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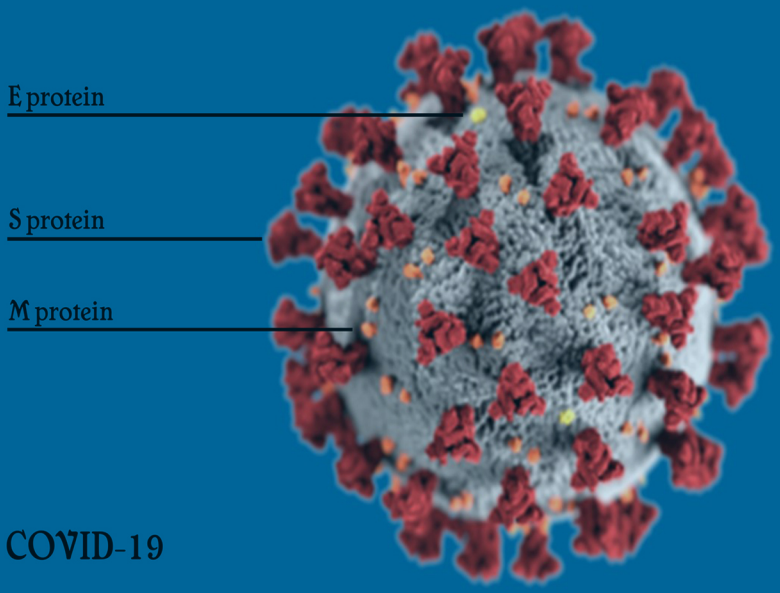
BİLGE INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY RESEARH

Year / Yıl 2020 | Volume / Cilt 4 | Number / Sayı 1

p-ISSN: 2651-401X
e-ISSN: 2651-4028

In The Memory of L. Wenliang



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BİLGE INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY RESEARCH

VOLUME: 4 ISSUE: 1 2020 ISSN: 2651-401X e-ISSN: 2651-4028

Press:
Kutbilge Association of Academicians
Distribution, Sales, Publisher; Certificate No: 42086
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BİLGE INTERNATIONAL JOURNAL OF SCIENCE AND TECHNOLOGY RESEARCH

CİLT: 4 SAYI: 1 2020 ISSN: 2651-401X e-ISSN: 2651-4028

Baskı:
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CİLT: 4 SAYI: 1 2020 ISSN: 2651-401X e-ISSN: 2651-4028

A peer reviewed international journal, published
biannually by Kutbilge Association of Academicians.

Yılda iki sayı olarak yayınlanan uluslararası hakemli bir dergi olup,
Kutbilge Akademisyenler Derneği tarafından yayınlanmaktadır.

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VOLUME: 4 ISSUE: 1 2020 ISSN: 2651-401X e-ISSN: 2651-4028

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Research Articles / Araştırma Makaleleri

Bilge International Journal of Science and Technology Research

2020, Volume: 4, Issue: 1, 1-6
ISSN: 2651-401X
Received: 29.01.2020; Accepted: 09.03.2020
e-ISSN: 2651-4028
DOI: 10.30516/bilgesci.680500

Treatment of Rose Processing Wastewater by Sunlight/TiO_2 Photocatalysis Process

Melda Başbuğ Çancı[1*], Mehmet Kılıç[1]

Abstract: The objective of this study was to investigate the photocatalytic treatment of rose processing wastewater by using sunlight and TiO_2. Rose processing wastewater contains high concentrations of chemical oxygen demand, high amount of solid matters and dark color. The effect of various operating conditions such as irradiation time, catalyst loading and pH on COD and color removal were determined. The highest color removal and COD removal was found to be 51.7 % and 15.7%, respectively with 2 g/L TiO2 catalyst dose at pH 4. Sunlight was used as an economic irradiation source for photocatalytic treatment of rose processing wastewater.

Keywords: Photocatalysis, rose processing wastewater, sunlight, TiO_2.

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Citation: Başbuğ Çancı, M., Kılıç, M. (2020). Treatment of Rose Processing Wastewater By Sunlight/TiO_2 Photocatalysis Process. Bilge International Journal of Science and Technology Research, 4 (1): 1-6.

1. INTRODUCTION

Rose flower is seen as a symbol of purity, beauty, love and faith all over the world and it is grown in many regions especially Turkey, Bulgaria, Iran, India, China, northern African countries and Europe (Rusanov, 2011; Göktürk Baydar and Baydar, 2013; Nayebi et al., 2017). Rose flowers bloom in May-June and harvesting period continues for about 40-45 days. During this period, rose flowers are collected daily and processed in facilities for producing rose oil, rose concrete, absolute and rose water. Turkey and Bulgaria are main rose oil producer countries (Anonymous, 2019). All of the rose oil and rose extracts produced in both countries are used as important additives in the world perfume and cosmetics industries (Kovatcheva et al. 2011; Anonymous, 2019).

Steam distillation process is used for producing rose oil. Rose flowers and water are filled in the boilers and distilled at 2-3 atm pressure. The amount of water is 3 times by the weight of the rose flowers. During the rose oil distillation process rose flowers absorb about 33% of water and 67% of water is discharged as wastewater. After distillation process waste rose petals and wastewater are discharged to the drainage channel. When 1 kg of rose flower is processed, about 2 kg of waste occurs on wet weight basis (Schieber et al., 2005). In many facilities, wastewater is separated from waste rose petals and collected in lagoons (Fig. 1). These darky wastewater contains a high concentration of chemical oxygen demand (COD).

Distillation process and as a result wastewater formation continues until the middle of July. This period usually coincides with the clear, cloudless, sunny days, allowing the use of sunlight as a natural light source for photocatalytic oxidation processes. Because the accumulated wastewaters are exposed to sunlight all the summer.

Figure 1. Discharge of waste rose petals and wastewater to the drainage channel and lagoon (Başbuğ Çancı, 2017).

