **2**-*Beta-pinene,* **3**-*Myrcene,* **4**-*Camphor,* **5**-*Isoborneol,* **6**-*Beta-caryophyllene,* **7**-*Alpha-humulene,* **8**-*Essential oil content*

Figure 7. *Essential oil content and main components of wild and cultivated Salvia tomentosa L. (%)*

CONCLUSION

Genotype leads to large differences in secondary metabolite synthesis. However, the method of collection (harvesting) and its duration is very important for an herbal drog to be as rich as possible in terms of the active ingredient. The chemical composition of essential oil in medicinal and aromatic plants is an important factor that determines quality. Therefore, it is important to determine the best harvest time throughout the day to improve the quality of essential oils from plants. On the other hand, the most important factor determining the quality of the part of the plant to be used as a medicine in medicinal and aromatic plants is the amount of essential oil it contains. This is also the most important factor in determining the part of the plant to be used as a drog. Because different plant organs contain essential oils in different amounts and contents.

The differences in the ecological conditions (temperature, precipitation, relative humidity, irradiation time, light intensity and day and night temperature differences, etc., and the physical, chemical and biological properties of the soil, etc.) also change the essential oil ratio and composition to be obtained from that plant.

The amount and composition of the essential oil contained in the plant is an indicator of the economic value of that product. Considering the change of bioactive substances in plants, it should be well known which part of the plant (morphogenetic variance), at what stage (ontogenetic variance) and at what time (daily variance) can be collected or harvested. Considering all these, it is seen that the factors that cause changes in the essential oil rate in aromatic plants are well known and how important it is to manage these factors positively.

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Chapter 7

EFFECT OF ROASTING PRETREATMENT ON THE FUNCTIONAL CHARACTERISTICS OF PHASEOLUS VULGARIS L.

Burcu ÇABUK[1], Gülşah ÇALIŞKAN KOÇ[2]

1 Doktor Öğretim Üyesi , Department of Gastronomy and Culinary Arts, Alanya Hamdullan Emin Paşa University, burcucabuk@ahep.edu.tr

2 Doktor , Department of Gastronomy and Culinary Arts, Alanya Hamdullan Emin Paşa University, gulsah_calisan86@hotmail.com

1. Introduction

Beans is one of the most ancient legumes and has been one of the most widely used pulse crops especially in India and Middle East region as it is a good plant-based protein source, rich in proteins, soluble and insoluble fibers and low in fat (Ceyhan, Harmankaya, & Kahraman, 2014). Bean has also a significant place in diet in Turkish cuisine because like in many developing countries where consumption of animal proteins is scarce and expensive, pulse crops are used as a main protein sources meeting the needs of almost 10% of the daily protein and 5% of the daily energy intake. Turkey also hosts hundreds of local landraces of common pulse crops due to its favourable climate and environmental conditions (Yeken, Kantar, Çancı, Özer, & Çiftçi).

As the population of the world increases rapidly, sufficient food production levels to meet the food security is decreasing. As a result, food insecurity and poverty increase the risk of malnutrition; especially deaths among children are linked to malnutrition mostly occurring in low and middle-income countries (Popelka, Terryn, & Higgins, 2004). High-quality protein requirements met with animal proteins which are expensive and therefore tend to be out of reach for much of the population however, pulse crops can effectively meet the nutritional energy requirements. Therefore, use of plant sources as an alternative to animal proteins seems to be promising approach (Prasad, 2010; Tontisirin, Nantel, & Bhattacharjee, 2002). Not only this but also higher levels of cholesterol and risk for cardiovascular diseases associated with consumption of animal proteins are widely revealed in growing number of studies and such studies have contributed significantly to a growing interest in producing plant-based products for food industry due to high protein content (Hu, 2003; Micha, Michas, & Mozaffarian, 2012; Thorogood, Mann, Appleby, & McPherson, 1994). As a result, better and more efficient use of legumes will become critical if animal proteins reach their maximum production capacity. Moreover, the production of animal proteins causes more natural resource waste than producing equal amounts of plant and insect protein sources, therefore plant protein-based meat and milk substitutes can be effective steps in reducing greenhouse gas emissions and destroying forest land by livestock while providing quality equivalent to animal proteins (Garnett, 2009; Van Huis et al., 2013).

Consumption of pulse crops such as beans in food industry can be increased by the use of these pulse flours as an ingredient in bakery products, snacks, sauces, processed meats and soups for improving their nutritional value without adversely altering the sensory properties (Boye, Zare, & Pletch, 2010; Tiwari, Gowen, & McKenna, 2011). Functional properties have a direct influence on various consumption areas of pulse flours therefore play a critical role helping to predict how these pulse flours can be used for replacement of the conventional ingredients and how novel food products may behave in specific systems (Duranti, 2006; Toews & Wang, 2013).

There have been many methods including conventional heat treatment or biotechnological methods such as fermentation widely used processes to produce desirable functional changes. Although effects of conventional heat treatment on composition, nutritional value, and functional properties such as increased emulsion stability (Çabuk, Stone, Korber, Tanaka, & Nickerson, 2018), decreased foam stability (Hussain, Anjum, Butt, & Sheikh, 2008), increased inhibitory enzyme activity (Çabuk, Nosworthy, et al., 2018), reduced bulk density (Jogihalli, Singh, Kumar, & Sharanagat, 2017) of different pulse crops have been reported earlier, information regarding the effect of microwave assisted roasting power and roasting time on functional properties of beans is very limited. Compared to other modification methods, mainly conventional heat treatment, microwave heating delivers high efficiency due to being time-energy saving.

The objectives of this study were therefore, to comprehensively investigate the microwave power and roasting time of the microwave assisted roasting process in terms of functional, physical and powder properties of bean flours. The outcomes of this study will provide a foundation for the use of bean flours in a wide range of food applications and contribute to our knowledge of both microwave treatment method on further developing functional foods.

2. Materials and methods

White navy beans and sunflower oil used in this study were purchased from a local supermarket; whereas all other chemicals used were of reagent grade.

2.1. Microwave heat treatment and flour preparation

For the microwave treatment, locally supplied bean seeds (30g) were placed in a glass petri dish and roasted in a domestic microwave oven (Arçelik MD574, Turkey) at 5 different microwave powers (120, 350, 460, 600, and 720W) and roasting time (15s, 30s, 45s).The microwave roasted beans were processed into flours by grinding (Custom Grind, model 80365; Hamilton Beach, Glen Allen, VA, USA) and then passed through a 40-mesh sieve and stored in an airtight container for further utilization in different applications.

2.2. Proximate and powder properties

The moisture and ash contents of the bean powders were determined according to AOAC (1995). The bulk and tapped density values and average wettability (s) time of the bean powders were determined using the method explained by Jinapong, Suphantharika, and Jamnong (2008) and Adamopoulos (2008), respectively. The flowability and cohesiveness values of the powders were evaluated in terms of the Carr Index (CI, Carr, 1965) and Hausner Ratio (HR, Hausner, 1967), respectively.

2.3. Oil holding (OHC) and water hydration capacity (WHC)

OHC and WHC values were determined according to Stone, Karalash, Tyler, Warkentin, and Nickerson (2015) with some modifications. Briefly, 1.0 g of bean flour sample was mixed with 10 mL of sunflower oil (for OHC experiment) or 10 ml of deionized water (for WHC experiment) in 50 mL of a centrifuge tube for 10 s every 5 min for 30 min. The mixture was then centrifuged at 10.000 rpm for 15 min at 25 ◦C. The weight change in samples after removing the supernatant relative to the dry sample weight (1.0 g) was calculated. The water hydration and oil holding capacities were expressed as g of water or oil, absorbed per g of the sample on a dry-weight basis.

2.4. Emulsification properties

The emulsification activity (EA) and stability (ES) was determined according to methods of Yasumatsu et al. (1972). Briefly, 1.0 g of bean flour sample was mixed with in 14.3 mL of Milli-Q water for 30 min using a mechanical stirrer (500 rpm) at room temperature. This mixture then was added to 14.3 mL of sunflower oil, and homogenized (Janke-Kunkel Ultra Turrax T25, Staufen, Germany) at 7.500 rpm for 1 min. Then 10 mL of this emulsion was centrifuged at 10.000 rpm for 5 min (Eppendorf, Model 5810R, Mississauga, ON, Canada). The emulsification activity was determined as following Eq. (1):

$$EA = \frac{H_1}{H_0} x100 \tag{1}$$

Where H_0 is the total height of the emulsion layer prior to centrifugation and H_1 is the total height of the emulsion layer after centrifugation.

Emulsification stability was determined by preparing the emulsion as previously described, except the emulsion was heated at 80°C for 30 min using a water bath in centrifuge tubes. The tubes were then cooled rapidly under running tap water. Afterwards, the tubes were centrifuged at 10.000 rpm for 5 min. ES was determined by the following Eq. (2):

$$ES = \frac{EA_H}{EA} x100 \quad (2)$$

Where EA_H is the emulsification activity of the heated emulsion and EA is the emulsification activity of the unheated emulsion.

2.5. Foaming properties

The foaming capacity (FC) and stability (FS) we determined according to S. Liu, Elmer, Low, and Nickerson (2010). One g of bean flour sample was stirred in 25 mL of Milli-Q water for 30 min on a mechanical stirrer (500 rpm) at room temperature. Then 15 mL of this solution was homogenized in 400 mL beaker at 7.600 rpm for 5 min. The homogenized samples were then poured into a 100 mL graduated cylinder. The foam volume was recorded at time 0 and after 30 min of homogenization. FC and FS was calculated by following Eq. (3 and 4):

$$FS = \frac{V_{F30}}{V_{F0}} x100 \quad (3)$$

$$FS = \frac{V_{F30}}{V_{F0}} x100 \quad (4)$$

Where V_{F0} is the volume of the foam at time 0 min, V_0 is the initial volume of sample used (15 mL), and V_{F30} is the foam volume after 30 min.

2.6. Statistical analysis

Data was analyzed by one-way ANOVA using Minitab Statistical Software (Minitab 17.0 for Windows, Minitab, USA). All analyses were carried out in triplicates. Data were presented as a mean ± standard deviation. Tukeys' test was used for comparison of means with a level significance of 0.05.

3. Results and discussion

3.1. Proximate and powder analysis

The powder properties, moisture and ash content of bean powders are given in Table 1. The moisture contents of bean powders are below 10% which is sufficient to make foods microbiologically safe (Tze et al., 2012) . The moisture content values of bean flours were found to be significantly lower than the moisture content of bean flour (10.41±0.01%) which was presented by Kohajdová, Karovičová, and Magala (2012). The effect of microwave power and treatment time were generally not found to be significant on the moisture content of the beans ($p>0.05$) except for 700W for 15s treatment ($p<0.05$). The moisture content of bean powders decreased depending on the increasing treatment time at 700W microwave power. It may be due to the higher evaporation rate of water (which is related to drying) or damaging of the bean tissues. The ash content of the samples was not significantly changed depending on the microwave power and treatment time ($p>0.05$). The ash content values of bean flours were found to be higher than the ash content of bean flour (3.49±0.07%) which was presented by Kohajdová et al. (2012). In addition, Siddiq, Ravi, Harte, and Dolan (2010) reported that the ash content values of different types of beans (red kidney, small red kidney, cranberry, and black) ranged between 4.60±0.09% and 5.00±0.18, respectively which is also consistent with the results of this study.

Microwave roasted beans were grounded that to have a uniform size for further utilization in different applications. The bulk and tapped density values of samples which were roasted at 700W were generally found to be higher compared to the samples which were roasted at 350W. Kratchanova, Pavlova, and Panchev (2004) reported that the energy of the super-high frequency (2450 MHz) electromagnetic field is converted into heat in substances made up of polar molecules. As a result of intensive vapor formation in the capillary-porous structure, a large pressure is built up which modify the physical properties of the material. The changes in the capillary-porous properties of the beans may be the reason of the higher tapped density values which is calculated according to the compressibility of the powder. In addition, Krokida and Maroulis (2019) reported that the porosity of the freeze-dried product is always higher (80-90%), and the microwave dried product (75%) follows it. It can be assumed that the bean flour roasted at 700W have a more porous structure which further resulted in higher tapped density values. The bulk and tapped density values decreased when the treatment time was increased from 15 to 30s, however, the opposite effect was observed for further increase except for 700W microwave power. Higher bulk density values are desired due to low packaging and transportation costs. For this reason, the bean flour that treated at 700W for 45 s have advantages of low packaging and transportation costs. Siddiq et al. (2010) reported that the bulk density values of different types of beans (red kidney, small red kidney, cranberry, and black) ranged between 515±17kg/m^3 and 556±16kg/m^3, respectively which is also consistent with the control sample, however, significantly higher values were observed for microwave treated samples ($P<0.05$).

The flowability and cohesiveness values of the flours were evaluated in terms of the Carr Index and Hausner Ratio, and the bean flours were found to be in Good-Fair and Low-Intermediate levels, respectively. Similarly, Çalışkan Koç, Nur Dİrim, and Akdogan (2017) reported that the flowability and cohesiveness values of microwave dried (180-900W microwave powers) corn husk powder ranged between fair-very good and low-intermediate levels, respectively The bean flours which were heated at 700W have superior flow properties compared to the 350W. Carr Index and Hausner Ratio values increased when treatment time was increased from 15s to 30s, however, the opposite effect was observed for further increase.

The average wettability time of control was found to be as 232.00±19.80s and the wettability times of microwave-roasted samples are shown in Figure 1. The wettability times of bean flours significantly decreased depending on the increasing of the microwave power and treatment time ($p<0.05$). The higher bulk density values (which is also related to sinking behavior) of bean flours which were roasted at 700W resulted in lower wettability times. The higher water hydration capacity of the samples which were roasted at 700W may also be the reason for fast wetting behavior (Table 3). Freudig, Hogekamp, and Schubert (1999) claimed that low tapped density values of the flours resulted in higher wettability time. Similar results (Average Tapped Density for 350W= 762.36kg/m^3 and for 700W=782.97kg/m^3) were also obtained in this study.

Table 1. Powder properties, moisture, and ash content of control and roasted flours.

Microwave Power (W)	Roasting Time (s)	Moisture Content (%, Wet Basis)	Ash Content (%, Wet Basis)	Bulk Density (kg/m^3)	Tapped Density (kg/m^3)	Flowability (Carr Index, CI)	Cohesiveness (Hausner Ratio, HR)
Control	-	5.62±0.29^{a}	4.33±0.63^{a}	555.56 ±0.00^{a}	741.76±8.85^{ab}	25.00±3.93^{bc} (Fair)	1.34±0.06^{bc} (Intermediate)
350	15	5.58±0.39^{a}	4.57±0.61^{a}	618.06±46.06^{ab}	787.54±57.43^{cd}	21.31±6.70^{bc} (Fair)	1.27 ± 0.10^{ab} (Intermediate)
	30	6.03±0.28^{ab}	4.33±0.12^{a}	563.73 ± 16.34^{a}	728.02±27.47^{ab}	22.54±0.65^{bc} (Fair)	1.29 ± 0.01^{bc} (Intermediate)
	45	5.42±0.25^{a}	4.62±1.29^{a}	612.59±5.28^{ab}	771.52±48.67^{bc}	20.75±5.69^{b} (Fair)	1.26 ± 0.09^{ab} (Intermediate)
700	15	7.08±1.59^{b}	4.26±0.12^{a}	615.80±18.38^{ab}	714.28±0.00^{a}	13.78±2.57^{a} (Good)	1.16 ± 0.03^{a} (Low)
	30	6.51±1.48^{ab}	4.23±0.41^{a}	598.44±33.43^{ab}	833.33±0.00^{d}	28.18±4.01^{c} (Fair)	1.39±0.07^{c} (Intermediate)
	45	5.53±0.22^{a}	4.73±0.61^{a}	647.32± 44.64^{b}	801.28±0.00^{cd}	19.19±4.40^{ab} (Good)	1.24 ± 0.06^{ab} (Intermediate)

Data represent the mean ± one standard deviation (n =3). Data with different superscript letters in the same column indicate significant differences ($p < 0.05$).