Advanced Oxidation Processes (AOPs) are widely used to remove recalcitrant, non-biodegradable, toxic and

hazardous organic contaminants from water and wastewater (Deng and Zhao, 2015). Among AOP processes heterogeneous photocatalysis has emerged as a promising efficient, economical and environmentally friendly process for removing organic impurities (Mecha et al., 2016; Szczepanik, 2017). Heterogeneous photocatalysis depends on the use of light source and semiconductor. During process, semiconductor surface is illuminated by the light with specific wavelength and a reaction occurs on activated surface then hydroxyl radicals (°OH) are generated (Borges et al., 2016; Mecha et al., 2016; Szczepanik, 2017). Hydroxyl radicals are highly reactive oxidizing agents with 2.8 V (pH 0) oxidation potential. It is able to react with all types of organic compounds and mineralize them to CO_2 and H_2O or form more biodegradable intermediates (Glaze et al., 1987; Tchobanoglous et al., 2003; Deng and Zhao, 2015; Rubio-Clemente et al., 2014). Titanium dioxide (TiO_2) is extensively used semiconductor photocatalyst owing to its versatility, nontoxicity, inertness to chemical environment, long-term photostability, oxidative power and low cost (Wen et al., 2015; Cai and Feng, 2016; Mecha et al., 2016). In heterogeneous photocatalysis, sunlight or artificial UV lamps can be used as light sources. Sunlight can be more economical irradiation source than artificial UV lamps because it does not require electricity consumption (Ghaly et al., 2011).

There is no sufficient information in the literature regarding the treatment of rose processing wastewater. In recent years, some researchers have carried out studies on polyphenol recovery from wastewater (Rusanov et al., 2014; Slavov et al., 2017a; Slavov et al., 2017b). But, there is only one study on the treatment of rose processing wastewater was carried out by Avşar et al. (2007).

The objective of this study was to investigate the photocatalytic treatment of rose processing wastewater. TiO_2 was used as photocatalyst and sunlight was used as irradiation source. This photocatalytic study on rose distillation wastewater is the first application, a similar study has not been encountered before.

2. Material and Method

Rose processing wastewater was supplied from a rose oil production facility in Isparta, Turkey. To separate waste rose petals, wastewater was filtered by cartridge filters and stored at +4 °C. In light-based oxidation processes, the light transmission of the medium is very important factor affecting the process. Therefore all experiments were carried out with filtered (0.45 µm) and 10 fold diluted wastewater to provide light transmission. The wastewater pH was 4. The initial COD concentration of the wastewater was 1254 mg/L (Başbuğ Çancı, 2017). Distilled water was used for preparing all solutions. The wastewater pH was adjusted with HCl (Sigma Aldrich, 37%) and phosphate buffer. TiO_2 was (21 nm particle diameter (TEM), ≥ 99.5%) purchased from Sigma-Aldrich.

Photocatalytic oxidation experiments were carried out in July under clear sky at 32 °C, between 12: 00-14: 00 at noon when the sunlight came directly to the earth. The luminous flux was measured 2264 µmol / m^2 s (for 400-700 nm range) with the HD 2102.2 radiometer. 500 mL beakers were used as photocatalytic reactor. The beakers were placed on magnetic stirrers (Velp, Daihan MSH-20 A), TiO_2 and wastewater were stirred homogeneously at 120 rpm during the 90 min. reaction time (Fig. 2). 10 ml samples were taken from the beaker at certain reaction times and centrifuged with Hettich ROTOFIX 32 A. COD and color removal were analyzed with Hach-Lange DR5000 spectrophotometer. The experimental conditions were selected as irradiation time (0, 10, 20, 30, 60, 90 minutes), catalyst dose (0.25, 0.5, 1, 2, 3) and pH (3, 4, 6, 9) based on preliminary experiments.

Figure 2. Experimental setup

Color removal % was calculated using Equation 1.

$$\text{Color Removal} = 1 - \left(\frac{A}{Ao}\right) \times 100 \qquad (1)$$

where A_0 is the initial absorbance and A is the absorbance at time t.

COD removal % was determined with Equation 2.

$$\text{COD removal \%} = 1 - \left(\frac{C}{C_0}\right) \times 100 \qquad (2)$$

where C_0 is the initial COD concentration and C is the COD concentration at time t.

The kinetics of heterogeneous photocatalytic reactions are usually defined by the Langmuir Hinshelwood kinetic model (Eq. 3) (Vasanth Kumar et al., 2008)

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1+KC} \qquad (3)$$

where r, C, t symbolizes the reaction rate, concentration and the reaction time, respectively. k_r and K are constants. At low concentration KC is negligible and the rate of reaction follows pseudo first order model (Eq. 4);

$$-ln\left(\frac{C}{Co}\right) = k\,t \qquad (4)$$

where k symbolizes the reaction rate.

3. RESULTS AND DISCUSSION

3.1. Irradiation Time Effect

In the presence of 1g /L TiO_2, the effect of irradiation time on sunlight/TiO_2 process was determined. In the first 30 min of photocatalytic oxidation, color removal rapidly reached 41% (Fig. 3) and COD removal reached 11% (Fig. 4). After 30 minutes, the reaction rate decreased with

increased reaction times. This may have been caused by colored intermediates formed as a result of oxidation. The competition of these colored intermediates with the main molecules reduced the reaction rate. Similar results have been found in previous studies (Ghaly et al., 2011; Borges et al., 2016). Ghaly et al. (2011) concluded that the degradation rate was slow down at the end of the process due to the formation of intermediates during the treatment of paper mill wastewater. Borges et al. (2016) stated that the removal of methylene blue was 95% within 2 hours and longer irradiation times were required when the light intensity was low.

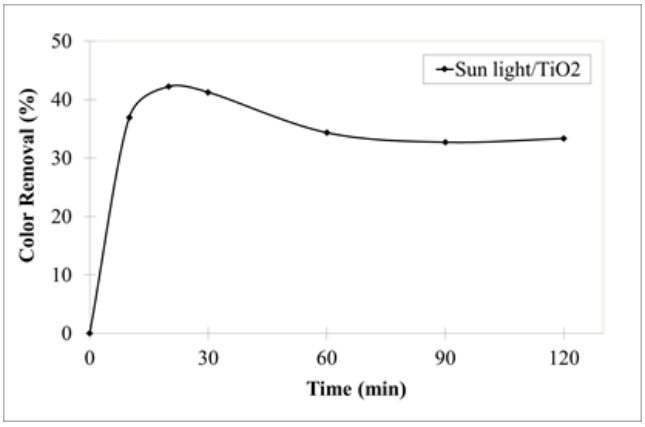

Figure 3. The time effect on color removal

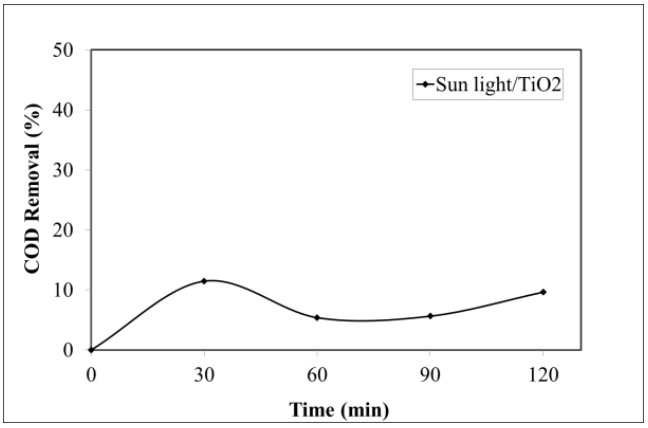

Figure 4. The time effect on COD removal

3.2. Catalyst Loading Effect

The catalyst loading is one of the most important parameters affecting photocatalytic degradation. In order to achieve effective treatment and avoid the use of excess catalyst, the optimum dose must be applied. To determine the effect of photocatalyst dose, experiments were conducted with 5 different doses in the range of 0.25-3 g. As shown in Figure 5, the color removal decreased when the photocatalyst dose was less than 1 g/L. Even if high light transmission is provided to the reactor at low catalyst dose, light was not effective for photocatalytic reactions due to the lack of active sites. The color removal increased when the catalyst dose increased. Because adsorption of photons increased and more active sites occurred. As the catalyst dose increases, the amount of organic molecules adsorbed onto the catalyst surface increases. Thereby the particle density increased in the illuminated area (Autin et al., 2012). However the removal efficiency was decreased with 3 g/L catalyst dose. Also, COD removal increased with catalyst loading in the range of 0.25 - 2 g / L (Fig. 6) but decreased when 3 g/L catalyst dose was used. Excess catalyst dose caused turbidity and reduced the light transmission. If the catalyst dose is too high, it causes turbidity, reduces light transmission, aggregates TiO_2 particles, reduces active surface areas and adversely affects photocatalytic oxidation. In this case, the catalyst surface becomes unavailable for photon adsorption and the reaction rate decreases. Similar results have been obtained in previous studies (Terazian and Serpone, 1995; Stafford et al., 1997; Sun et al., 2008; Ghaly et al., 2011; Ahmed et al., 2011; Mechaa et al., 2016). The optimum catalyst dose was found to be 2 g/L for the photocatalytic treatment of rose processing wastewater with sunlight/ TiO_2 process. In the presence of 2 g/L TiO_2, the highest color removal was found as 51.7 % (Fig 5) and the highest COD removal was 15.7 % (Fig 6).

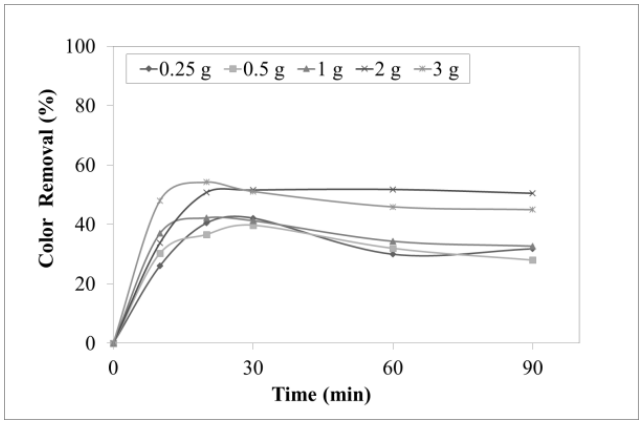

Figure 5. The catalyst loading effect on color removal

Table 1 shows the effect of catalyst dose on first order kinetic rate constant. The value of reaction rate constant increased with increasing catalyst dose. When 2 g/L TiO_2 dose was loaded, the rate constant reached 0.028 min^{-1}.

Table 1. The catalyst loading effect on first order kinetic rate constant

Catalyst dose (g/L)	k' (min^{-1})	R^2
0.25	0.021	0.87
0.5	0.019	0.76
1	0.022	0.56
2	0.028	0.85
3	0.031	0.52

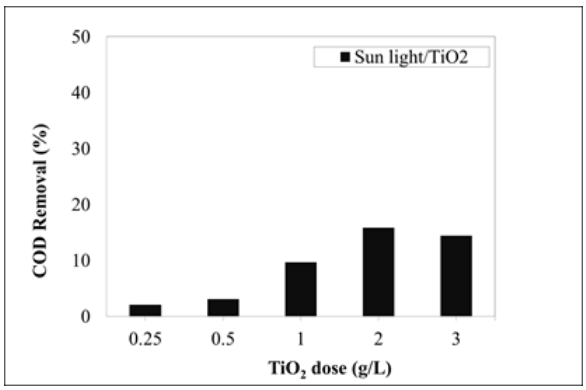

Figure 6. The catalyst loading effect on COD removal

Optimum catalyst loading is related to the type of pollutant, concentration and the operating conditions of the photoreactor (Liu, et al., 2006). Hence the most accurate catalyst dosage varies for various wastewaters and reactor configurations.

3.3. pH Effect

pH value is the main parameter governing the adsorption of the impurities to the catalyst surface in heterogeneous photocatalysis process. Figure 7, shows that the highest color removal was 51% at natural pH (pH 4). Color removal decreased to less than 20% at higher pH. The positive effect of the acidic pH can be explained by the fact that the main constituents (flovanols; OH group containing phenols) of rose treatment wastewater prefer adsorption to the catalyst surface under acidic conditions.

Since the pHpzc (the point of zero charge) of TiO_2 is in the range of pH 5.6-6.4, the changes in the wastewater pH affects the TiO_2 surface properties (Abella´n et al., 2007; Pereira et al., 2011; Speltini et al., 2015). TiO_2 surface is negatively charged at lower pH and hydroxyl ion concentration increases in the medium. In addition to higher OH ion concentration, the electrostatic repulsion between the substrate and negatively charged catalyst surface caused lower adsorption and decreased color removal. The original pH of the wastewater was found to be optimum.