3.2. Water hydration and oil holding properties

Water hydration capacity (WHC) and oil holding capacity (OHC) of the control and roasted bean flours are presented in Table 3. It can be implied from the results that WHC for control sample was 1.38 ± 0.03g/g flour (in dry basis) which was lower than those the previously reported values by Wani, Sogi, Wani, and Gill (2013) and Aguilera, Estrella, Benitez, Esteban, and Martín-Cabrejas (2011). In comparison with the unroasted control sample, the roasted bean flours exhibited significantly higher ($P<0.05$) WHC. The highest WHC of 2.04±0.09 g/g bean flour (in dry basis) was obtained when microwave power was applied at 700W for 45 s. This effect could be associated with dissociated protein subunits which have more water binding sites favoring more hydrogen bonding and greater water absorption (Siddiq, Kelkar, Harte, Dolan, & Nyombaire, 2013). Moreover, several authors have indicated that higher degree of starch damage, amylopectin break down and fracture of the seed with microwave treatment allows greater absorption of water (Chau, Wen, & Wang, 2006; Gallegos-Infante et al., 2014).

OHC value is a significant parameter which affect the product texture (crispness), appearance, sensory profile, fat uptake during frying, and storage (Siddiq et al., 2010). Control sample was found to have OHC of 0.70±0.01g/g flour (in dry basis) which was different to the previously reported values of various bean flours varying between 1.23±0.08 to 1.52±0.11 g/g dry bean flour (Siddiq et al., 2010). OHC of the bean flour was found to be increased with the treatment time at 350W roasting power from 0.69±0.01 to 0.59±0.01. The highest oil holding of 0.76±0.03 was observed with the sample roasted at 700W for 30s. The increased OHC of roasted samples compared to control sample can be explained due to the changes in the structure of the starch molecules with microwave treatment (Bashir & Aggarwal, 2016; Chung & Liu, 2010).

Table 3. Water hydration and oil holding capacity values of control and roasted bean flour samples.

Microwave Power (W)	**Roasting Time (sec)**	**WHC (g/g flour, in dry basis)**	**OHC (g/g flour, in dry basis)**
Control	-	1.38 ± 0.03^{c}	0.70 ± 0.01^{b}
350	15	1.62 ± 0.06^{bc}	0.69 ± 0.01^{b}
	30	1.72 ± 0.03^{b}	0.63 ± 0.01^{cd}
	45	1.64 ± 0.01^{bc}	0.59 ± 0.01^{d}
700	15	1.73 ± 0.15^{b}	0.67 ± 0.01^{bc}
	30	1.78 ± 0.06^{ab}	0.76 ± 0.03^{a}
	45	2.04 ± 0.09^{a}	0.73 ± 0.01^{ab}

Data represent the mean ± one standard deviation (n =3). Data with different superscript letters in the same column indicate significant differences ($p < 0.05$)

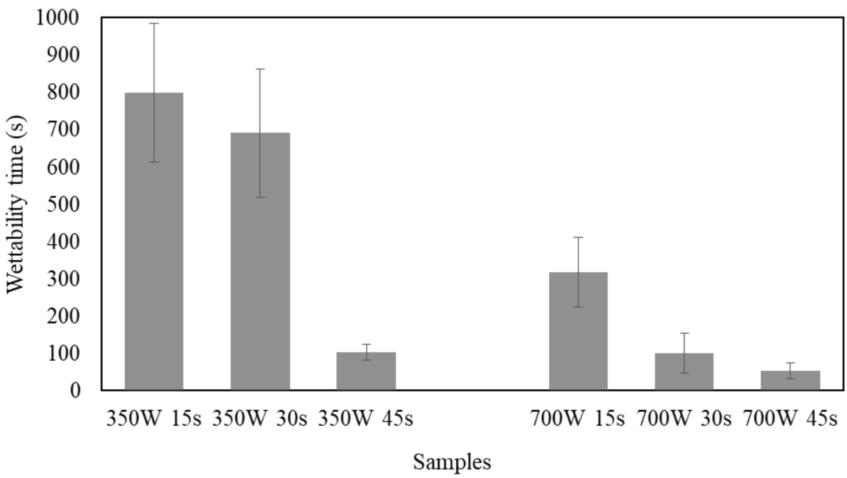

Fig.1. *The average wettability times of roasted flour samples.*

3.3. Emulsification properties

Emulsification properties are important parameters for the development of functional food ingredients and gluten free food products. Table 2 represents the results of emulsification activity (EA) and stability (ES) analysis of unroasted (control) and roasted bean flours. According to the results, microwave roasting increased the EA of bean flour in between 3.91% (at 700W for 45s) to 5.90% (at 700W for 15s). On the other hand, no significant differences in the results were observed between the microwave roasted sample flours (P>0.05). It can be stated that further microwave treatment observed to have no positive impact on improving emulsification activity. The roasted bean flours showed ES in the range from 89.88±2.28% to 102.24±1.48% as compared to unroasted control (74.81±0.89%). Furthermore, emulsification stability was observed to increase significantly (P<0.05) with increase in roasting time dose from 89.88±2.28% to 100.88±5.28% at 350W while an opposite trend of was observed at 700W with the increase in roasting time. The highest ES was obtained with the samples roasted at 700W for 15s. It has been reported that configurational changes of protein structure due to microwave heat treatment of various pulses including different types of beans resulting in an altered emulsification properties were reported in many studies (Hernández-Infante, Sousa, Montalvo, & Tena, 1998; Karunakaran et al., 2017; Z. Liu & Wang, 2018).

Table 2. *Functional properties of control and roasted bean flour samples.*

Microwave Power (W)	Roasting Time (s)	Emulsification Activity (%)	Emulsification Stability (%)	Foaming Capacity (%)	Foaming Stability (%)
Control	-	34.76±0.21^{b}	74.81±0.89^{c}	63.46±2.35^{a}	11.44±0.89^{e}
350	15	39.74±0.51^{a}	89.88±2.28^{b}	63.33±0.72^{a}	95.28±0.04^{a}
	30	39.69±0.59^{a}	96.55±2.96^{ab}	61.79±0.28^{ab}	82.21±0.07^{b}
	45	39.74±0.36^{a}	100.88±5.28^{a}	55.71±0.86^{b}	70.85±0.83^{c}
700	15	40.66±1.49^{a}	102.24±1.48^{a}	55.05±1.51^{bc}	95.00±2.19^{a}
	30	38.70±0.23^{a}	97.10±1.94^{ab}	37.55±1.64^{d}	24.04±1.36^{d}
	45	38.67±1.47^{a}	94.74±1.50^{ab}	48.08±2.42^{c}	25.86±0.65^{d}

Data represent the mean ± one standard deviation (n =3). Data with different superscript letters in the same column indicate significant differences (p < 0.05).

3.4. Foaming Properties

The impacts of microwave treatment on foaming properties are presented in Table 2. The results showed that foaming capacity of bean flour differed significantly ($P<0.05$) when roasted under different microwave powers. The foaming capacity (FC) decreased as the microwave treatment time increased, from 63.46±2.35% (control, 0s) to 48.08±2.42 (700W, 45s) ($P<0.05$).

Foam stability (FS) is generally described as the ability to form a strong and cohesive film around air bubbles. The results showed the FC values of roasted samples which ranged from 95.28±0.04% to 24.04±1.36% were significantly different ($P< 0.05$) from unroasted sample (11.44±0.89%). It is noted that some microstructural changes might have taken place during microwave roasting that larger protein aggregates, starch aggregates and modified interactions between protein and starch may form which further can lead to decreased viscosity and protein solubility lowering the film strength formed between air-water interphase around air bubbles (Sawada et al., 1972; Wani, Hamid, Hamdani, Gani, & Ashwar, 2017). Similar results have been reported by Saini (2016) and Jogihalli et al. (2017) for over roasted flaxseed and chickpea, respectively.

4. Conclusions

Microwave assisted roasting resulted in the alteration of both powder and functional properties. Results indicated that roasting provided enhanced bulk density, flow properties, emulsification stability, foaming stability and water hydration capacity values. Samples treated at 700W for 45s have advantages of smaller storage area, lower packaging and transportation costs due to lower bulk densities than other samples. According to the wettability experiment, roasted samples at 700W microwave power dispersed faster in water compared to both control and 350W treated ones. Experiment showed that roasting time played a significant role ($P<0.05$) in modification of foaming and water hydration properties in microwave roasted bean flour samples; increase in roasting time at 700W revealed a drastic reduction in foam stability. On the other hand, all microwave treatments resulted in an improved foaming stability compared to control sample. It can be concluded that, results of this study could be the basis for the development of new products. Overall, microwave assisted roasting can be successfully applied in order to modify desired functional and powder properties of bean flours, and further to develop novel food formulations.

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Conflict of interest

The authors have no conflict of interests.

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Chapter 8

YENİ NESİL FONKSİYONEL KARBON MALZEMELER "BİYOKÖMÜR"

Ayfer DÖNMEZ ÇAVDAR[1]

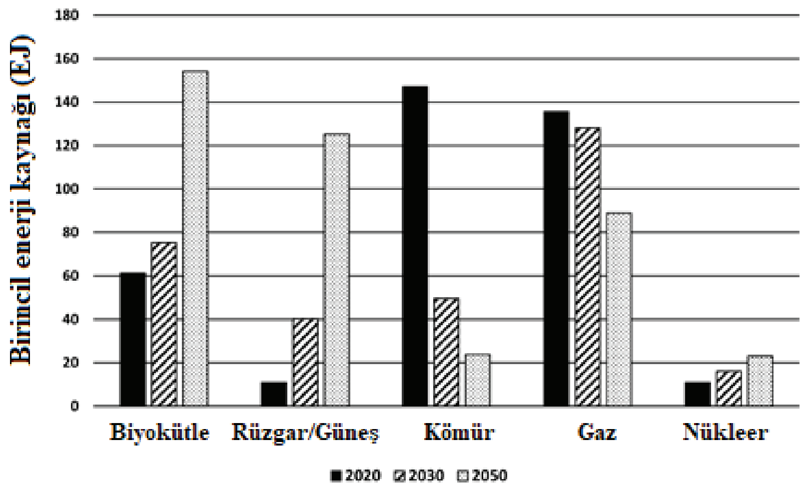
1 Doç. Dr., Karadeniz Teknik Üniversitesi, adonmez@ktu.edu.tr

GİRİŞ

Bu bölümde, yeni nesil fonksiyonel karbon malzemeler kategorisinde biyokömürün yeri, üretim teknikleri ve aktivasyon süreçleri hakkında bilgiler sunulmuştur. Bu bilgilerin, bundan sonraki süreçte ülkemizin stratejik planlarına katkı sağlayacak fikirlerin oluşmasında ve hayata geçirilmesine katkıda bulunması temenni edilmektedir.

Yenilenebilir biyokütle, Dünya üzerindeki yaygınlığından ve kolayca diğer ürünlere dönüştürülebildiğinden ötürü yeni nesil karbon malzemeler ve enerji kaynağı için olası bir adaydır. Kömür ile karşılaştırıldığında, biyokütlenin avantajları (i) karbon-nötr ve sürdürülebilir yapısı (ii) biyolojik dönüşüm süreçlerindeki reaktivitesini, (iii) yüksek oksijen içeriği nedeniyle hızlı piroliz ile biyo-yağ (yaklaşık% 75 verimle) üretme potansiyeli, (iv) düşük kükürt ve düşük istenmeyen kirletici madde içeriği (ör. metaller, azot vb.), (v) geniş coğrafi dağılımı ve (vi) enerji mahsulü üretim ve dönüştürme tesislerinde, istihdam ve sanayi yaratma potansiyeline sahip olması şeklinde ifade edilebilir. Birçok araştırmacı, hükümet, araştırma kurumu ve endüstri, odunsu ve otsu biyokütle dahil olmak üzere biyokütlenin kimyasallara, biyoyakıtlara ve kompozit malzemelere dönüştürme aşamasında birçok çalışma yürütmektedirler.

Yıllık küresel biyokütle üretimi son 10 yılın verilerine bakıldığında, yaklaşık 220 milyar kuru ton veya 4.500 EJ'dir (1 EJ=1.055 × 10^{18} joule), 2014 yılında dünyanın enerji tüketiminin 8,3 katına eşittir (543 EJ). Öte yandan, 2017 yılı sonunda dünyaca kanıtlanmış petrol rezervleri, 1.7 trilyon varile ulaşmıştır ki bu sadece 50 yıllık küresel üretimi karşılayabilecektir. Bu nedenle, kimyasallar ve petrol bazlı malzemeler için alternatif kaynaklara ihtiyaç vardır. Öyle ki hazırlanan raporlarda dünyanın önümüzdeki tahmini 50 yıllık birincil enerji kaynakları arasında biyokütle en önemli kaynak olacağı belirtilmektedir (Şekil 1) (Reidl vd. 2020).



Şekil 1. 2020-2050 yılları arasında beklenen birincil enerji kaynak miktarları (Reidl vd. 2020)

Gelecekteki ekonomiler için gerekli yeni "biyorafineri" süreçleri geliştirme üzerine yeni bir yarış başlamaktadır. Mevcut doğrusal ekonominin yerini, enerji ve yakıtın doğadan hasat edileceği ve aşırı miktarda sera gazı veya atık üretmeden çevreye iade edileceği dairesel bir "biyoekonomi" alabilir. Mevcut tüm teknikler arasında termokimyasal yol, biyokütleden biyoyakıt ve biyoenerji elde etmek için umut verici sonuçlar göstermiştir (Mohan vd. 2006, Menon ve Rao 2012). Bu gelişmeler ormancılık sektörü, biyoteknoloji, malzemeler ve kimyasal işleme endüstrisi ve tarıma teşvik için dikkate değer fırsatlar yaratacak, yenilenebilir ve karbondan bağımsız kaynaklar kullanan sürdürülebilir bir toplum ve endüstriler yaratmaya yardımcı olacaktır (Zang vd. 2019).

Bu gelişmeler ışığında, biyokütle giderek daha değerli bir ürün olarak kabul edilmektedir. Özellikle, yeryüzünde en bol bulunan organik maddeler olan lignoselülozik biyokütle, yakıt, ısı ve elektrik enerjisi üretimi için bir hammadde olarak büyük bir potansiyele sahiptir. Dünyadaki ekonomik ve çevresel kirlilik konularını ciddi bir şekilde göz önünde bulundurarak bu alandaki araştırmalar yoğunlaşmıştır. Özellikle lignoselülozik biyokütle dönüşümünün katı kalıntısı olan "Biyokömür" e ilgi giderek artmaktadır. Biyokarbon (biocarbon) ya da biyokömür (biochar), yeni nesil fonksiyonel karbon malzemelerinin geliştirilmesi için en uygun maliyetli platform olarak tanımlanmaktadır. Biyokarbon tek başına bir malzeme olarak ya da kompozit malzeme içerisinde bir bileşen olarak çevre ıslahından sürdürülebilir enerjiye kadar etkinliğini ve kullanım avantajını kanıtlamıştır. Bu yan ürün ana uygulamasını toprak ıslahı olarak bulmuştur, ancak son zamanlarda alternatif uygulamalar önerilmiştir (Giorcelli vd. 2019). Nanda vd. (2016) Enerji, Agronomi, Karbon Tutulması, Aktif Karbon ve kompozitler olarak farklı alanlarda Biyokömür uygulamasının sonuçlarını özetlemektedir. Biyokömür karbon açısından zengin olduğundan, çeşitli çalışmalar özelliklerini araştırmaya ve örneğin elektronik uygulamada daha pahalı karbon malzemeyle karşılaştırmaya çalışmaktadır (Giorcelli vd. 2016). Ayrıca, sadece geleneksel karbon malzemelerin uygulandığı sensörler gibi alanlarda biyokömür uygulama olasılığı da gösterilmiştir (Noman vd. 2014, Ziegler vd. 2017). İnşaat gibi diğer alanlarda ekonomik yönü göz önüne alınarak biyokömür dikkate alınmıştır (Khushnood vd. 2016). Khan vd. (2018) biyokömürün polimer kompozit sektöründeki uygulamaları değerlendirmiştir ve bu alanda biyokömür; malzemenin mekanik, elektriksel ve termal özellikleri arttırabilmiştir.

Yeni nesil polimerik kompozit malzemeler; fiziksel özellikleri, hafifliği ve maliyeti nedeniyle araçlarda kullanılan metaller gibi diğer geleneksel baskın malzemelerden daha fazla kullanım bulmaktadır. Polimerik malzemelerin kullanımı, takım maliyetleri metal sistemlere göre daha düşük olabileceğinden ve kalıp tasarımları kolayca değiştirilebildiğinden, parça tasarımı değişikliğinde önemli esneklik sağlamaktadır. Uygun polimerik malzemeler birkaç arzu edilen özelliğe sahip olabilir. Polimerik yakıt sistemi bileşenleri, yakıt depoları, hortumlar, borular, manifoldlar, raylar, filtreler, pompalar, karbüratörler ve enjektörler gibi bir dizi bileşeni içerir. Bu yakıt sistemleri için geliştirilecek malzemenin; statik enerji tüketen özellikler (elektriksel olarak iletken); yakıt geçirgenliği direnci; darbe ve kimyasal dirençlerinin iyi olması ve yüksek sıcaklıklarda birçok yakıt sistemi bileşeninin gereksinimlerini karşılayabilecek iyi fiziksel özelliklere sahip olması arzu edilir. Çoğu polimerik malzeme yakıt sistemi bileşenleri için kendinden elektriksel veya termal olarak iletken değildir. İletken polimerik malzeme bileşimleri bazı durumlarda polimerlere biyokütleden dönüştürülen biyokömür ilave edilerek yapılabilir (Biron 2007).

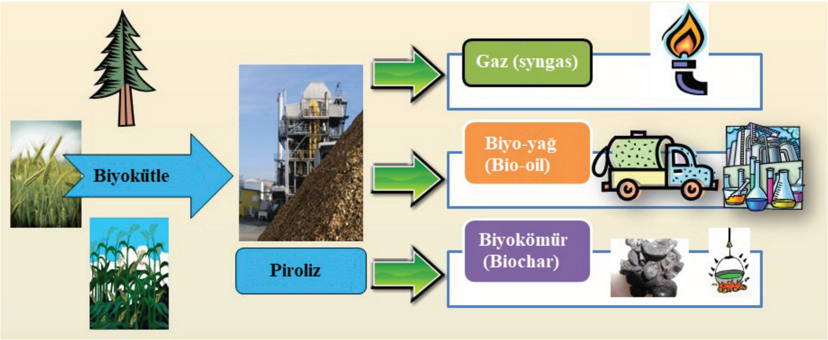
Biyokömürün geniş bir kullanım alanı potansiyeline ait olduğunu gösteren başarılı sonuçlar elde edilmiş olsa da, bu potansiyelin tam olarak gerçekleştirilmesi ile ilgili birçok zorluk vardır. Yapılandırılmış bir karbon malzemesi olarak, biyokömür ailenin grafit, grafen ve karbon nanotüpler gibi iyi bilinen diğer üyelerinden farklıdır. Biyokömür, biyokütle prekursörlerinin karmaşıklığına ve doğal varyasyonuna (iki odun parçası aynı değildir) ve karbonizasyon koşullarındaki belirsizlikten kaynaklı hem karbon matrisinin hem de gözeneklerinin kimyasında ve yapılarında farklılık yaratmaktadır. Sonuç olarak, mekanik mukavemet, termal ve elektriksel iletkenlik dahil olmak üzere biyokömürün ortak özelliklerinde önemli bir bilgi boşluğu vardır. Bu bilgi boşluğuna ek olarak biyokömürün yapı özelliklerinin birbirleri ile olan ilişkilerinin henüz net olarak anlaşılamamaktadır.

Bu ilişkileri geliştirmek ve anlamak için tutarlı ve tekrarlanabilir ölçümler gereklidir, ancak büyük ölçüde biyokömür karakterizasyonu için standart protokollerin eksikliği büyük bir sorundur. Biyokütlenin çeşitli ölçeklerin yapıları hakkında zengin bir bilgi birikimi olsa da, biyokütle pirojenik veya hidrotermal olarak biyokömüre dönüştüğünde bu yapısal özelliklerin nasıl korunabileceği ve bu dönüşümün nasıl olduğu, karbonizasyon işlem koşullarından nasıl etkilendiği hakkında çok az şey bilinmektedir. Bu zorluklar, ormancılıktan malzeme bilimine ve kimya mühendisliğine kadar ilgili alanlarda uzmanlaşmış bilim adamları ve mühendisler arasında yakın işbirliğini ve daha fazla çalışma yapılmasını gerektirmektedir.

BİYOKÖMÜR ÜRETİM YÖNTEMLERİ

Biyokömürün fonksiyonel bir malzeme olarak potansiyeli, arzu edilen birçok niteliğinden, bulunabilirliğinden ve çok çeşitli prekursör malzemelerden kaynaklanmaktadır. Pamuk sapı, palmiye ağacı atığı, ayçiçeği tohumu kabukları ve hatta kanalizasyon çamuru gibi atık biyokütlesinden odunsu biyokütle gibi diğer atık olmayan prekursörlere kadar değişen biyokömür için geniş bir hammadde rezervi bulunmaktadır. Bu farklı prekursörler ve kontrol edilebilir piroliz koşulları ile spesifik uygulamalar için ince ayarlanabilen özelliklere sahip biyokömür üretimleri gerçekleştirilebilir. Bu özellikler arasında yığın yoğunluğu (bulk density) ve yüzey kimyasal bileşimleri, kristallik, yapışma yapısı ve elektriksel iletkenlik gibi fiziksel özellikler kullanılan biyokütlenin türüne ve elde edilme yöntemine göre farklılık göstermektedir. Örneğin, bazı uygulamalar biyokömürün elektriksel iletkenliğine kayıtsız olabilirken, biyokömürü elektrot olarak enerji depolama uygulamaları ve önerilen projede araçların yakıt sistemi bileşenleri; yüksek bir elektrik iletkenliğine sahip malzemeye ihtiyaç duyar. Bir diğeri örnek biyokömürdeki kül; tarımsal uygulama için kül kritik bir bileşen iken, enerji uygulamaları için çıkarılması gereken safsızlık olarak kabul edilmektedir.

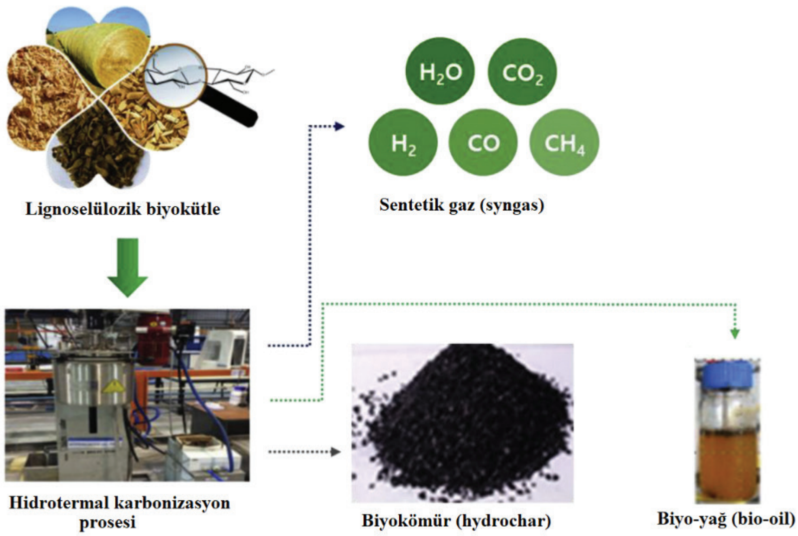
Piroliz en yaygın ve tartışmasız biyokömür üretmenin en basit yöntemidir. Piroliz, biyokütlenin oksijensiz bir ortamda ısıl işlemden geçmesi anlamına gelir ve "biyokömür", "biyo-yağ" ve "sentez gazlar" olarak katı, sıvı (Şekil 2) ve gaz formlarına dönüştürür (Manya 2012, Ronsse vd. 2013).



Şekil 2. Temel piroliz prosesi (Spokas, 2012).

Piroliz normalde kuru biyokütle üzerinde yapılırken, hidrotermal karbonizasyon işlemi yüksek basınçta suyla ıslatılmış biyokütle üzerinde yapılır, böylece su kullanılan sıcaklık aralığında sıvı halde kalır. Piroliz normalde kuru biyokütle üzerinde yapılırken, hidrotermal karbonizasyon işlemi yüksek basınçta suyla ıslatılmış biyokütle üzerinde yapılır, böylece su kullanılan sıcaklık aralığında sıvı halde kalır (Cha vd. 2016). Hidrotermal karbonizasyon bir kurutma işlemine olan ihtiyacı ortadan kaldırdığı için bu, biyokütle besleme stoğu kuru olmadığında avantajlı hale gelir (Ngan vd. 2019).

Pirolize benzer şekilde, **hidrotermal karbonizasyon** tekniğinde de, işlem koşullarına bağlı olarak farklı oranlarda biyokömür, biyo-yağ ve sentetik gaz (syngas) üretilebilir (Şekil 3). Sıcaklık anahtar parametredir. 250 ° C'nin altındaki düşük sıcaklıklar, biyokömür üretimini destekler ve katı ürünlerin verimini maksimuma çıkarır (Roman vd. 2012, Xiao vd. 2012). Sıvı ürünlerin biyo-yağ üretimini desteklemek için 250 ° C ile 400 ° C sıcaklık aralığı kullanılır (Chan vd. 2014). Son olarak, gazlı ürünleri veya sentez gazlarını tercih etmek için 400 ° C'nin üzerindeki sıcaklıklar kullanılır (Sabio vd. 2016).



Şekil 3. Lignoselülozik biyokütleden hidrotermal karbonizasyon yöntemi ile karbonca zengin biyokömür üretimi (Khan vd. 2019)

Selülozik doğal lifler, PAN (Poliakrilonitril) ve zift lifleriyle karşılaştırıldığında, daha fazla hidroksil grubu ve daha düşük karbon içeriği (ağırlıkça % 44.4) içerir. Karbonizasyon derecesi kesinlikle biyokömürün en önemli karakterleri arasındadır, çünkü alternatif uygulamalarla ilgili özellikleri büyük ölçüde etkiler. Biyokömürün elektriksel iletkenliği, yakıt sistem bileşenleri için önemlidir. Karbonizasyon derecesi elektrik iletkenliğini kontrol eden önemli bir parametredir (Davies ve Yu, 2011).

BİYOKÖMÜRÜN AKTİVASYONU

Biyokömür karbonizasyon işleminden sonra aktivite edilmesi; genel olarak biyokömür veya gözenekli karbonun gözenekliliğini daha da arttırmak için kullanılan bir işlemdir, ancak bu işlem biyokömürün yüzey kimyasını da değiştirebilir. Aktivasyon, daha önce bahsedilen yöntemler gibi biyokömür üretmek için bir yöntem olmasa da, genellikle biyokömür üretiminden sonra yapılır (piroliz gibi). Biyokömürü başarılı bir şekilde aktive etmek için birçok farklı aktivasyon prosedürü kullanılmakta olup ve fiziksel aktivasyon veya kimyasal aktivasyon olarak kategorize edilebilir. Her iki durumda da, malzeme bir aktifleştirici madde ortamında termal olarak muamele edilmektedir. Aktifleştirici maddenin tipi, prosedüre fiziksel mi kimyasal mı diye karar verir. Kimyasal aktivasyon, kömürü dehidrasyon ve oksidasyon reaksiyonları yoluyla aktive etmek için genellikle katı veya sıvı formda farklı kimyasal ajanlar kullanır. Kimyasal aktivasyon, aktive edilmiş biyokömürü üretmek için doğrudan biyokütleye veya pirolizden sonra biyokömüre uygulanabilir. Kimyasal aktivasyon, fiziksel aktivasyondan daha yüksek sıcaklıklarda gerçekleştirilir ve daha pahalıdır, ancak daha yüksek spesifikasyon alanı değerlerine sahip biyokömür ürünleri verir - daha yüksek aktivasyon verimliliğine sahiptir. Aktivasyon için kullanılan birçok kimyasal aktive edici ajan vardır. Bunlar arasında alkali özellikte olan KOH, NaOH, NH_3, K_2CO_3 ve $ZnCl_2$ ve asidik özellikte yer alan HNO_3, H_3PO_4 ve H_2SO_4 öne çıkmaktadır. Bunlar arasında, KOH özellikle mikro gözenekler oluşturmada ve spesifik yüzey alanını artırmada etkilidir (Otova vd. 1997, Basta vd. 2009, Wang ve Kaskel 2012).

Şekil 4'de nitrik asit ile biyokömürün aktivasyonu gösterilmektedir. Aktivasyon rutin olarak biyokömürün gözenekliliğini arttırmak ve değiştirmek için kullanıldığında, aynı işlem karbon yüzeye yabancı elementler ekleyebilir. Bu ilave elemanlar (örneğin O, N ve S), karbon ile kimyasal bağlar oluşturarak yüzey pH'ını, potansiyelini ve ıslanabilirliği değiştiren fonksiyonel yüzey grupları oluşturabilir. Bu özellikler, özellikle su saflaştırma ve sulu elektrolit ile enerji depolama gibi sulu faz içerenler olmak üzere birçok uygulamada biyokömürün etkinliğinin belirlenmesinde önemli rol oynamaktadır. Dahası, aktivasyon ürünleri bilerek ayrı fazlar halinde bırakılabilir, bu da çeşitli fonksiyonlara sahip biyokömür kompozitler ile sonuçlanır. Aynı amaçla, yabancı elementler, biyokömürün işlevselliği arttırmak için uyarıcı gibi çeşitli işlemlerle biyokömüre bilerek eklenir (Chen 2017).

Şekil 4. Biyokömürün HNO_3 kimyasalı ile aktivasyonu (Kalinke vd. 2017)

Selülozun 400 °C'nin altındaki sıcaklıklarda N_2'de ısıtılmasıyla önemli ağırlık kaybı, daralma ve yapısal değişiklikler gözlenmektedir. Bu tür termal (ayrışma / piroliz) işlemlerde birçok karmaşık reaksiyon söz konusudur. Sıcaklık arttıkça, fiziksel olarak emilen su önce buhara dönüşür. (<150 °C). 150-240 °C' de su selüloz ünitesinde bulunan –H ve -OH fragmanlarından kaynaklanan dehidrasyon reaksiyonu nedeniyle evrilir. 240-400 °C'de selüloz oksitlenmeye gerek duymadan, diğer C, O ve bazı C-C bağlarının glikozidik bağının termal bölünmesi ve parçalanmasıyla ayrışmaya başladığında büyük miktarlarda katran, H_2O, CO ve CO_2 yayılır (Tang ve Bacon, 1964, Kilzer ve Broido, 1965). İstenmeyen levoglukozan üretilir (Liu vd., 2005, Jakab vd., 2010), bu da daha düşük bir karbon verimi ile sonuçlanır ve oksijen veya hava varlığında yanıcı ürünler vermek için ayrışırlar (Parks vd. 1955). Piroliz sırasında daha yüksek N_2 gazı akışı, oluşan levoglukozanın buharlaşmasını kolaylaştırır ve bu da kömür veriminde bir azalmaya neden olur (Bohra ve Saxena, 1991).

Selülozun önceden oksitlenmesi karbon verimini artırabilir. Oksidasyonun erken aşamalarında, moleküller arası çapraz bağlama reaksiyonlarını destekleyen aldehit veya keton grupları oluşur. Cl_2 (Mayer vd., 1967; Gutzeit, 1969), HCl (Shindo, 1970; Shindo vd., 1969; Shindo ve Sawada, 1987) ve O_2 (Bacon, 1974) daha düşük bir ayrışmaya başlar sıcaklık ve karbon verimini artırır. Bununla birlikte, etkinlik, lifin iç kısmında oluşan reaktif gazların difüzyon hızı sınırlıdır (Donnet, 1984).