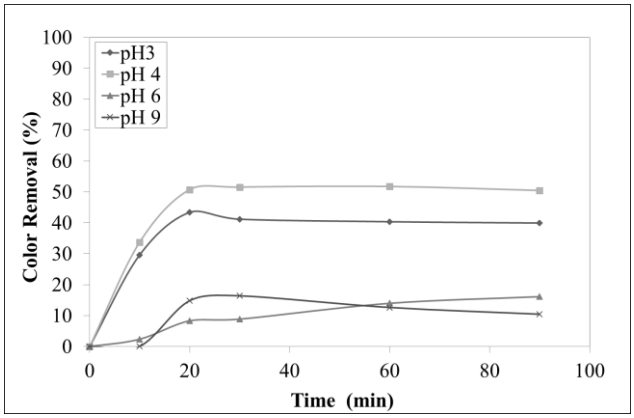

Figure 7. The catalyst loading effect on color removal

The pH effect on first order kinetic rate constant was shown from Table 2.

Table 2. The pH effect on first order kinetic rate constant

pH	k' (min^{-1})	R^2
3	0.022	0.75
4	0.028	0.85
6	0.006	0,82
9	0.003	0.91

Table 2 shows that the original pH value of the wastewater was more favorable for the photocatalytic treatment of rose processing wastewater.

4. CONCLUSIONS

The following results can be drawn from photocatalytic treatment of rose processing wastewater by sunlight / TiO_2 process:

- Sunlight was used as an economical irradiation source for the photocatalytic treatment of this wastewater. Because, rose processing wastewater have been discharged into the lagoons and exposures sunlight all the summer at the sampling facility.
- In the presence of 2 g/L TiO_2, the color removal reached 51.7 % and the COD removal reached 15.7 %.
- The photocatalytic treatment of wastewater was higher at acidic pH values.
- Further research can be done with artificial irradiation sources and different catalysts.

ACKNOWLEDGEMENTS

This research has been financially supported by Scientific Research Project Commission of Süleyman Demirel University, Isparta, Turkey (SDU-BAP Project No: 3673-D1-13). The authors thank the Gülbirlik Company for providing the rose processing wastewater.

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Bilge International Journal of Science and Technology Research

ISSN: 2651-401X
e-ISSN: 2651-4028

2020, Volume: 4, Issue: 1, 7-13
Received: 27.01.2020; Accepted: 12.03.2020
DOI: 10.30516/bilgesci.680487

Predators and Parasitoids of Pine Processionary Moth (*Thaumetopoea wilkinsoni* Tams) in Western Mediterranean Region in Turkey

İsmail Erkaya*[1]

Abstract: The pine processionary moth, *Thaumetopoea wilkinsoni* Tams, 1924 (Lepidoptera: Notodontidae) is the most important defoliator pest of pine forests in the Mediterranean Basin and Turkey. Natural enemies of the pine processionary moth are various species of predators and parasitoids. In this study, field studies were performed in nine study areas which were chosen from four provinces (Isparta, Burdur, Antalya, Muğla) in the Western Mediterranean Region of Turkey to determine the potential predators, larva and egg parasitoids of pine processionary moth. Wintering nests and egg batches of the pine processionary caterpillars were sampled from selected study stations throughout 2018. *Calosoma sycophanta* (L.) and *Forficula smyrnensis* Serville were determined as predator species and *Phryxe caudata* (Róndani), *Trichogramma* sp., *Ooencyrtus pityocampae* (Mercet) and *Anastatus bifasciatus* (Geoffroy) were determined as parasitoids. *Forficula smyrnensis* is recoreded for the first time as a predator of *T. wilkinsoni*. Results may contribute to the literature on ecology, forestry studies and biological control efforts

Keywords: *Forficula smyrnensis*, parasitoid, pine processionary moth, *Thaumetopoea wilkinsoni*, western mediterranean region.

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Citation: Erkaya, İ. (2020). Predators and Parasitoids of Pine Processionary Moth (*Thaumetopoea wilkinsoni* Tams) in Western Mediterranean Region in Turkey. Bilge International Journal of Science and Technology Research, 4 (1): 7-13.

1. INTRODUCTION

Pine Processionary Moth (PPM), *Thaumetopoea wilkinsoni* Tams, (Lepidoptera: Notodontidae) is the most important leaf defoilator pest of Southwest Europe, North Africa and the Near East (Battisti et al., 2000). It is the common pest in the Mediterranean Basin and in southern, western and northern parts of Turkey. Pine processionary larvae feed with pine needles in forest ecosystems, weaken the pines and make them vulnerable to secondary pests. Although PPM causes damage to other pine species, its main host is Turkish red pine (*Pinus brutia* Ten.) and its development on each pine species varies (Hodar et al., 2002). In addition to causing serious economic and ecological losses, the setae of the larvae cause allergic reactions and respiratory disorders such as asthma in humans and mammals (Ziprkowski and Roland, 1966; Lamy, 1990). Two species distributed in Turkey are *Thaumetopoea pityocampa* (Den. & Schiff.) and *T. wilkinsoni* (Barbaro and Battisti, 2011). *Thaumetopoea wilkinsoni* is mostly found in pine forests in the south, west and north of Anatolia, while *T. pityocampa* generally occurs in Thrace and northwestern Anatolia, and there is a potential hybrid zone of these two twin species in this region (İpekdal et al., 2015).

In the studies to determine the parasitoids using PPM as a host, nine species of egg parasitoid, all belonging to Hymenoptera, were identified. The most common two egg parasitoids are generalist *Ooencyrtus pityocampae* (Merc.) (Hymenoptera, Encyrtidae) and host specific *Baryscapus servadeii* (Dom.) (Hym., Eulophidae). *Anastatus bifasciatus* (Fonsc.) (Hym., Eupelmidae), *Trichogramma embryophagum* (Hbg.) (Hym., Trichogrammatidae), *Trichogramma dendrolimi* Matsumura (Hym., Trichogrammatidae), *Baryscapus transversalis* Graham (Hym., Eulophidae), *Pediobius bruchicida* (Rondani) (Hym., Eulophidae), *Eupelmus* (*Macroneura*) *seculata* (Ferrière) (Hym., Eulophidae) and *Eupelmus* (*Macroneura*) *vesicularis* (Retzius) (Hym., Eulophidae) are parasitoid species with a lower frequency (Tsankov, 1990; Tsankov et al., 1999; Öztemiz et al., 2013; Battisti et al., 2015).

The known larva parasitoids are *Phryxe caudata* (Rondani) (Diptera, Tachinidae), *Compsilura concinnata* (Meigen) (Dipt., Tachinidae), *Exorista segregata* (Rondani) (Dipt., Tachinidae), *Erigorgus femorator* Aubert (Hym., Ichneumonidae), *Cotesia vestalis* (Haliday) (Hym., Braconidae), *Pteromalus chrysos* Walker (Hym.,

Chalcididae) and *Dibrachys lignicola* Graham (Hym., Chalcididae) belonging to Hymenoptera and Diptera (Battisti et al., 2015). Pupa parasitoids are determined in the previous studies as *Villa brunnea* Beck. (Dipt., Bombyliidae), *Coelichneumon rudis* (Fonscolombe) (Hym., Ichneumonidae) and *Conomorium pityocampae* Graham (Hym., Pteromalidae) (Battisti et al., 2015).

The known natural predators of the PPM include some birds, amphibians, reptiles, spiders and predator insects. *Upupa epops* and *Clamator glandarius* (Aves), *Bufo viridis* and *Hyla arborea* (Amphibia) *Agamia stellio* (Reptilia), *Thomisus citrinellus (*Arachnida*), Carabus graecus*, *Calosoma sycophanta*, *Chrysoperla carnea*, *Coccinella septempunctata*, *Chilocorus bipustulatus*, *Synbarmonia conglobata*, *Forficula auricularia*, *Formica rufa*, *Monomorium dentiger*, *M. gracillimum*, *Ephippiger ephippiger*, *Dermestes lardarius*, *Sphodromantis viridis*, *Labidura riparia* and Tettigonidae species of Insecta are predators of PPM (Mirchev and Tsankov, 2005). Pathogens include a variety of viruses, bacteria and fungi (Battisti et al., 2015). In the Mediterranean basin, extensive control studies are conducted with vertebrate and invertebrate predators, pathogens such as *Bacillus thuringiensis kurstaki* and pesticides such as insect growth inhibitors in the control against PPM (Barbaro and Battisti, 2011). However, it is stated that these predators and pathogens do not have a significant effect on population control except epidemic periods (Way et al., 1999). Pesticides have various damages in biological control. Pesticides can also have adverse effects on non-target organisms, target natural predators of the pest and cause phytophagous insect to develop resistance (Jansen and Sabelis, 1995). For these reasons, parasitoid species should be preferred in biological control. Parasitoids do not have the disadvantages of pesticides and have an important role in controlling harmful herbivore insect populations (Lewis et al., 1997; Stiling and Cornelissen 2005). In fact, it was determined that egg parasitoids increase PPM mortality by 72% (Mirchev et al., 2004).

In this study, it is aimed to determine the potential parasitoids and predators of *T. wilkinsoni* that uses Turkish red pines as hosts in the western Mediterranean region of Turkey.

2. MATERIALS AND METHODS

Nine study stations selected from the Western Mediterranean region were visited during 2018 in order to collect samples from PPM (*Thaumetopoea wilkinsoni* Tams), taking into account the density of red pine (*Pinus brutia* Ten.). The stations were selected from three different elevation intervals (0-100 m, 400-650 m and 900-1100 m) within four different provinces (Isparta, Burdur, Antalya, and Mugla). Map of nine selcted study stations are shown in Figure 1.

Figure 1. Satellite image of study stations.

Sampling date, localities, coordinates, altitude and area characteristics of nine study stations are shown in Table 1.

Table 1. Localities and area characteristics of study stations.

St.No	Sampling Date	Location	Coordinates and Altitude	Area Characteristics
1	18.02.2018	Isparta-Antalya highway 30th km	37°37'29" N 30°43'58" E 600-630 m	Near highway, pine forest
2	18.02.2018	Isparta-Antalya highway 80th km	37°13’53’’ N 30°48’7’’ E 90-100 m	Near highway, pine forest
3	10.03.2018	Burdur-Fethiye highway	36°45’36’’ N 29°27’31’’ E 980 m	Short pines on highway edge, clear area
4	10.03.2018	Fethiye, Gemiler	36°33’49’’ N 29°3’6’’ E 0-70 m	Sloping terrain, dense pine forest
5	23.03.2018	Burdur, Ağlasun	37°38’35’’ N 30°42’7’’ E 1020 m	Near highway, sloping area
6	23.03.2018	Budur, Ağlasun	37°33’12’’ N 30°31’8’’ E 940 m	Near highway, short pines
7	13.02.2018	Isparta, Sütçüler	37°32’14’’ N 30°56’44’’ E 1080 m	Sloping area, near marble quarry
8	02.03.2018	Antalya-Kemer highway	36°43’42’’ N 30°33’23’’ E 10 m	Near highway and urban area, sparse pine forest
9	02.03.2018	Beycik Village, Kemer	36°29’32’’ K 30°26’11’’ D 440-600 m	Pine forest on a slope

Samplings were carried out at nine selected stations in the Western Mediterranean region during 2018. In February and March, nests containing last instar larvae of PPM were collected. Pupae were sampled in May and June. Eggs were collected in August and September.

At each station, one nest from each 15 pine trees infested with PPM was collected with the help of high branch pruning shears and taken to three-liter pet bins. The 30x30 cm cut tulles were stretched to the openings of the bins by using rubber for the insects can continue to breathe. The pupae were searched by digging pits at a depth of 20 cm at the bottom of the infested trees. The pupae were taken together with the soil in which they were placed and put in 1 L canisters. Eggs in cylindrical clusters on the young pine needles were plucked together with the leaves and kept in 1 L bins with tulle on their openings. Samples were brought to Süleyman Demirel University, Faculty of Arts and Sciences, Entomology Laboratory within the same day.

The larvae and nests of PPM larvae were kept in bins in the climate chamber at 25 °C and 55% humidity. In order to observe parasitoid emergence, larvae were conserved under suitable conditions. Therefore, in addition to establishing favorable conditions, the larvae were regularly fed with *Pinus brutia* needles. The collected pupae and egg clusters were also stored under the same conditions.