Selüloz liflerinin Lewis asitleri, bazları, güçlü asitleri ve halojenürleri gibi alev geciktiricilerle ön işlemden geçirilmesi, dehidrasyonu etkin bir şekilde teşvik edebilir ve üretilen levoglukozan miktarını azaltabilir, böylece verimi artırabilir ve muamele süresini azaltabilir. Bu işlem genellikle liflerin sulu alev geciktiricilerin sulu çözeltileri ile emprenye edilmesi veya lif üzerine alev geciktirici çözeltinin püskürtülmesi, daha sonra liflerin N_2 veya havada kurutulması ve oda sıcaklığından 250-400 °C sıcaklığa ısıtılmasıyla gerçekleştirilir. Alev geciktiricilerin varlığında, selüloz dehidrasyona başlar ve daha düşük bir sıcaklıkta daha hızlı bir oranda ayrışır ve ön-karbonizasyon olarak tanımlanmaktadır.

İki tür alev geciktirici vardır: biri katalizör görevi görür ve –OH gruplarının uzaklaştırılmasını destekler ve ikincisi –OH grupları ile reaksiyona girer (Goodhew vd., 1975). Hidroksil gruplarının uzaklaştırılması ile moleküller arası hidrojen bağı zayıflar veya yok olur, böylece piroliz üzerinde erime olasılığı olan lifler önemli hale gelir. Bu, sadece hidroksil gruplarını uzaklaştırmakla kalmayıp aynı zamanda kovalent olarak bağlanmış çapraz bağlama oluşturan alev geciktiriciler kullanılarak önlenebilir (Goodhew vd., 1975). Selüloz esaslı aktif karbon lifler üretilirken, karbonizasyon ve aktivasyondan önce, lifin / kumaşların alev geciktiricilerle emprenye edilmesi veya püskürtülmesi ve daha sonra lifin N_2 veya havada <400 ° C sıcaklıkta ısıtılması sadece karbon verimini arttırmakla kalmaz, aynı zamanda elde edilen aktif karbon liflerinin mukavemeti, gözenek yapıları ve adsorpsiyon özelliklerini de arttırır (Chen 2017).

Sulu bir H_3P0_4 ve NaCl çözeltisi (Wu vd., 2006, Chen vd.,2013) ile muamele, oldukça gelişmiş mezo gözeneklere (2-50 nm) ve hatta makro gözeneklere (> 50 nm) sahip aktif karbon lifleri verir. Selüloz esaslı lifler primer karbonizasyon sıcaklığını düşürerek karbon verimini arttırmak için, H_2SO_4 ve $ZnCl_2$ ile muamele edilebilirler (Kim vd., 2001).

Selülozun karbonlaşması sırasında 500 ° C sıcaklıktan , ~1000 °C'ye ulaşılana kadar devam eden elektrik direncinde belirgin bir azalma vardır, bu elektrik iletkenliğinin artması anlamına gelmektedir. Artan sıcaklık muamelesi sürecince, oluşan hidrojen kaybı ve karbonca zenginleşme ile kademeli olarak aromatik halka yapıları oluşur (Chen, 2017). Karbonize fiberde grafit benzeri bir yapı oluşur.

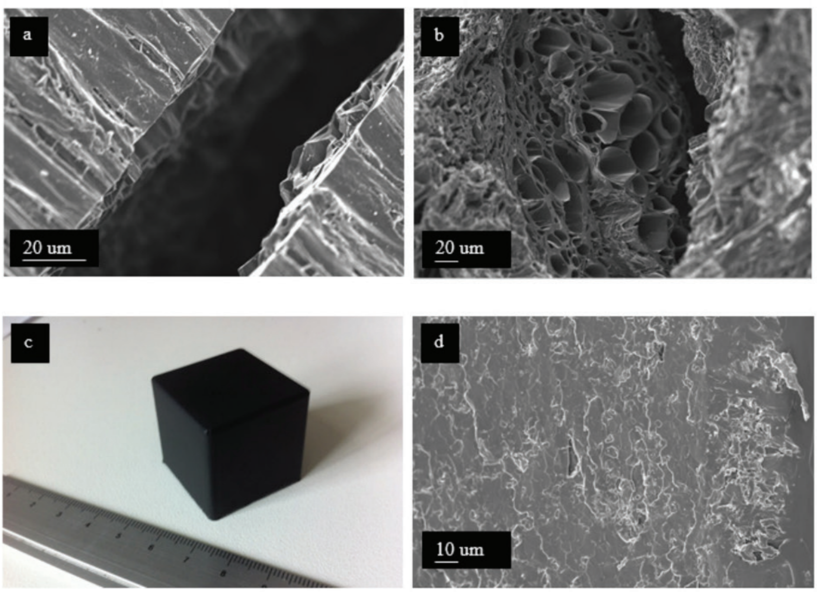
SONUÇ ve ÖNERİ

Bu bölümde yeni nesil fonksiyonel karbon malzeme üretimi açısından biyokömürü konu alan bilimsel çalışmalar incelenmiş ve önemli noktaları ele alınarak değerlendirilmiştir.

Biyokarbon ya da biyokömürler; biyoenerji, yakıt pili üretimi, toprak ıslahı vb. birçok farklı alanda yoğun çalışmalara konu olmaktadır. Her alan için istenilen biyokömür özellikleri farklı üretim yöntemlerinin geliştirilmesine neden olmaktadır. Özellikle aktive edilmiş biyokömürler (aktif karbonlar); bugün kozmetikten gıda sanayine kadar birçok farklı sektörde karşımıza çıkmaktadır. Büyük yüzey alanı, yüksek yüzey reaktivitesi, büyük gözenek hacmi, uygun gözenek dağılımı, mekanik dayanıklılık aktif karbonun önemli özelliklerindendir.

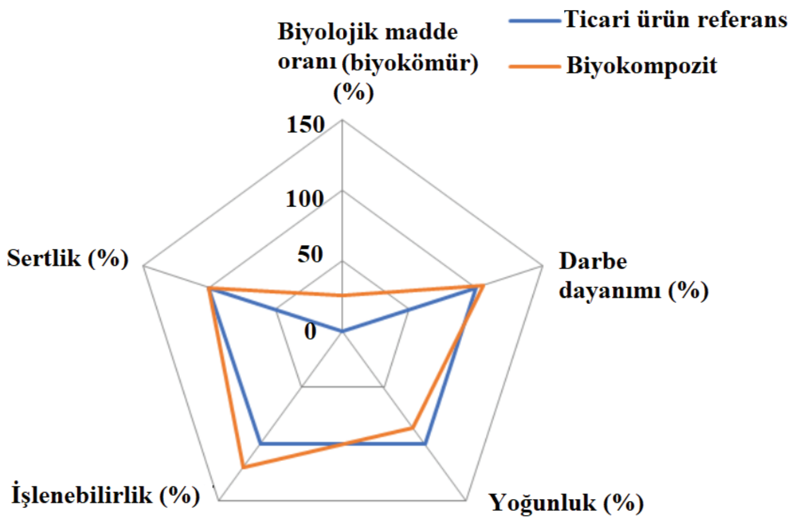
Biyokömürün yeni nesil fonksiyonel kompozit üretiminde değerlendirilmesi sektörel açıdan son dönemde özellikle otomotiv üreticilerinin yakın markajındadır. Dünyanın doğrusal petrol bazlı ekonomisi, yenilenemeyen kaynakların aşırı kullanılmasına, biyolojik olarak parçalanamaz atıkların üretilmesine ve mevcut ve gelecek nesiller için ciddi sürdürülebilirlik sorunlarını gündeme getiren sera gazlarının (GHG) emisyonuna yol açmıştır (Owusu ve Asumadu-Sarkodie, 2016). İstatistiki veriler, ulaştırma sektörünün toplam dünya petrol talebinin %60'ından sorumlu olduğunu bu oranın da gelecekte büyümeye devam edeceğini göstermektedir (Atabani vd. 2011). Bu durumda yeni yakıt ekonomisi standartlarının uygulanması ve ulaşım-enerji sektörleri için yenilenebilir yeni yakıt üretimleri zorunluluğunu gündeme getirmiştir. Aynı zamanda, kurumsal ortalama yakıt ekonomisi (CAFE) gibi yakıt ekonomisi standartları gereği araçların yakıt tüketimini azaltmaları ile ilgili yaptırımları; hafiflik avantajına sahip, spesifik dayanımı yüksek sürdürülebilir ve yenilenebilir yeni nesil biyo-kompozitlerin geleneksel petrol bazlı malzemeler yerine kullanılmasına zemin oluşturmaktadır.

Biyo kompozitlerde piroliz yan ürünü olarak elde edilen biyokömürün kullanımı, daha az petrol bazlı polimer kullanımı ile daha hafif ağırlıklara neden olabilir. Parçaların daha hafif olması otomobiller için daha iyi yakıt ekonomisine katkıda bulunur. Genel olarak, bu yaklaşım biyo-rafinerilerin sürdürülebilirliğine katkıda bulunarak, araçlardaki yakıt tüketimini azaltarak ve kompozitlerin petrol bazlı içeriğini azaltarak küresel ekonomi konseptiyle uyumlu olacağı düşünülmektedir. Otomotiv sanayinde, polimer kompozit üretiminde takviye elmanı olarak kullanılacak biyo karbon ya da biyokömürden beklenen özellikler; "düşük kül oluşumu, yüksek karbonlaşma miktarı, yüksek iç yüzey alanı, mekanik dayanıklılık, yüksek elektriksel ve ısıl iletkenlik" sayılabilir. Giorcelli vd (2016) tarafından yapılan çalışmada biyokömürün aktivasyonun yüzey özellikleri üzerine olumlu etkisini elektron mikroskopu ile net bir biçimde ifade etmişlerdir (Şekil 5 a,b). Yine aynı çalışmada aktif biyokömür ile üretilen kompozit ürünün yüzey yapısının oldukça homojen, polimer matrisi içerisinde oldukça iyi dağılım sağladığı rapor edilmiştir (Şekil 5 b,c).



Şekil 5. FESEM görüntüleri a) Biyokömür, b) aktif biyokömür ve c,d) aktif karbon ile güçlendirilmiş kompozit malzeme (Giorcelli vd. 2016).

Berzan vd. (2017) tarafından yapılan çalışmada; otomotiv parçaları için kompozit formülasyonlarda biyokömürün dolgu maddesi olarak kullanılması, partiküllerin boyutu ve partiküllerin matris ile uyumluluğu açısından araştırılmıştır. Bilyalı öğütme ile yapısal kusurların azaltılmasının polimer matrisi içerisinde dağılımını önemli ölçüde iyileştirilebileceği bulunmuştur. Uyumlaştırıcı ve yüksek sıcaklıkta aktive edilmiş biyokömür kombinasyonu, en iyi darbe dayanımı sağladığı rapor edilmiştir. Referans olarak %30 talk takviyeli polimer kompozit ürün ile elde edilen biyokompozitin performan karşılaştırılmasına göre (Şekil 6), sertleştirilmiş PP kompozitlerde geleneksel dolgu maddesinin yerine biyokömürün potansiyel performansa sahip olduğu belirtilmiştir.



Şekil 6. % 30 talk takviyeli ticari kompozit ürünü ile biyokömür bazlı biyokompozitler arasındaki performans karşılaştırması (Berzani vd. 2017).

Özetle, otomotiv plastik parçalarında biyokömür kullanımı, bu malzeme için yüksek talep ve katma değer uygulaması bulmak için olası bir çözüm olabilir. Otomotiv uygulamaları için yeni nesil biyokömür katkılı biyo-kompozitler üretilmesindeki ana zorluk, talk veya cam elyafı gibi mineral dolgu maddeleri içeren geleneksel kompozitler ile aynı performans seviyesine ulaşmaktır. En önemli husus mekanik özellik gereklilikleri, özellikle de sertlik-tokluk dengesini karşılamak olacaktır (Behazin vd. 2017). Bu bölümde mevcut bazı çalışmalara yer verilmiş olsa da araştırmacılar tarafından bu konuyla ilişkin daha fazla çalışma yapılmasına ve literatürdeki bu boşluğun doldurulmasına ihtiyaç duyulmaktadır.

Bunların yanısıra; ülkemizde biyokömür üretimi için yeterli prekusörlere (biyokütle) sahiptir. Özellikle kenevir liflerinin ülkemiz açısından biyokömür üretimi için aşağıda belirtilen hususlar dikkate alındığında iyi bir prekursör olacağı düşünülmektedir.

Kenevir lifleri yenilenebilir olması, dört ay gibi kısa bir sürede hasat edilebilmesi, çok farklı alanlarda kolay yetişebilmesi ve üretmiş oldukları sağlam lifleri dolayısıyla odak noktası olmuştur. Ülkemizde 2016 yılında yayınlanan ―Kenevir Yetiştiriciliği ve Kontrolü Yönetmeliği ile 19 ilde sanayi keneviri ekimine izin verilmiş olup Tarım ve Orman Bakanlığı Tarımsal Araştırmalar Politikalar Genel Müdürlüğüne (TAGEM) bağlı Karadeniz Tarımsal Araştırma Enstitüsü Müdürlüğünde 2017'den itibaren bu alanda yoğun çalışmalar başlanmıştır. Bu anlamda Kenevirin liflerinin katma değeri yüksek alanlarda değerlendirilmesinin artırılması yönündeki çalışmaların teşvik edilmesinin ülkemizin stratejik kalkınma planlarının arasında olduğunun göstergesidir (URL, 2020).

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Chapter 9

THE EFFECT OF DIFFERENT MULCHING MATERIALS IN SEEDLING PERFORMANCE OF ORIENTAL TOBACCO (NICOTIANA TABACUM L.)

Dursun KURT [1]

1 Dr. Researcher Assistant , Department of Plant and Animal Production, Vocational School of Bafra, Ondokuz Mayis University, dursun.kurt@omu.edu.tr

INTRODUCTION

Tobacco leaves are mostly used in cigarette manufacture. Each year, 6.5 trillion cigarettes are produced and about 82% of this production is consumed by developed countries. Leaf tobacco production is practiced in 128 countries of the world over 4.3 million ha land area with an annual production of 7.49 million tons. Of this production quantity, 68% is performed in Asia and China is the leading producer meeting about 36% of world production alone. China is followed by Brazil, India, the USA and Indonesia. Turkey with an annual production of 72 thousand tons has the 10^{th} place in world tobacco production, but has the first place in world oriental tobacco production (FAO, 2018; GTCI, 2018). About 17% of Turkish tobacco production comes from Black Sea region. Samsun-type tobacco is produced almost over 60% of Black Sea region and this type is used in blends at ratios of between 4-12% (TAMRA, 2018). Oriental-type tobaccos have a significant place in world cigarette industry. With their special aroma and technical characteristics, they became essential component of world famous blends (Gumus, 2008; Ekren and Ilker, 2017).

Since oriental-type tobaccos are small ones, they are planted closer as compared to the other tobacco types. About 180.000-220.000 seedlings are planted per hectare. As compared to the conventional growing methods, oriental type tobacco seedlings are grown over seedbeds in open fields. Since there is a need for many seedlings and such a need should be met with quality seedlings, seedling place should be carefully selected and prepared in oriental type tobaccos (Camas et al., 2011). For a successful production season, optimum environments should be provided in seedling stage. About 3500-4000 seedlings are desired from a square meter of nursery. Seedbeds are usually arranged in one meter wide and long beds and mulching is a significant factor effecting seedling growth and quality in seedbeds (Caliskan, 2006).

Type of mulch applied over the seedbed directly influence seed germination ratios, seedling nutrition levels, soil moisture levels, water holding capacity, control of disease agents, temperatures to which seedlings are exposed and growth rates (Maurya and Lal, 1981; Gurbuz, 1994; AEA, 2012). Mulches increase soil temperature, slow down soil moisture losses and control weed growth and development (Ramakrishna et al., 2006). Type of mulch also influence dry weight of above ground parts, dry weight of roots per plant, root/shoot ratio, number of the first lateral roots per plant, number of the second lateral roots per plant, the first lateral root thickness and bleeding intensity of basal internodes of tobacco seedlings (Lu et al., 2008).

Several methods have been practiced about the seedling growth environments of seedling-propagated plants and seedbeds have been recommended based of plant species. Several researches have focused on seedling growth environments and such researches are still going on since production of seedlings with well-developed root system is the primary issue for guaranteed yields. Jones and Terrill (1984) indicated that growth and yield of tobacco plants largely depended on initial seedling sizes. Briefly, high yields and quality is directly related to initial seedling quality (Kabranova et al., 2014). Early seedling growth may also allow producers to benefit from spring precipitations and thus to have positive impacts on plant growth and development in filed. Mulches generally increase soil temperature and water holding capacity, thus accelerate seedling growth and development (Li et al., 2001; Duan et al., 2006; Jia et al., 2006).

Wrong practices of tobacco growers especially in nurseries limited tobacco growing lands or growers usually try to establish their own nurseries and most of the time they were unsuccessful and had to buy seedlings from outside. This study was conducted to determine the effects of different mulching treatments on seedling quality and to find out the mulching material with the best seedling performance in oriental tobacco cultivars.

MATERIALS AND METHODS

Plant Materials

Nail tobacco line and Canik 190-5 and Canik Sıtmasuyu 10821 tobacco cultivars, which have long been used as local population in tobacco production lands of Samsun province and with quite high export potential as Samsun-type, were used as the plant material of this study.

Nail tobacco line had a plant height of 80-90 cm, number of leaves of 25-30 per plant, leaves have a webby butt and pointed tip, leaf size is medium and dried leaf color is dark red. Ovality coefficients vary between 1.6-1.9 and the leaves are bulgy. Leaf tissue has a medium thickness and it is an aromatic tobacco line. Dry leaf yield per hectare is between 900-1100 kg (Camas and Esendal, 2001).

Canik 190-5 (190-5) tobacco cultivar is resistant to drought and blue mold. It is an early and high yield oriental type tobacco cultivar. Plants have medium-long plant height and have 30-35 leaves. The leaf size is small, leaves are not bulgy and have webby butt, pointed tip, elliptical-cow tongue shape and leaf diameter is 2.6 cm. Dried leaves have a thin texture and bright dark red color. Elasticity, burning and performance are high. Aromatic leaves have a sweet-full taste (Camas et al., 2011; Peksuslu et al., 2012).

Canik-Sıtmasuyu 10821 (Canik) tobacco cultivar has a plant height of 80 cm and number of leaves is about 25-30 per plant. Long leaves are not bulgy (cow tongue) and have webby butt and pointed tip. Diameter ratios vary between 2.3-3. Leaves have thin texture, red and dark red color and dried leaves have a small size. Leaves have high elasticity, burning characteristics and performance. Sweet full-taste leaves have a specific spicy aroma (Camas et al., 2011; Peksuslu et al., 2012).

Mulching Materials

Rice husk (R), fermented livestock manure (M) and 1:1 mixture (R+M) were used as the mulching material in this study. Rice husk has an organic carbon content of 46.9%, nitrogen content of 1.6%, moisture content of 9.3%, bulk density of 0.01 g cm^{-3} and water holding capacity of 21% (Balci et al., 2017). Fermented livestock manure has an organic matter content of 45.4%, total nitrogen content of 2.3% and a pH of 8.5.

Methods

Experiments were conducted in Gökçekent village of Bafra in 2015 and in Çetinkaya village of Bafra in 2016 in randomized blocks factorial experimental design with 5 replications. Experiments were carried out over open seedbeds. Experimental plots were 5 m long and 1.2 m wide. About 1 m distance was left between the plots and blocks as to consider side effect (Fig. 1). In both years, the first plough was performed at the last week of March and the second plough was performed at the first week of April. Following the formation of farrows, 20-20-20 NPK composed fertilizer was applied to all plots (2 kg da^{-1}). Seedbed surfaces were processed with a cultivator. Cylinders were rolled over the seedbeds and prepared for seeding. Mulching materials were laid over the seedbeds at 2 cm thickness. Seeding was performed with sprinkling cans at 1 g m^{-2} density. Sprinkler irrigation was performed twice a day until emergence and once every day later on. Irrigations were terminated 4 days before planting for maturation. Manual weed control and chemical pests and disease controls were practiced throughout the nursery period. About 25 cm side effect was considered from 4 sides of the plots and 20 mature seedlings were sampled from each plot. Seedling roots were throughly washed with distilled water before to dry them in an oven (Fig. 1).

Seedling height (SH; from the root collar to shoot tip), root length (RL; from root collar to tip of the root), stem diameter (SD; about 3-4 cm above the root collar), below-ground fresh weight (BGFW), above-ground fresh weight (AGFW), total fresh weight (TFW), below-ground dry weight (BGDW; drying at 105°C until a constant weight), above-ground dry weight (AGDW), total dry weight (TDW), below-ground weight ratio (BGWR), above-ground weight ratio (AGWR) and total dry/fresh weight ratio (TWR) parameters were investigated (Caliskan, 2006; Ekren and Ilker, 2017). Experimental data were subjected to variance analysis (ANOVA) with SPSS statistical software. Correlation analysis was performed to determine the relationships between the observed and measured attributes.

Figure 1. *General view from the nursery, samples washing with distilled water*

RESULTS AND DISCUSSION

Just because of seed characteristics, seedling production is the first and the mandatory stage of tobacco culture. The seedling characteristics directly influence yield, quality and performance criteria. Therefore, vigor of seedlings transplanted from the nursery to the field totally designates the overall product characteristics. Several studies have been conducted about tobacco seedling production. The primary target is to produce ideal strong and healthy seedlings with desired size dimensions. In this study, effects of different mulching materials on seedling growth, physiology and vigor were investigated.

Significant differences were observed in seedling height, root length, stem diameter, below-ground fresh weight, above-ground fresh weight, total fresh weight, below-ground dry weight, above-ground dry weight of the cultivars and mulching materials. Differences in below-ground weight ratios and above-ground weight ratios of the cultivars were found to be significant and the differences in total dry weights and total dry/fresh weight ratios of the mulching materials were also found to be significant.

Among three oriental tobacco cultivars, the shortest seedling height (14.32 cm) was observed in Nail cultivar and the longest seedling height (17.73 cm) was observed in 190-5 cultivar. The lowest root length (5.43 cm) was observed in Nail cultivar and the greatest root length (7.36 cm) was observed in Canik cultivar. The thinnest stem diameter (3.53 mm) was observed in Nail cultivar and thickest stem diameters (4.61 mm) was observed in 190-5 cultivar.

Table 1. *Seedling height, root length and stem diameters of three tobacco cultivars*

	Seedling height (cm)				Root length (cm)				Stem diameter (mm)			
	Nail	190-5	Canik	Mean	Nail	190-5	Canik	Mean	Nail	190-5	Canik	Mean
R	14.32	15.54	15.49	15.12^{b}	5.43	6.78	6.81	6.34^{b}	3.53	4.49	4.26	4.09^{a}
M	16.47	17.73	16.63	16.94^{a}	6.75	7.02	7.36	7.04^{a}	3.88	4.61	4.06	4.18^{a}
R+M	15.79	17.10	16.18	16.36^{a}	5.85	6.69	6.87	6.47^{b}	3.68	4.04	4.14	3.95^{b}
Mean	15.53^{b}	16.79^{a}	16.10^{ab}	16.14	6.01^{b}	6.83^{a}	7.01^{a}	6.62	3.69^{c}	4.38^{a}	4.15^{b}	4.08

Values followed by different letters in each column are significantly different ($P<0.01$) according to Duncan Test.

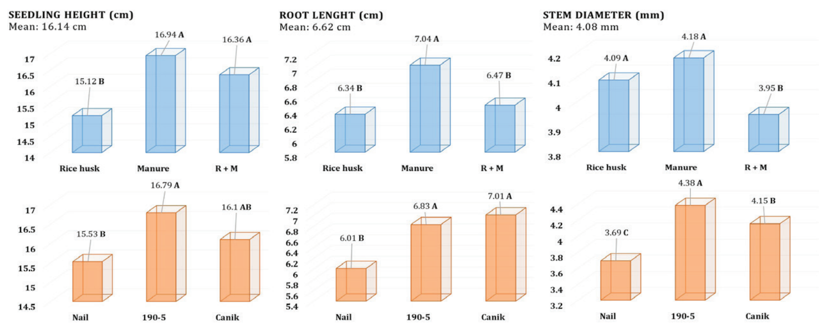

Figure 2. *Seedling height, root length and stem diameters of three tobacco cultivars*

Table 2. *Below-ground, above ground and total fresh weights of three tobacco cultivars (g)*

	Below-ground fresh weight				Above-ground fresh weight				Total fresh weight			
	Nail	190-5	Canik	Mean	Nail	190-5	Canik	Mean	Nail	190-5	Canik	Mean
R	0.35	0.43	0.48	0.42^{b}	6.53	7.05	7.19	6.92^{b}	6.88	7.48	7.67	7.34^{b}
M	0.47	0.53	0.56	0.52^{a}	7.71	8.17	7.30	7.73^{a}	8.18	8.70	7.87	8.25^{a}
R+M	0.46	0.50	0.53	0.50^{a}	7.41	7.71	7.77	7.63^{a}	7.86	8.22	8.30	8.13^{a}
Mean	0.43^{b}	0.49^{a}	0.53^{a}	0.48	7.22^{b}	7.65^{a}	7.42^{b}	7.43	7.64^{b}	8.13^{a}	7.95^{ab}	7.91

Values followed by different letters in each column are significantly different ($P<0.01$) according to Duncan Test.

Figure 3. *Below-ground, above ground and total fresh weights of three tobacco cultivars*

With regard to seedling height and root length, 190-5 and Canik cultivars were identified as the best ones. On the other hand, 190-5 cultivar was prominent with stem diameter. With regard to mulching materials, fermented livestock manure and rice husk + fermented livestock manure treatments were placed in the same statistical group for seedling height and fermented livestock manure had the greatest positive effects on root length and stem diameter. Rice husk and mixture mulching had similar effects on root length and stem diameter (Table 1; Fig. 2).

The lowest below-ground, above-ground and total fresh weights (respectively as 0.35 g, 6.53 g and 6.8 g) were obtained from Nail cultivar. The greatest below-ground, above-ground and total fresh weights were respectively observed as 0.56 g (Canik), 8.17 g (190-5) and 8.70 g (190-5). While Canik and 190-5 cultivars were found to be prominent with below-ground fresh weight and total fresh weight and such greater values were mainly resulted from fermented livestock manure and rice husk + fermented livestock manure mixture. With regard to above-ground fresh weights, the greatest effects of fermented livestock manure and rice husk + fermented livestock manure mixture were observed in 190-5 cultivar (Table 2; Fig. 3). Manure-type mulches both increase soil temperature and provide nutrients to the plants (Lu et al., 2008; Maurya and Lal, 1981; Teasdale et al., 2000). Therefore, above-ground and below-ground seedling characteristics of manure containing mulches were greater than the single rice husk mulches.

The findings on below-ground, above-ground and total dry weights were similar with the findings on fresh weights. With regard to weight ratios, the lowest below-ground weight ratio (6.27%) was obtained from Nail cultivar and the greatest value (8.84%) was obtained from Canik cultivar.

Table 3. *Below-ground, above ground and total dry weights of three tobacco cultivars (g)*

	Below-ground dry weight				Above-ground dry weight				Total dry weight			
	Nail	190-5	Canik	Mean	Nail	190-5	Canik	Mean	Nail	190-5	Canik	Mean
R	0.04	0.05	0.06	0.05[b]	0.63	0.69	0.69	0.67[c]	0.67	0.74	0.74	0.72[c]
M	0.06	0.07	0.07	0.06[a]	0.82	0.86	0.77	0.82[a]	0.88	0.93	0.84	0.88[a]
R+M	0.06	0.06	0.06	0.06[a]	0.74	0.79	0.71	0.75[b]	0.80	0.86	0.77	0.81[b]
Mean	0.05[b]	0.06[a]	0.06[a]	0.06	0.73[ab]	0.78[a]	0.72[b]	0.74	0.78	0.84	0.78	0.80

Values followed by different letters in each column are significantly different (P<0.01) according to Duncan Test.

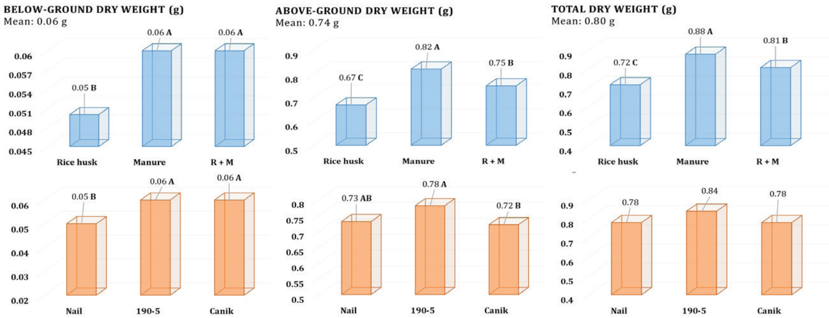

Figure 4. *Below-ground, above ground and total dry weights of three tobacco cultivars*

Table 4. *Below-ground, above-ground and total weight ratios of three tobacco cultivars (%)*

	Below-ground weight ratio				***Above-ground weight ratio***				Total dry/fresh weight ratio			
	Nail	190-5	Canik	Mean	Nail	190-5	Canik	Mean	Nail	190-5	Canik	Mean
R	6.27	6.81	8.00	7.03	93.73	93.19	92.00	92.97	9.85	9.87	9.87	9.87[b]
M	6.37	7.11	8.37	7.28	93.63	92.89	91.63	92.72	10.73	10.60	10.68	10.67[a]
R+M	7.40	7.34	8.84	7.86	92.60	92.66	91.16	92.14	10.10	10.39	9.30	9.93[b]
Mean	6.68[b]	7.09[b]	8.40[a]	7.39	93.32[a]	92.91[a]	91.60[b]	92.61	10.23	10.29	9.95	10.16

Values followed by different letters in each column are significantly different (P<0.01) according to Duncan Test.

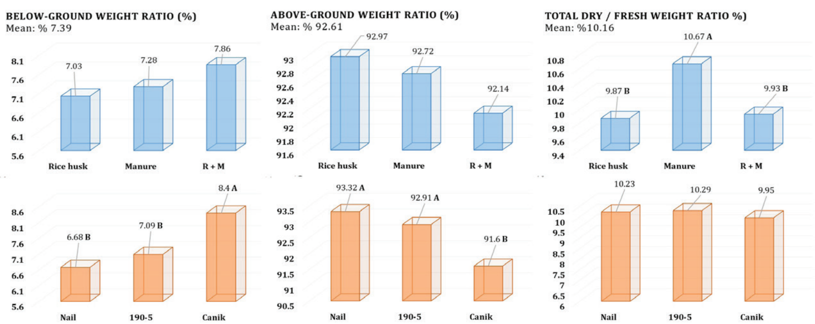

Figure 5. *Below-ground, above-ground and total weight ratios of three tobacco cultivars (%)*

The lowest above-ground weight ratio and total dry/fresh weight ratios were observed in Nail cultivar and the greatest values were observed in Canik cultivar. While Canik and 190-5 cultivars were prominent with below-ground dry weights, Nail and 190-5 cultivars were prominent with above-ground dry weights. Fermented livestock manure was quite effective in having such differences. The differences in total dry weights of the cultivars were not significant (Table 3; Fig. 4).

While the mulching treatments did not have significant effects on below-ground weight ratios, the greatest ratio (8.40%) was obtained from Canik cultivar. Mulching treatments also did not have significant effects on above-ground weight ratios, but Nail and 190-5 cultivars were significantly different from Canik cultivar. The differences in total fresh/dry weight ratios of the cultivars were not found to be significant and the greatest value (10.67%) was obtained from fermented livestock manure treatment (Table 4; Fig. 5).