A predator coleopteran and a dermapteran species, which were observed to be fed by larvae in nests, prepared for identification. In addition, larva parasitoids (Diptera:Tachinidae) were sampled from the nests that brought to the laboratory and hymenopteran parasitoids were obtained from egg containers and kept for identification. Samples were sent to experts for identification. Also Chopard (1922), Jeannel (1941), Askew and Aldrey (2004) and Samra et al. (2018) were used as diagnostic keys.

3. RESULTS

During 2018, 24,660 larvae from 135 nests of *Thaumetopoea wilkinsoni*, 40 pupae and 58 egg clusters were sampled from nine stations. Some of the pupae mature under laboratory conditions. As a result, six species were determined as the natural enemies of *Thaumetopoea wilkinsoni*. One of them is *Calosoma sycophanta* (L., 1758), a natural predator of the PPM. Another potential

predator species is *Forficula smyrnensis* Serville, 1839. *Phryxe caudata* (Róndani, 1859) is a larval parasitoid. *Trichogramma* Westwood, 1833 sp., *Ooencyrtus pityocampae* (Mercet, 1921) and *Anastatus bifasciatus* (Geoffroy, 1785) are egg parasitoids. No pupae parasitoid emergence was observed from 40 pupae collected.

***Calosoma sycophanta* (L., 1758) (Coleoptera: Carabidae)**

Preys: *Lymantria dispar* L., *L. monacha* L., *Dendrolimus pini* L., *Thaumetopoea processionea* L., *T. pityocampa* (Denis ve Schiffermüller, 1775), *T. wilkinsoni* Tams, 1924, *T. solitaria* (Freyer, 1838), *Euproctis chrysorrhoea* L., *Dasychira pudibunda* L., *Hyphantria cunea* (Drury, 1773), *Tortrix viridana* L. (Weseloh, 1985; Mirchev and Tsankov, 2005; Kanat and Mol, 2008; Goertz and Hoch, 2013).

Geographical distribution: European countries, Western Palaearctic, Nearctic, Near East, Mid-Asia, Northern Africa (Kanat and Özbolat 2006; Stolbov et al., 2018).

***Forficula smyrnensis* Serville, 1839 (Dermaptera: Forficulidae)**

Preys: According to some researchers, it is thought to be herbivorous, but other authors believe that it is omnivorous (plant material, aphids, spiders, insect eggs, dead insects) species like *Forficula auricularia* L. (Haas and Henderickx, 2002; Tezcan and Kocarek, 2009).

Geographical distribution: Turkey (terra typica), Albania, Bulgaria, Greece, Iran, Israel, Lebanon, Syria, former Yugoslavia (Albouy and Caussanel, 1990; Haas and Henderickx, 2002).

***Phryxe caudata* (Róndani, 1859) (Diptera: Tachinidae)**

Hosts: *Thaumetopoea pityocampa* (Denis and Schiffermüller, 1775), *Traumatocampa ispartaensis* (Doğanlar and Avcı, 2001) (Pekel, 1999; Avcı and Kara, 2002; Mirchev and Tsankov, 2005).

Geographical distribution: Mediterranean countries, Southern Europe and Northern Africa (Lutovinovas et al., 2018).

***Trichogramma* sp. Westwood, 1833 (Hymenoptera: Trichogrammatidae)**

Hosts: *Cydia pomonella* L., *Cydia molesta* (Busck, 1916), *Hedya nubiferana* (Haw. 1811), *Spilonota ocellana* (Denis and Schiffermüller, 1775), *Thaumetopoea pityocampa* (Denis and Schiffermüller, 1775), *T. processionea* L., *Archips* Hubner, 1822 spp. (Mirchev and Tsankov, 2005; Öztemiz and., 2013).

Geographical distribution: Cosmopolitan (Buchori vd., 2010).

***Ooencyrtus pityocampae* (Mercet, 1921) (Hymenoptera: Encyrtidae)**

Hosts: *Stenozygum coloratum* (Klug, 1845), *Thaumetopoea pityocampa* (Denis and Schiffermüller, 1775), *T. wilkinsoni* Tams, 1924, *T. bonjeani* (Powell, 1922) (Mirchev and Tsankov, 2005; Samra et al., 2018).

Geographical distribution: Eastern Mediterranean, Middle East ve Eastern Africa (Samra et al., 2018).

***Anastatus bifasciatus* (Geoffroy, 1785) (Hymenoptera: Eupelmidae)**

Hosts: *Thaumetopoea pityocampa* (Denis and Schiffermüller, 1775), *T. wilkinsoni* Tams, 1924, *T. processionea* L., *Lymantria dispar* L. (Mirchev and Tsankov, 2005; Avcı, 2009).

Geographical distribution: Europe, Asia and Africa (Narendran, 2009).

Table 2 shows the number of sampled parasitoid and predator species in the studty stations.

Table 2. Sampled natural enemies in nine study stations.

Station	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Ooencyrtus pityocampae	-	-	24	4	12	18	-	30	-
Anastatus bifascatus	-	-	8	1	-	-	-	-	-
Trichogramma sp.	-	-	108	1	-	-	-	-	-
Phryxe caudata	21	32	60	54	47	49	-	32	22
Calosoma sycophanta	2	2	3	1	-	-	-	-	-
Forficula smyrnensis	-	-	-	-	-	-	-	2	-

The 3rd station was determined to have the highest parasitoid density, while station 7 was the only area without natural enemies. This may be caused by antropogenic activities (marble mine) nearby. Nearly all *Trichogramma* individuals were sampled from 3rd station. *Forficula smyrnenis* was sampled only from 8th station. Percentages of individuals belonging to parasitoid and predator species were given in Figure 2.

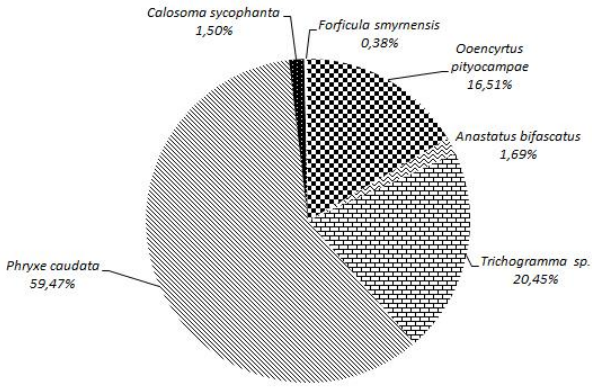

Figure 2. Percentages of individuals belonging to six natural enemy species.