Table 5. Correlation analysis results for investigated parameters

	SH	*RL*	*SD*	*BGFW*	*AGFW*	*TFW*	*BGDW*	*AGDW*	*TDW*	*BGWR*	*AGWR*	*TWR*
SH	1											
RL	0.61**	1										
SD	0.52**	0.42**	1									
BGFW	0.27**	0.26**	0.28**	1								
AGFW	0.23**	0.21**	0.18**	0.19**	1							
TFW	0.33**	0.31**	0.27**	0.28**	0.98**	1						
BGDW	0.58**	0.57**	0.48**	0.35**	0.21**	0.35**	1					
AGDW	0.18**	0.09	0.11	-0.01	0.34**	0.34**	0.11	1				
TDW	0.27**	0.22**	0.21**	0.12*	0.32**	0.35**	0.27**	0.79**	1			
BGWR	0.41**	0.47**	0.29**	0.22**	-0.05	0.07	0.77**	-0.19**	-0.11	1		
AGWR	-0.41**	-0.47**	-0.29**	-0.22**	0.05	-0.07	-0.77**	0.19**	0.11	-1.00**	1	
TWR	0.08	-0.02	0.11*	-0.02	-0.12	-0.09	0.11	0.41**	0.49**	-0.43**	0.43**	1

* Correlation is significant at 0.05 level, ** Correlation is significant at 0.01 level

Correlation analysis was performed to determine the relationships among the investigated parameters. Seedling height had the greatest positive correlations with root length and stem diameter. There were generally positive week correlations between the other parameters at 0.01 level. While the correlations of AGWR with AGFW, TFW and TDW were not significant, correlations of AGWR with the other parameters were weak but negative at 0.01 level. There was a weak positive correlation between TWR and SD at 0.05 level (Table 5). Shi et al. (2007) indicated that different mulching materials increased water-holding capacity of nursery seedbeds and had positive impacts on plant nutrition. Livestock manure and rice husk + livestock manure treatments had positive effects on physical attributes of the seedlings. Similar effects were also reported by several researchers and livestock manure and mixtures with the other husk materials were recommended to provide proper growth mediums in root zone (Wells and Loy 1985; Jia et al., 2006; Wu, 2006; Fan et al., 2014, Svotwa et al., 2014).

CONCLUSION

The above-mentioned criteria are the characteristics effecting field performance of the seedlings and indicating their physiological vigor. There is a need for about 200.000 seedling per hectare in oriental-type tobaccos. To have a good production season and to grow high quality tobacco, optimum seedling growth mediums should be supplied and maximum number of seedlings with desired characteristics should be obtained from each unit area. With regard to seedling characteristics of three oriental tobacco cultivars, fermented livestock manure was found to be prominent as a mulching material. Also 1:1 rusk husk: livestock manure mixture can also be used as an appropriate mulching material for tobacco seedlings. In cases where quite large areas required for nurseries and with insufficient livestock manure sources, rusk husk can be used as a supplementary mulching material. Rusk husk can also be used in places in where rice culture is common and livestock manure is purchased. Rice husk can constitute an attracting, efficient, environment-friendly and economic mixture material. In places where rice culture is not performed, other plant residues can be incorporated into livestock manure. Further research is recommended about the other plant residues to be used as mulching material.

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Chapter 10

STONE WATER (HUMAN/FRIENDLY ENVIRONMENT) THERMAL (THERMOGRAVIMETRIC-TGA) COMBUSTION PROPERTIES IN SOME WOOD

Hatice ULUSOY[1], Hüseyin PEKER[2]

1 Dr.Öğr.Üyesi , Department of Forest , Köyceğiz Vocational School, University of Muğla Sıtkı Koçman University , haticeulusoy@mu.edu.tr

2 Department of Forestry, University of Artvin Çoruh University ,

1.INTRODUCTION

One of the negative properties of wood material is that it is an organic material. Therefore, burning is one of the important negative properties in case of proper conditions. Apart from the flammability of wood material, other negative properties cause only material losses, while life-threatening of wood material also occurs. The flames and gases created by the burning of wood material threaten human life and may cause [1].

The study on the pyrolysis is process of fire-retardant treated wood may help to understand the mechanism of fire-retarding. Since fire-retardant treatment possibly affects wood pyrolysis, using the catalysis of flame–retardants can cause the pyrolysis reaction to form more char and lower the temperature of pyrolysis as well as reduce the yield of the flammable gas which helps to restrain wood burn [2].

Nowadays, due to the rapidly increasing world population and the increasing needs of humankind due to developing technology and living standards, natural resources are decreasing as a result of unconscious consumption. This forces producers to engage in studies on how they can use natural resources more efficiently and in a variety of ways. Wood material, which has a wide range of usage, is a natural and renewable raw material that can be applied to all areas. Due to its light weight compared to concrete, iron, aluminum, PVC and various other construction materials, being easy to be processed, having continuous production, having superior physical and mechanical properties in various places for use; the wood has a wide range of unique uses in construction techniques, many industries such as paper and cellulose, sheet, furniture. At the same time, due to the sensitivity towards fire safety, it is emphasized that fire resistance of wood material is provided in the most effective way. In addition to the known combustion properties of wood material, it is of great importance to determine the effect of impregnation process on combustion resistance. Wood is a flammable material since it is an organic based material containing carbon and hydrogen. The temperature must be increased to 275 ° C to able to burn for wood. However, it can ignite in any kind of flame source even at much lower temperatures. In order to burning of wood, there must be one of the three; oxygen, a source of burning heat and a flammable substance. If this trio is not available, there will be no ignition [3]. Combustion properties of scotch pine wood treated with a mixture of boric acid and borax, various natural sepi materials as an anti-combustion or retarding agent in wood material were investigated. It was found that natural sepi substances had a negative effect on the examined combustion parameters, the combustion properties of scotch pine treated with natural sepi substances were similar to control or worse than the control and it has been determined that some of the burning characteristics of the scotch pine wood treated with natural sepi substances have improved significantly statistically [4].

İn a study; TGA of particle boards treated with some fire retardants were examined. They found that fire retardants altered the reaction of thermal decomposition of particleboard. More specifically, retardant chemicals altered the pyrolysis of particleboards, increasing the amount of char residuals and reducing the amount of volatile, combustible vapors [5]. İn one study, they investigated thermal behavior of borate treated Scots pine wood. They found that weight loss of wood reduced while char yield increased in the charring phase of the pyrolysis in the boron preservative treated wood accompanying with pyrolysis temperature lowered [6].

İn one a study, he studied thermal characteristics of BA impregnated Scotchs pine. He found that decomposition started earlier for BA impregnated Scots pine than untreated wood and proceeded at lower temperature levels [7].

2. MATERİALS AND METHODS

2.1 Material (Wood and Chemical)

In this study, Black pine (Pinus nigra Arn. Subsp pallasiana var. pallasiana), fir (Abies nordmanniana) material was preferred, stone water (firetex) was used at a concentration of 100% in the impregnation process.

2.2 Preparation of Test Samples

Wood sample of Black pine (Pinus nigra Arn. Subsp pallasiana var. pallasiana), fir (Abies nordmanniana) were taken as wood chips to represent the whole mass of the sample, milled in laboratory Willey mill and sieved in 40 and 60 mesh sieves. The obtained samples were subjected to impregnation process.

2.3.Thermal Analysis

In conditions with heating rate of 10 ° C/min and a purge rate of 50 mL / min (Argon) by using a LABSYS TG-DTA analyzer between room temperature to 600 °C, thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) were implemented under nitrogen atmosphere. 10 mg of the sample was analyzed and weight loss of the sample was noted continuously for each individual experiment. By using TG curve as a function of time, derivative TG (DTG) curves were applied [4].

3. RESULTS AND DİSCUSSİONS

3.1 Experimental Results

The solution properties are given in (Table 1).

Table 1. The solution properties

Impregnation material	Solvent material	Temperatur(⁰C)	pH		Density	
			BI	AI	BI	AI
Stone Water (% 100)	Distilled water	22 ⁰C	1.65	1.65	1215	1215

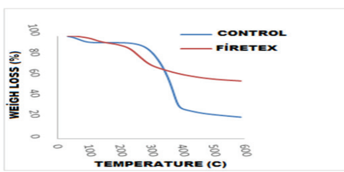
BI: Before impregnation, AI: After impregnation

The solution concentration was used as 100% and the pH/density values were determined before and after impregnation. It has been reported in the literature that acidic structure may cause adversities in anatomical/technological structure of wood.

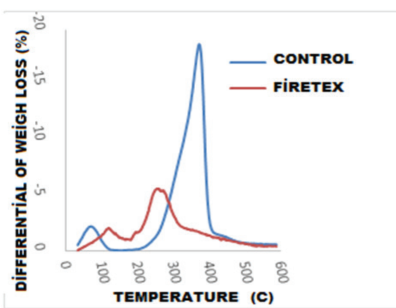
3.2 Thermogravimetric (TGA) Analysis

3.2.1. Black Pine Wood

Samples impregnated using two different tree species were compared with control (non-impregnated) samples. TGA analysis was applied for thermal strength of the samples and DTG curves were generated. The results of thermogravimetric (TGA) analysis of Black pine wood are given below. Figure 1 shows the TGA (1-a) and DTG (1-b) curves of firetex-treated Crimeann wood and control sample. While the turning point temperature of the control sample was 373.71 °C, the decomposition temperature of the firetex applied samples decreased to 251.73 °C.

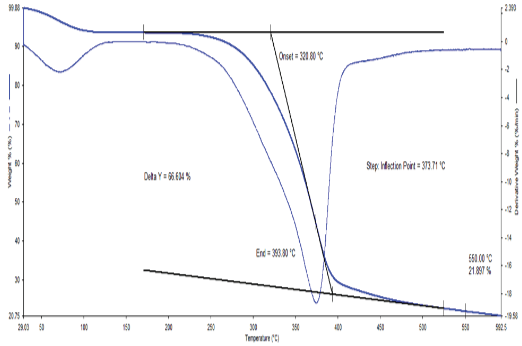


(1-a)

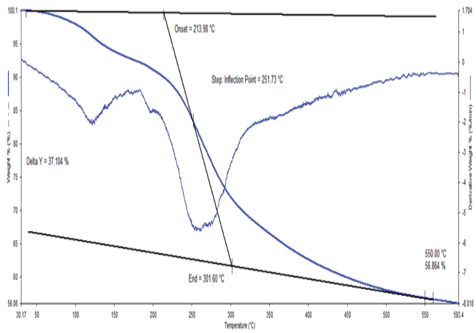


(1-b)

Figure 1. *TGA (a), and DTG (b) curves in Black pine*



(2-a) Control



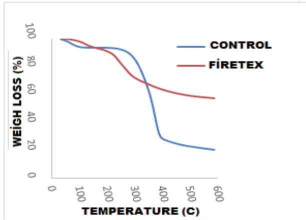
(2-b) Treatment

Figure 2. *Mass Loss in The Control/Treatment Sample*

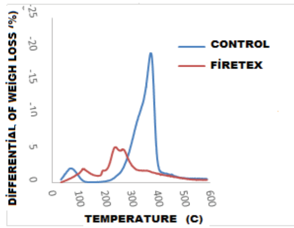
While the amount of residues from combustion result of the control sample was 21.97%, the amount of residue from carbonization result in the sample containing firetex increased to 56.86 %.

3.2.2. Fir Wood

Samples impregnated using two different tree species were compared with control (non-impregnated) samples. TGA analysis was applied for thermal strength of the samples and DTG curves were generated. The results of thermogravimetric (TGA) analysis of Fir wood are given below. Figure 3 shows the TGA (3-a) and DTG (3-b) curves of firetex-treated Fir wood and control sample. While the turning point temperature of the control sample was 361.24 °C, the decomposition temperature of the firetex applied samples decreased to 409.20°C.

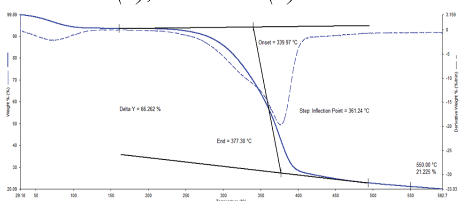


(3-a)

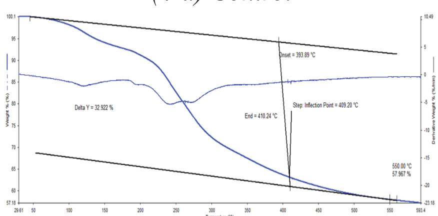


(3-b)

Figure 3. *TGA (a), and DTG (b) curves in Fir Wood*



(4-a) Control



(4-b) Treatment

Figure 4. *Mass Loss in The Control/Treatment Sample*

While the amount of residues from combustion result of the control sample was 21.22%, the amount of residue from carbonization result in the sample containing firetex increased to 57.96 %.

Degradation of the hemicelluloses also causes the organic acid especially acetic acid formation. Acetic acid formation accelerates the decomposition of polysaccharides by means of acting as depolymerization catalyst [8, 9, 10](Brosse et al. 2010; Esteves and Pereira 2008). Kesik et al.(2015) In a study, according to the results of the combustion test carried out on scotch pine wood treated impregnation with stone water using immersion process, significant differences were found in the remaining mass and released CO gas ratios.

4. CONCLUSİONS

Due to their anatomical structure and texture differences, the resistance of wood material against burning is also different. In this study, the thermal properties of wood impregnated with stone water were investigated. In this study, TG/DTG analyzes of defective woods of Black pine (Pinus nigra Arn. Subsp pallasiana var. pallasiana), fir (Abies nordmanniana) woods; It has been determined that the effects of stone water against combustion are also thermally demonstrated. When the variations were compared with the control samples in itself, increases in mass losses were observed depending on species. On the other hand, it showed different rates depending on the physical and anatomical structure of the wood. It was observed that stone water affects thermal properties. To clarify this situation, comparisons can be made with the results of thermal analysis by calculating the impregnated stone water at different times (2, 4, 6, 12 hours).

TGA results can be applied in the production of wood material such as medium-density fiberboard (MDF), particle board, plywood and wood/plastic composites, to explain some of the behavior of wood material against combustion, to evaluate the performance of fire retardants and to obtain fuel from biomass.

All chemical compounds are effective on the combustion, physical and mechanical properties of wood. The fireproofing ability, color, density, odor, taste and resistance to pressure of wood vary depending on the amount of extractive material. As the amount of extractive material decreases in wood, its ability to burn decreases. The increase in lignin and inorganic material (ash) ratio decreases combustion resistance. For further, studies can be conducted on how these substances affect TGA results.

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Chapter 11

FARMERS' MAIN MOTIVATIONS FOR COOPERATIVE PARTNERSHIP AND FACTORS AFFECTING PARTNER PARTICIPATION IN MANAGEMENT: THE CASE OF MERSIN PROVINCE, TURKEY

Seyit HAYRAN[1], Ahmet Duran ÇELİK[2], Aykut GÜL[3]

1 Dr., Cukurova University, seyithayran@gmail.com
2 Dr., Mustafa Kemal University, acelik_01@hotmail.com
3 Prof. Dr., Cukurova University, aykutgul@gmail.com

1. INTRODUCTION

The concept of cooperative is mainly based on helping each other out that is as old as human history. Since the first ages, it is known that people gain mutual benefits by cooperating on things that they can't cope with individually.

In today's context, the idea of modern cooperative dates back to the year of 1816 in England, and in Turkey, beginning of modern cooperatives was based on ''Conventional Agricultural Unions Law'' which was published in 1924 (Güreşçi and Gönç, 2017). According to International Co-operative Alliance (ICA), the definition of cooperatives are; ''people-centered enterprises jointly owned and democratically controlled by and for their members to realize their common socio-economic needs and aspirations''. It is estimated that there are around 3 million of cooperatives and 1.2 billion of cooperative members in the world (ICA, 2020). Moreover, 279.4 millions of total global employment (9.46%) is provided by cooperatives as directly or indirectly (CICOPA, 2017), and the turnover value of the largest 300 cooperatives is approximately 2.1 trillion USD (ICA, 2020).

In terms of Turkey, there are 53,259 cooperatives and around 7.5 million of cooperative members. Among those cooperatives, 12,269 (23%) of them are agricultural cooperatives, and the number of agricultural cooperative members are around 3.9 million which is more than half (52.3%) of the total cooperative members in Turkey (Republic of Turkey-Ministry of Trade, 2017).

Agricultural production, includes many risk and uncertainties in its own nature, therefore, it is important for producers to act as organized in order to minimize risk and uncertainties, and to utilize limited resources effectively.

In most of the developed countries, agricultural production is carried out under limited number of big agricultural cooperatives. According to the report released by ICA in 2018, first five countries in terms of cooperative turnover values are respectively as followed; USA (64.08 billion USD), Japan (58.12 billion USD), South Korea (36.45 billion USD), Germany (31.06 billion USD) and Denmark (26.83 billion USD) (ICA, 2018).

Agricultural cooperatives face some problems in Turkey in certain topics such as financial, supreme organization, education, legislation and supervision. Especially, there is an issue in efficiency due to outnumbered and disorganized structure of cooperatives (Tan and Karaönder, 2013). However, the number of cooperative partners of Turkey is around 8 million, this number is around 19 million in Germany, and it is known that every one of the 3rd EU citizens is a partner of a cooperative. This issue that low level of cooperative participation in Turkey, was a subject of some studies. There are some factors that drive farmers to become a cooperative partner. Especially, farmers' level of awareness is one of the main motivations of participating to a cooperative, for instance, one study indicates that 80% of the cooperative partners don't know what cooperative really means (Güreşçi and Gönç, 2017).

Some of the studies which were aimed to determine the main motivations of farmers' to become a cooperative partner are summarized. In a study that was carried out across the Turkey, farmers' sense of association, their level of willingness, and trust in management were found as the most important factors that affect to participate in a cooperative. Also, it was found out that success of a cooperative was affected by enterprise scale, irrigated land size, animal existence, need of loan and input (Şahin et.al., 2013). In another study, inputs that provided by cooperatives was found as the main reason of becoming a cooperative partner. Moreover, willingness to participate in management was found that getting higher along with the education level of a farmer (Everest, 2015). In a study that was carried out on 257 of dairy cattle enterprises, the main factors that drive farmers to become a cooperative partner were found as age and experience level of farmers, non-agricultural income amount, number of animal, and subsidy amount that is provided (Ertek et.al., 2016). Yercan and Kınıklı (2018) carried out a study on 142 partners of milk cooperatives, and level of participation in management was found low, in the meantime willingness of participation in management was found higher in young and educated partners. Gashaw and Kibret (2018) carried out a study in Ethiopia about factors that affect participation in cooperatives, according to research results, factors such as age, need of loan and input, benefit perception of dividend distribution, awareness of socio-economic benefits, and trust in management were found significant. In another study that was carried out by Balgah (2019) on partners of coffee cooperatives, land size, payment on time by cooperatives, household size, experience and main income source were found as the factors that affect participating in cooperatives,

This study was carried out in Mersin Province – Turkey, and the main purpose of this study was to determine both farmers' main motivations for being a cooperative partner and factors affecting partner participation in management.

2. MATERIALS AND METHODS

Research area and data: The data used in the study obtained from the cross-sectional survey conducted in Mersin Province. The main farmers' survey was conducted face-to-face with farmers during the period of

December 2019 and January 2020 to obtain research data in Mersin. 77 randomly selected farmers were visited to obtain research data. Within the research the proportional distribution of the farmers based on cooperative partnerships were as follows; agricultural development cooperative was 33.77% (n:26), agricultural credit cooperative was 23,38% (n: 18), agricultural sale cooperative was 7,79% (n: 6), and irrigation cooperative was 35,06% (n:25).

A structured questionnaire used for data collection instrument. The questionnaire consisted of information on farms and farmers' characteristics, farmers' main motivations for being a cooperative partnership prepared using a Likert-type five-point continuum, and items that reflect farmers' participation in cooperative management.

Data analysis: In this research, multiple statistics methods used which consist of descriptive statistics, factor analysis, multiple regression analysis, and binary logistic regression analysis. A scale of 10 items was used to determine the main motivations of farmers to become cooperative partners. In order to reduce this scale to fewer components, factor analysis using varimax rotation was run. Then, multiple regression analysis, in which factor scores obtained from factor analysis were included in the model as the dependent variable, was used to investigate the relationship between farmers' cooperative partnership motivations and their socioeconomic variables. In the last part of the study, binary logistic regression analysis was used to analyze the factors affecting farmers' participation in cooperative management (Greene, 1997; Gujarati, 2009; Hair et al., 1994). The ındependent variables used in regression analysis represented in Table 1.

Tablo 1. Independent variables used in regression analysis

Variables	Definition	Min	Max	Mean	SD
Age	Farmer's age as year	32.00	72.00	52.65	10.39
Education	Farmer's educational level	1.00	3.00	1.43	0.62
Internet	1 if farmers can use internet; 0 other	0.00	1.00	0.51	0.50
Training	1 if farmers participated in an training program on agricultural cooperative; 0 other	0.00	1.00	0.12	0.32
Non-Agricultural Income	1 if farmers had an non-agricultural income sources; 0 other	0.00	1.00	0.35	0.48
Land	Total farmland as da	1.00	130.00	20.42	24.47

Economic Motivations	Factor scores derived from factor analysis
Information and Technological Motivations	

3. RESULTS AND DISCUSSION

3.1. Farmers' socio-economic characteristics

The basic socioeconomic characteristics of the sample farmers are presented in the Table 2. 97.40% of the sample farmers were male. Farmers' mean age was 52.65 years old. Farmers carry out their agricultural activities in an area of 20.42 on average; their greenhouse agriculture experience was on average 29.60 years. The educational level of farmers was not satisfactory. 63.60% of the farmers were primary school graduates. About half of the farmers were actively using the internet, and 88.30% of the farmers participated in a training program on agricultural cooperatives. 35.10% of farmers have non-agricultural income sources

Table 2. Farmers socio-economics characteristics

Farmer's age (year) (Mean - SD)		52.65	10.39
Farmer's experience (year) (Mean - SD)		29.60	11.35
Agricultural land (da) (Mean - SD)		20.42	24.47
Gender	Male (n - %)	75	97.40
	Female (n - %)	2	2.60
	Total (n - %)	77	100.00
Education	Primary education (n - %)	49	63.60
	High school (n - %)	23	29.90
	University (n - %)	5	6.50
	Total (n - %)	77	100.00
Internet	No (n - %)	38	49.40
	Yes (n - %)	39	50.60
	Total (n - %)	77	100.00
Training about cooperatives	No (n - %)	68	88.30
	Yes (n - %)	9	11.70
	Total (n - %)	77	100.00
Non-Agricultural Income	No (n - %)	50	64.90
	Yes (n - %)	27	35.10
	Total (n - %)	77	100.00

3.2. Farmers' main motivations and their determinants

3.2.1.Farmers' main motivations

Farmers become partners in agricultural cooperatives to achieve different motivations and expectations. The main reasons for farmers to become a partner in the agricultural cooperatives are to increase the economic performance of their farms and to improve their financial situations. In addition, some farmers maybe become partners with the agricultural cooperatives to realize their social motivations as well as economics, and financial motivations (Yercan and Kınıklı, 2018). In this case, the main motivations of farmers to be an agricultural cooperative partner were examined with a scale that consists of 10 items. The scale's internal reliability coefficient (Cronbach's Alpha) was 0.930. The motivations of farmers to be a partnership in agricultural cooperatives in Mersin Province are presented in Table 3. As a result of this study, it was found that the most important motivations of farmers are economic-based. It has been determined that the most important motivations of farmers to be cooperative partners are to obtain quality input, to find marketing opportunities under more favorable conditions, and to obtain a more favorable output price in the research area. As similar to our results, Gashaw and Kibret (2018) stated that the credit and input needs of farmers and the needs for marketing and training through cooperatives were factors affecting their decision to be a partnership with cooperatives in Ethiopia. In another study conducted in Uganda, infrastructural access such as district produce market, local input shop, extension worker, nurseries, and all year gravel road affected farmers' partnership decisions with a cooperative (Adong, 2012). Grece (2011) stated that farmers to be a partnership with cooperatives in order to get access to market and services, to get access to production and processing equipment, to get access to training opportunities that are offered by the cooperative and other supporting organizations. These results line with findings in this case.

Factor analysis was applied to the scale in order to be interpreted scale sub-dimensions and, to obtain factor scores used in multiple regression analysis. As a result of factor analysis, two factors were derived which explaining 77.73% of the total variance. Two factors were identified as "economic motivations" and, "information and technological motivations" based on factor loadings Table 3 Factor 1, economic motivations, loaded significantly on quality input opportunities, better marketing opportunities better output price opportunities, credit opportunities, and creating a public-pressure group. Factor 2, information and technological motivations, have high loadings on technical information support, the common use of agricultural tools and machinery, benefiting from agricultural training and seminars, opportunity to access written materials such as agricultural handbooks and brochures easily, and infrastructural support on product processing and storage

Table 3. Farmers' main motivations for being a cooperative partner

Motivations	Mean	SD	Component	
			Economic Motivations	Information and Technological Motivations
Quality input opportunities	4.31	1.12	**0.910**	0.256
Better marketing opportunities	4.40	1.05	**0.913**	0.250
Better output price opportunities	4.51	1.00	**0.906**	0.263
Credit opportunities	4.25	1.27	**0.759**	0.158
Technical information support	3.99	1.37	0.581	**0.628**
Creating a public-pressure group	4.06	1.37	**0.721**	0.391
Common use of agricultural tools and machinery	3.45	1.40	0.070	**0.808**
Benefiting from agricultural training and seminars	3.88	1.28	0.386	**0.808**
Opportunity to access written materials such as agricultural handbooks and brochures easily	3.42	1.44	0.240	**0.900**
Infrastructural support on product processing and storage	3.96	1.36	0.540	**0.683**
Explained Variance (%)			44.210	33.520
KMO Measure of Sampling Adequacy.			0.868	
Bartlett's Test of Sphericity			0.000	
Cronbach's Alpha			0.930	

Note: 5 Very Important, 4 Important, 3 Moderately Important, 2 Slightly Important, 1 Unimportant

3.2.2. The determinants of farmers' main motivations

As a result of factor analysis, two sub-dimensions were derived. In this part of the study, the relationship between socioeconomic variables and the motivations of farmers' cooperative partnership was investigated using multiple regression analysis, in which factor loadings derived from factor analysis were included in the model as the dependent variable. Two multiple regression models were analyzed to investigate the relationship between the "economic motivations" and "information and technological motivations" of farmers, and socioeconomic variables. Two models and variables were significant at p-values < 0.10 were discussed. According to the results of the first model, there were positive relationships between the economic motivations of farmers to be cooperative partners and their ages, and sources of non-agricultural income. These results indicated that older farmers prioritize their economic motivations than their young colleagues. In addition, farmers with non-agricultural income sources give more attention to economic motivations. According to the results of the second model, more educated farmers attached more importance to information and technological motivations to be a cooperative partner (Table 4).

Table 4. The determinants of farmers' main motivations for being a cooperative partner

Independent Variables	Economic Motivations		Information and Technological Motivations	
	Coef.	Std. Error	Coef.	Std. Error
Constant	-1.903**	0.732	-1.354***	0.704
Age	0.027**	0.012	0.006	0.011
Education	0.134	0.219	0.628*	0.210
Internet	0.441	0.288	0.178	0.277
Training	-0.260	0.39	0.208	0.375
Non-Agricultural Income	0.455**	0.241	0.008	0.232
Land	-0.002	0.005	0.002	0.005
Adjusted R Square	0.078***		0.148**	

Note: Variables and models significant at *p < 0.10, **p < 0.05, ***p < 0.01.

3.3. Farmers' participation in cooperative management

Agricultural cooperatives are established with the Cooperative Articles of Association in Turkey. The articles of association are important documents that contain information such as the working area of the cooperative, the conditions of partnership and withdrawal from the partnership, the cooperative capital, partner responsibility, the choice of cooperative management, and supervisory bodies. As a result of reading the articles of association of the cooperative, the partners can achieve information on the cooperative more closely. In this study, the farmers were asked whether they have read the articles of association of the cooperative that they are partners in. 42.86% of the partners stated that they had read the main contract of the cooperative (Table 5). Logistic regression analysis was carried out to determine the factors affecting whether farmers read the cooperative articles of association or not. According to the results of logistic regression analysis, the variables of education, training, non-agricultural income, and information and technological motivation had positive and statistically significant coefficients (Table 6). According to the results, more educated farmers, and farmers who attend training on agricultural cooperatives were more likely to read cooperative articles of association. Another research finding showed that the possibility of reading of cooperative articles of association by farmers who had non-agricultural income sources was higher than other colleges. Farmers who placed more emphasis on information and technological motivations were more likely to read cooperative articles of association. Yercan and Kınıklı (2018) reported that 42.30% of the farmers who they examined were read the cooperative article of association, and their age and non-agricultural income were affected it.

To achieve informed about agricultural cooperatives, it is useful to read in the Cooperatives Law No 1163, as well as the cooperative articles of association. In this study, it was determined that only 27.27% of farmers read the aforementioned law (Table 4). Factors affecting the possibility of farmers to read the Cooperatives Law No 1163 determined as education and training on agricultural cooperatives (Table 6).

Table 5. Farmers' participation in cooperative management

Items	**No**		**Yes**		**Total**	
	n	**%**	**n**	**%**	**n**	**%**
I1 - Have you read the Cooperative's Articles of Association before becoming a member of the cooperative?	44	57.14	33	42.86	**77**	100.00
I2 - Have you read the Cooperatives Law No. 1163?	56	72.73	21	27.27	**77**	100.00
I3 - Have you attended the last cooperative general assembly?	20	25.97	57	74.03	**77**	100.00
I4 - Did you ever speak at the general assembly meeting?	38	49.35	39	50.65	**77**	100.00
I5 - Have you ever been a candidate for board of directors' membership?	63	81.82	14	18.18	**77**	100.00
I6 - Have you ever been a candidate for board supervisory membership?	70	90.91	7	9.09	**77**	100.00

I7 - Are you aware of the decisions taken by the board of directors?	28	36.36	49	63.64	**77**	100.00
I8 - Are you aware of the financial transactions and records of the cooperative?	43	55.84	34	44.16	**77**	100.00
I9 - Do you know the establishment date of the cooperative?	23	29.87	54	70.13	**77**	100.00

Farmer's attention to and attend to the general assembly meetings of the cooperatives that they are partners are an important indicator of their participation level in management. Therefore, in this study, farmers were asked whether they attended the last general assembly meeting. It was determined that a large part of the farmers (74.03%) attended the last general assembly meeting. This research finding showed that farmers were closely interested in the general meetings of the agricultural cooperative they are partners in the research area.

Table 6. Factors affecting farmers' participation in cooperative management

Variables	**I1^X**	**I2^X**	**I3^X**
Age	0.014 (0.038)	-0.016 (0.035)	-0.002 (0.035)
Education	**1.574 (0.735)	*1.076 (0.648)	-0.507 (0.757)
Internet	1.147 (0.821)	0.065 (0.847)	**2.416 (0.939)
Training	**3.807 (0.729)	**2.956 (1.182)	-0.104 (1.349)
NAI	**1.758 (0.788)	-1.076 (0.750)	-0.348 (0.703)
Land	-0.027 (0.018)	-0.011 (0.014)	0.010 (0.019)
Economic Motivations	-0.147 (0.334)	0.174 (0.408)	-0.012 (0.281)
Information and Technological Motivations	**0.840 (0.387)	0.582 (0.408)	0.522 (0.332)
Constant	-3.105 (2.422)	-1.800 (2.172)	0.957 (2.268)
-2 Log likelihood	64.049	64.161	70.097
Cox & Snell R Square	0.414	0.287	0.210
Nagelkerke R Square	0.555	0.416	0.307
Chi-square	***41.119	**26.076	18.112**

Note: Variables and models significant at *p < 0.10, **p < 0.05, ***p < 0.01.

^{X} Yes:1, No: 0

Another important indicator of the farmers' participation in cooperative management is whether or not they ever speak about the agenda at the general assembly meeting. In this study, the ratio of farmers who speak at least once a time in the past general assembly meetings regarding the cooperative agenda was determined as 50.65%.

Partners who have been candidates and/or have served in the board of directors and supervisory bodies are more closely concerned with cooperative problems and are making more efforts to develop the cooperative than other partners. Therefore, whether farmers have been a candidate for the board of directors and supervisory bodies gives information about their feeling of the belonging level of the cooperatives. 9.09% of the partners were candidates for the supervisory board, and 18.18% for the membership of the board of directors.

It is important for the farmers to follow the decisions of the cooperative board of directors and the financial records of the cooperative and to have information about them to maximize the advantage they gain from the cooperative partnership. 63.64% of the farmers stated that they were aware of the decisions of the cooperative board of directors, and 44.16% of them stated that they were aware of the cooperative's financial records in the research area. Logistic regression analysis results showed that more educated farmers and farmers with large farmland closely monitor and be informed of the decisions of the cooperative board of directors. In addition, farmers who more attention to knowledge and technological motivations to become a partner of the agricultural cooperative are more interested in and informed about the financial transactions and records of the cooperative.