The most frequent parasitoid species was *Phryxe caudata* (59.47%) and was emerged from the eggs in all study stations except Number 7.

4. DISCUSSION AND CONCLUSİONS

The PPM has a wide range of natural enemies in terms of predators and parasitoids. Six of them were sampled in this study. Mirchev and Tsankov (2005) published a checklist and according to this checklist natural enemies that recorded from Turkey are *Ooencyrtus pityocampae*, *Baryscapus (Eutetrastichus) servadeii*, *B. (E.) transversalis*, *Anastatus bifasciatus* and *Trichogramma* sp. In addition, tachinid parasitoids *Exorista segregata* and *Phryxe caudata* were found in Turkey by Pekel (1999) and Avcı and Kara (2002). *Ooencyrtus pityocampae* is recorded by Mirschev et al. (2004) in southwestern Anatolia. Kanat and Mol (2008) stated that *Calosoma sycophanta* is used as an effective predator in the biological control of PPM in our country. In addition, Özçankaya and Can (2004) reported *Forficula* species in the PPM nests.

Calosoma sycophanta, which is frequently used in the biological control of this pest in Turkey (Kanat and Özbolat, 2006; Stolbov et al., 2018), is the first predator species obtained from field studies. Eight individuals from four areas were found. According to Mirchev and Tsankov (2005), this species is the larvae predator of the PPM. However, it is known to feed on pupa (Kanat and Özbolat 2006; Toprak, 2014). *C. sycophanta* larvae fed by another harmful lepidopteran *Lymantria dispar* L. pupa has been demonstrated by Weseloh (1985).

Another predator species found in this study is *Forficula smyrnensis*, sampled in Kemer, Antalya with two individuals. Özçankaya and Can (2004), found *Forficula* sp. individuals on the PPM nests. They reported that they did not observe the feeding event, so they could not comment on whether they were predators or not. But it was known that these insects were omnivorous and therefore fed with soft bodied insects. On the other hand, it was reported by Kailidis (1962) in Greece that *Forficula auricularia* was a PPM predator and listed as a predator on the check-list of Mirchev and Tsankov (2005). Haas and Hendrickx (2002), in their study of the intestinal contents of the collected dermapterans, found some plant materials in the gut of *F. smyrnensis*, so they speculate that the species may be herbivore contrary to its close relatives. However, Tezcan and Kocarek (2009) emphasized that such an interpretation cannot be made from the intestinal contents of a single individual and *F. smyrnensis* is most likely omnivorous like *F. auricularia*. For this reason, *F. smyrnensis*, sampled in a larval nest in Kemer during field surveys, could potentially be a PPM predator and it is recorded for the first time.

Phryxe caudata, which is one of the most common tachinid species in Turkey (Lutovinovas et al., 2018) is sampled from all study sites except 7th station. Adults began to be observed in containers in which the nests were kept in the laboratory in June. Avcı and Kara (2002) also stated that adults emerged in the second half of June. In terms of the number of individuals, this species was the most sampled with 317 individuals.

Trichogramma species are egg parasitoids of PPM (Mirchev and Tsankov, 2005) and in this study 109 individuals were collected. The members of this Hymenopteran genus cause taxonomic difficulties due to their small size and are difficult to identify (Nagarkatti and Nagaraja, 1977). Thus, Trichogramma specimens sampled in this study could not be identified to species level. But only two species ocur in Turkey, *T. embryophagum* and *T. dendrolimi* are parasitoids of PPM (Öztemiz et al., 2013), so the sampled specimens are likely to belong to one of these two species.

Ooencyrtus pityocampae is another hymenopteran egg parasitoid sampled in this study. Samra et al. (2018) determined that three species of *Ooencyrtus* (*O. zoeae*, *O. telenomicida* and *O. pityocampae*) are distributed in Turkey. They emphasized that *O. pityocampae* is a generalist parasitoid, using both Hemiptera and Lepidoptera members as hosts, and also one of the best known natural enemies of *T. pityocampa* and *T. wilkinsoni* in the Mediterranean Basin. In this study, 88 individuals of this species were collected.

Finally, hymenopteran egg parasitoid *Anastatus bifasciatus* was represented in this study with 9 individuals. *Anastatus bifasciatus* is listed on the chcklist of Mirchev and Tsankov (2005) and previously sampled in Turkey by Pekel (1990).

Results of this study may contribute to the literature on pest ecology, forestry and biological control efforts.

ACKNOWLEDGEMENTS

We thank to Assoc. Prof. Dr. Turgut ATAY from Tokat Gaziosmanpasa University, Faculty of Agriculture, Plant Protection Departmant for tachinid identification; Dr. Viktor FURSOV from Ukraine National Sciences Academy, Institute of Zoology for hymenopteran parasitoid identifications and Dr. Petr KOCAREK from Ostrava University, Department of Biology and Ecology for dermapteran identification.

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Bilge International Journal of Science and Technology Research

ISSN: 2651-401X
e-ISSN: 2651-4028

2020, Volume: 4, Issue: 1, 14-20
Received: 19.12.2019; Accepted: 09.03.2020
DOI: 10.30516/bilgesci.659928

Isıl İşlem Görmüş Kızılçam (*Pinus brutia* Ten.) Yongalarından Üretilen Levhaların Bazı Özellikleri

Samim Yaşar [1*], Aytaç Uz[1], Abdullah Beram[1]

Özet: Bu çalışmada, 120, 160 ve 180 ºC'lerde ısıl işlem görmüş kızılçam (*Pinus brutia* Ten.) yongalarının FTIR spekroskopik ve termal özellikleri araştırılmış, devamında yongalardan elde edilen levhaların fiziksel, mekanik ve yüzey özellikleri değerlendirilmiştir. FTIR sonuçları, numunelerin kristallik indeksinde ısıl işlemden kaynaklı önemli bir değişmenin gerçekleşmediğini göstermiştir. TGA ve DTG eğrilerindeki esas bozunma aşamasında ısıl işlem görmüş yongalarda kontrol yongalarına göre daha az madde kaybı meydana geldiği görülmüştür. Bununla birlikte, TGA ve DTG sonuçlarına göre ısıl işlem sıcaklık derecesinin artışıyla yongalarda önemli düzeyde holoselüloz kaybı gerçekleştiği saptanmıştır. Yongalara uygulanan ısıl işlem sıcaklık derecesinin artışına bağlı olarak üretilen levhaların yüzey pürüzlülük değerlerinde sürekli bir düşüş gözlenmiştir. Elde edilen sonuçlarda, ısıl işlem görmüş yongalardan üretilen levhaların fiziksel özelliklerinde genel anlamda gelişme sağlanırken, mekanik özelliklerinde zayıflama kaydedilmiştir. Bu nedenle, ısıl işlem görmüş yongalardan üretilen levhaların dekorasyon amaçlı ve nemli ortamlarda, yani malzemede fiziksel özellik beklenen ve kısmen yanmaya dayanıklı yapılarda kullanılmasının önerilebileceği görülmüştür.