Table 6. Factors affecting farmers' participation in cooperative management (Continued)

Variables	I4^{X}	I7^{X}	I8^{X}
Age	-0.005 (0.030)	-0.014 (0.037)	0.012 (0.029)
Education	0.756 (0.574)	**2.570 (1.153)	0.624 (0.538)
Internet	0.906 (0.690)	0.600 (0.777)	1.094 (0.675)
Training	-0.026 (1.003)	1.979 (1.133)	-0.859 (0.910)
NAI	-0.111 (0.618)	0.197 (0.710)	-0.111 (0.587)
Land	**0.058 (0.027)	0.004 (0.019)	*0.026 (0.016)

Economic Motivations	-0.094 (0.291)	0.586 (0.385)	-0.001 (0.301)
Information and Technological Motivations	**0.595 (0.324)	0.390 (0.314)	*0.508 (0.305)
Constant	-2.133 (1.997)	-2.338 (2.483)	-2.729 (1.890)
-2 Log likelihood	79.32	64.417	85.098
Cox & Snell R Square	0.300	0.380	0.235
Nagelkerke R Square	0.400	0.520	0.314
Chi-square	27.500***	36.828***	20.593**

Note: Variables and models significant at *p < 0.10, **p < 0.05, ***p < 0.01.

[X] Yes:1, No: 0

4. CONCLUSION

Cooperatives are considered as the third sector besides the private and public sectors. In order to improve agricultural cooperatives, it is important to know the basic motivations of the farmers to be a cooperative partner and their level of participation in the management. In this study, the basic motivation and participation level of farmers in management levels were investigated in Mersin province, Turkey. Participation of farmers in managerial activities such as participation in the general assembly of the cooperative, awareness of decisions of the cooperative director's board and of the financial transactions and records of the cooperative was generally satisfactory. In general, the education of farmers and their training on cooperatives positively affected their participation in cooperative management. The basic motivations of farmers to be partners with agricultural cooperatives were based on economic motivations. However, farmers' information and technological motivations were also important.

In the research area, agricultural cooperatives should attach importance to cooperative training and meet their partners' information and technological motivations to enable their partners to participate more actively in management. Agricultural cooperatives can train their partners in cooperation with universities or through their superior associations. In addition, cooperatives may also engage in more interesting training activities, such as training materials such as training brochures, magazines, or mobile cooperative training. Increasing social interaction in this way may lead to a cooperation environment between the cooperative and its partners.

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Chapter 12

INVESTIGATE THE RELATIONSHIP BETWEEN CALCIUM ELEMENT AND CYTOKINE HORMONE

Diyar Abdullah Hassan HASSAN1, Özlem ÜZAL2, Fikret YAŞAR3

1 Van Yüzüncü Yıl Üniversitesi Fen Bilimleri Enstitüsü Bahçe Bitkileri Bölümü
2 Doç. Dr., Van Yüzüncü Yıl Üniversitesi Ziraat Fakültesi Bahçe Bitkileri Bölümü , ozlemuzal@yyu.edu.tr
3 Van Yüzüncü Yıl Üniversitesi Ziraat Fakültesi Bahçe Bitkileri Bölümü

1. INTRODUCTION

Calcium can easily enter the apoplasts and make changes in the cell wall. It is a plant nutrient that can be found in the forms and outer surface of the plasma membrane. It has long been known that Calcium is an essential element for plants, and that plant species differ in both the amounts of Calcium they require and their tolerance of Calcium in the rhizosphere. As the divalent cation (Ca^{2+}), it is required for structural roles in the cell wall and membranes, as a counter cation for inorganic and organic anions in the vacuole, and as an intracellular messenger in the cytosol. Calcium deficiency is rare in nature, but excessive Calcium restricts plant communities on calcareous soils. Calcium is taken up by roots from the soil solution and delivered to the shoot via the xylem. It may traverse the root either through the cytoplasm of cells linked by plasmodesmata or through the spaces between cells (the apoplast). The relative contributions of the apoplastic and symplastic pathways to the delivery of Calcium to the xylem are unknown (White, 2001). However, the movement of Calcium through these pathways must be finely balanced to allow root cells to signal using cytosolic Calcium concentration, control the rate of Calcium delivery to the xylem, and prevent the accumulation of toxic cations in the shoot. Deficiency symptoms are observed in young expanding leaves, such as in 'tipburn' of leafy vegetables, in enclosed tissues, such as in 'brown heart' of leafy vegetables or 'black heart' of celery, or in tissues fed principally by the phloem rather than the xylem, such as in 'blossom end rot' of watermelon, pepper and tomato fruit, 'bitter pit' of apples and 'empty pod' in peanut. They occur because Calcium cannot be mobilized from older tissues and redistributed via the phloem. This forces the developing tissues to rely on the immediate supply of Calcium in the xylem, which is dependent on transpiration. Transpiration is low in young leaves, in enclosed tissues and in fruit. Other physiological disorders, such as 'cracking' in tomato, cherry and apple fruit, occur in tissues lacking sufficient Calcium upon hypo-osmotic shock (following increased humidity or rainfall), presumably as a result of structural weaknesses in cell walls. When excessive calcium is present in the rhizosphere solution, plants may suffer calcium toxicity. This may prevent the germination of seeds and reduce plant growth rates. In cultivated tomato, one symptom of excess calcium is the development of tiny yellowish flecks or 'gold spot' in the cell walls around the calyx and shoulders of the fruit. These flecks are crystals of Calcium oxalate and their abundance is increased by high humidity and high Calcium fertilization (De kreij et al., 1992).

Since their discovery, cytokinins have been implicated in almost all aspects of plant growth and development (Hwang et al., 2012). Further, cytokinins play important roles in the interaction with both biotic and abiotic factors (Argueso et al., 2012). Naturally occurring cytokinins are adenine derivatives with distinct substitutions attached to the N^6 position of the adenine ring. The most common class of cytokinins have isoprenoid side chains, including the most abundant cytokinin in Arabidopsis, trans-zeatin (tZ). In higher plants, zeatin occurs in both the cis and the trans configuration. The trans form is an active cytokinin in all plant species; the cis form (cZ) is present ubiquitously in plants (Gajdošová et al., 2011), but is active only in a subset, and in Arabidopsis, the cis form shows at most only limited cytokinin activity (Heyl et al., 2012). Further, cytokinins can also be conjugated to sugar moieties, most commonly glucose. They are also produced by several strains of soil-living and phytopathogenic bacteria, such as Agrobacterium and Pseudomonas, which cause galls or tumors in plants, and by certain phytopathogenic fungi, such as *Helminthosporium* and *Ustilag* (Srivastava, 2002).

Cytokinins have been noted for their ability to stimulate cell division in plant tissue culture methods, nitrogen purin are some adenine derivatives (Özen and Onay, 1999). Zeatin, dihydroseatin, isopentenyl adenine and dimethylalladenin are naturally synthesized cytokines in various plants, as well as synthetic cytokines (kinetin (N6-furfurilamino purin), benzyladenine (BA) and tetrahydropyranylbenzyl adenine (PBA) (Ünsal, 1993). There are more than 200 natural and synthetic cytokines chemically and biologically (Salisbury and Ross, 1991). It is the most common cytokine zeate that occurs naturally in higher plants. Riboside (purine base + ribose sugar) or ribotid (purine base + ribose sugar + phosphate group) are located in the ninth position of zeatin and other natural cytokines. In addition to stimulating cell division, cytokinins are also effective on shoot and root differentiation in tissue culture, growth of lateral buds, leaf development, chloroplast development, and senescence. All of these events usually occur when used with auxin. Therefore, mixtures of auxin and cytokinin are added to the media (Özen and Onay, 1999). Cytokinin group hormones affect the activation and synthesis of proteins necessary for mitosis cleavage. Therefore, it increases cell division. It causes trunk formation and vascular tissue differentiation in morphogenesis. It has effects on bud dormancy. Cytokinins provide the breaking of apical dominance, which is promoted by auxin, because they increase the development of lateral bud (Özen and Onay, 1999). It is thought that cytokinins prevent the formation of proteases and nucleases in the leaf, prevent protein breakdown and delay aging in this way (Kaynak and Ersoy, 1997). Cytokinins promote chloroplast formation. They provide this by promoting chlorophyll synthesis and conversion of etioplasts (colorless pigments) to chloroplasts (Salisbury and Ross, 1991).

In this review, it is aimed to bring together the researchers' studies on calcium and cytokine hormone and to reveal the morphological and biochemical effects and importance of the relationship between calcium ion and cytokinin hormone in plants.

2. ROLES OF CYTOKININS IN PLANTS

2.1. Cytokinins and the Cell Cycle

Cytokinins are required, in concert with auxin, for cell division in culture in a wide variety of plant cells. There is also evidence that in vivo cytokinin may play a role in stimulating cell division. Immunocytochemistry and direct measurements of cytokinin revealed high cytokinin levels in mitotically active areas, such as the root and shoot meristems, and very low levels in tissues where the cell cycle is arrested (Dewitte et al., 1999). Application of exogenous cytokinin to some organs that normally lack this hormone has been shown to induce cell division and cytokinins have been linked to all stages of the cell cycle (Den Boer and Murray, 2000).

2.2. Cytokinin and the Shoot Apical Meristem

The shoot apical meristem (SAM) is a highly specialized group of cells from which the majority of the aerial portion of the plant is derived by reiterative development. The ability of cytokinins to initiate shoots from undifferentiated callus cultures and the initiation of ectopic meristems in transgenic plants engineered to overexpress cytokinins suggested a role for this hormone in SAM development. More recently, studies have shed light on the role of cytokinin in SAM function and its interaction with other hormonal and developmental signaling pathways (Durbak et al., 2012; Hwang et al., 2012).

2.3. Cytokinin in the Root Apical Meristem

Cytokinins have been known to inhibit root growth and development. While reduced cytokinin function in Arabidopsis leads to reduced shoot growth, it results in an increase in overall root mass, with longer roots, an increased number of lateral roots and an enlarged root apical meristem (RAM) (Riefler et al., 2006). The inhibitory role of cytokinin on primary root growth arises from effects on cell division in the root meristem and on cell expansion in the root elongation zone. Cytokinin-mediated inhibition of cell expansion occurs in part through stimulation of the ethylene signaling pathway, as inhibition of ethylene biosynthesis or signaling reduces the effects of cytokinin (Ruzicka et al., 2009).

2.4. Role of Cytokinin in Lateral Root Development

Auxin and cytokinin interact antagonistically to regulate the formation of lateral root primordia. Auxin is a positive regulator of lateral root formation, cytokinin inhibits the formation of lateral roots in Arabidopsis. Exogenous application of cytokinin results in fewer lateral roots. Consistent with this, mutants with decreased cytokinin signaling have an increased number of lateral roots, and mutants with increased cytokinin sensitivity have fewer (Riefler et al., 2006).

2.5. Cytokinin in Vascular Development

Cytokinin plays key roles in the development of the vasculature system, acting both to promote protoxylem differentiation and the development of the vascular cambium. The first demonstration of a role for cytokinin in vascular development in Arabidopsis came from the analysis of the woodenleg mutant, which is the result of an antimorphic allele of the AHK4 cytokinin receptor (Dettmer et al., 2009).

2.6. Cytokinin and Gametophyte Development

The life cycle of higher plants alternates between haploid gametophytic and diploid sporophytic phases. The female gametophyte is surrounded by the sporophyte and develops within the ovule of the maternal plant. Cytokinin has been shown to be required in the sporophytic tissue for female gametophyte development (Kinoshita-Tsujimura and Kakimoto, 2011).

2.7. Role in Leaf Development

The pavement cells of Arabidopsis leaves are puzzle-shaped with highly interdigitated lobes. Previous studies have indicated that auxin acts to coordinate this interdigitation through the activation of a ROP GTPase. A recent study has also linked cytokinin to this process (Xu et al., 2010).

2.8. The Interaction of Cytokinin and Light Signaling

Cytokinin and light responses interact in several contexts. The growth and developmental response of seedlings to light, called photomorphogenesis, can be partially mimicked by growth of seedlings in the presence of exogenous cytokinin or by elevation of endogenous cytokinin (Lochmanova et al., 2008).

2.9. Cytokinin and Leaf Senescence

Cytokinins have long been known to inhibit leaf senescence. Disruption of multiple type-A ARRs inhibits dark-induced senescence of detached leaves and increases the sensitivity of the leaves to the effect of exogenous cytokinin in delaying leaf senescence (To et al., 2004).

2.10 Cytokinin and plant defense

A number of plant pathogen interactions involve cytokinin. Some pathogens are capable of synthesizing cytokinins, and/or of directing the plant to elevate cytokinin biosynthesis, which has often been closely tied to the success of the pathogen. These include gall-forming pathogenic bacteria such as Agrobacterium and the biotrophic actinomycete Rhodococcus fascians, and biotrophic fungal and bacterial pathogens that form green bionissia (Naseem and Dandekar, 2012).

2.11. Cytokinin and abiotic stress

Cytokinin function has been linked to a variety of abiotic stresses. Cold stress rapidly up-regulates the expression of multiple type-A ARRs by an AHK2/AHK3-dependent mechanism that surprisingly does not appear to require cytokinin (Jeon et al., 2010). This suggests other potential inputs into the activation of these AHK hybrid sensor kinases. ARR1, AHP2, AHP3, and AHP5 were also involved in the induction of type-A ARRs by cold (Jeon and Kim, 2013).

3. CYTOKININ AND CALCIUM

Although cytokine provides cell division, little to culture medium it cannot stimulate cell division alone. Calcium must be added to the environment in order to stimulate division. The presence of calcium in the environment increases the sensitivity of cytokines to cells. However, compounds that increase the Ca permeability of 2 cells act like cytokinin and delay aging. Calcium was seen to enhance the ability of cytokinin to retard senescence, leaf abscission, and to promote cotyledon expansion. Calcium was also found to inhibit cytokinin stimulation of anthocyanin, and betacyanin synthesis. Yet other studies identified a Calcium/cytokinin/ ethylene connection, although there was disagreement between published reports on the nature of the interaction (Hepler, 2005).

It was suggested by Oliveira et al., (2010) that the evaluation of the effect of different sources of cytokinin on shoots obtained from cloned plants of *Annona glabra* demonstrated that the presence of 6-benzilaminopurine (BAP), thidiazuron (TDZ), kinetin (KIN), and zeatin (ZEA) reduced Calcium concentrations in buds of *A. glabra* during *in vitro* culture. Furthermore, reduction of the Calcium content in tissues cultivated in vitro is directly related to physiological disorders such as necrosis of the apex and vitrification.

Various results indicate that Calcium plays a role in cytokinin-induced responses. This includes the synergistic action of Calcium and cytokinin in ethylene production, increased cotyledon dry weight, membrane protein phosphorylation and betacyanin synthesis and cell division in the moss Funaria hygrometrica. The bud formation from the protonemata of this moss has been extensively studied. It begins with an asymmetric division of a cell several cells back from the tip and its development requires the continuous presence of cytokinin. Cytokinin-induced bud formation is inhibited in a Calcium-free medium and Calcium ionophores can substitute for cytokinin to initiate bud formation. These results indicate that cytokinin may act by increasing the cytosolic Calcium concentration by promoting Calcium uptake from the medium, since external Calcium is required (Aducci, 1993). It is documented that Calcium has a great effect on hormone's expression genes. In peanut, Calcium signal transduction pathway is involved in hormone regulation pathway including cytokinin. These results implied that seed development might be regulated by the collaboration of Calcium signal transduction pathway and hormone regulation pathway (Li et al., 2017). Studying barley and cucumber by Legocka and Sobieszczuk-Nowicka (2014) showed that Calcium has an effect on cytokinin inducing during the greening process. Cytokinin enhancement of chlorophyll accumulation induced by light apparently is dependent on the external pool of Calcium, whereas cytokinin stimulation of LHCPII (light-harvesting chlorophyll a/b-binding protein complex of photosystem II) accumulation induced by light is only partially dependent on that pool of Calcium.

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