Anahtar kelimeler: Isıl işlem, yongalevha, FTIR, TGA, fiziksel ve mekanik özellikler, yüzey pürüzlülüğü.

Some Properties of Boards Produced from Heat-Treated Brutian Pine (*Pinus brutia* Ten.) Particles

Abstract: In this study, FTIR spectroscopic and thermal properties of brutian pine (*Pinus brutia* Ten.) particles heat-treated at 120, 160 and 180 ºC were investigated and the physical, mechanical and surface roughness properties of the boards obtained from the particles were evaluated. FTIR results showed that no significant change in the crystallinity index of the samples caused by heat treatment were determined. In the main decomposition phase of the TGA and DTG curves, less material loss occurred in the heat-treated particles compared to the control particles. However, according to TGA and DTG results, it was found that there was a significant loss of holocellulose in the particles with increasing heat treatment temperature. A continuous decrease in the surface roughness values of the boards produced was observed due to the increase of the heat treatment temperature applied to the particles. The results showed that the physical properties of the boards produced were improved and the mechanical properties were weakened by heat treatment. For this reason, it can be suggested that the boards produced from heat-treated particles can be used in decoration structures and in humid environments, that is, physical properties expected in the material and partially resistant to fire.

Keywords: Heat treatment, particleboard, FTIR, TGA, physical and mechanical properties, surface roughness.

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Citation: Yaşar, S., Uz, A., Beram, A. (2020). Isıl İşlem Görmüş Kızılçam (*Pinus brutia* Ten.) Yongalarından Üretilen Levhaların Bazı Özellikleri. Bilge International Journal of Science and Technology Research, 4 (1): 14-20.

1. GİRİŞ

İlk çağlardan bu yana gerçekleşen endüstriyel ilerlemeler, kullanımı ve şekil verilmesi basit olan odunu en ilkel kullanım sürecinden, ileri teknolojik seviyelere getirmiştir. Ahşap ürünler günümüze kadar yoğun bir şekilde insanlık tarafından kullanılmış ve halen de gözde ürünler olarak hayatımızda yer almaktadırlar (Yalınkılıç, 1993; Hafızoğlu vd., 1994; Rowell, 1996).

Masif odunun yanı sıra, yongalevha ve liflevha gibi kompozit malzemeler üzerine gerçekleştirilen çalışılmalar ile elde edilen gelişmeler söz konusu ürünlerin günümüzde vazgeçilmez hale gelmesini sağlamıştır; özellikle mobilya sektöründe kullanılan yongalevhanın pazarda önemli bir yere sahip olduğu bilinmektedir (Bozkurt vd., 1993; Baharoğlu, 2010).

Ahşap malzemenin olumlu özelliklerinin daha ileri derecelere ulaştırılmasına yönelik çeşitli çalışmalar yapılmıştır. Bu çalışmalar "odun modifikasyon yöntemleri" olarak adlandırılmaktadır. Söz konusu yöntemlerden birisi de termal bir modifikasyon yöntemi olarak bilinen ısıl işlem tekniğidir. Isıl işlemin en önemli avantajları, proses sırasında herhangi bir kimyasal madde kullanılmaması ve buna bağlı olarak çevreye herhangi bir zararın verilmemesidir (Mayes ve Oksanen, 2002; Hill, 2006; Korkut vd., 2008).

Isıl işlem sırasında, ahşap materyalin kimyasal bileşenlerinin yüksek sıcaklıklarda bozunmasıyla elde edilen ürünlerin boyutsal kararlılığında iyileşme sağlanabilmektedir. Ahşap materyalin kimyasal bileşiminde meydana gelen söz konusu değişimler aynı zamanda ürünün renk, fiziksel ve mekanik özellikleri yanı sıra yüzey özelliklerine de önemli ölçüde etkilerde bulunabilmektedir (Bourgois vd., 1989; Obataya vd., 2000: Ünsal ve Ayrılmış, 2005; Gündüz vd., 2007, 2008; Özcan vd., 2012; Özdemir, 2016; Altun ve Esmer, 2017).

Çalışmamızda, kızılçam (Pinus brutia Ten.) odunundan elde edilen yongalara laboratuvar ortamında 120, 160 ve 180 ^{o}C'de ısıl işlem uygulanmıştır. Uygulama sonrası, tüm işlem gruplarına ait yongalardaki kimyasal ve termal özellik değişimleri kontrol grubuna göre ortaya konmuş ve ısıl işlemin üretilen levhaların fiziksel, mekanik ve yüzey özelliklerine etkileri değerlendirilmiştir.

2. MATERYAL VE YÖNTEM

2.1. Materyal

Çalışmada kullanılan kızılçam odunu yongaları, tutkal (üre formaldehit) ve sertleştirici (amonyum klorür) ORMA A.Ş./Isparta firmasından alınmıştır. Kullanılan üre formaldehit tutkalında, katı madde oranı % 65 ± 1, yoğunluk 1.27-1.29 g/cm^3, pH 25 oC'de 7.5-8.5, vizkozite 25 ^{o}C'de 150-200 cps, jelleşme süresi 25 ^{o}C'de 25-30 s, kullanım süresi 25 ^{o}C'de 60 gün, akışkanlık süresi 25 ^{o}C'de 20-30 s ve serbest CH_2O en fazla % 0.19 şeklindedir.

2.2. Yöntem

Isıl İşlem

Kızılçam yongaları laboratuvar ortamında etüvde 120 °C, 160 °C ve 180 °C'de 2 saat süreyle ayrı gruplar halinde ısıl işleme tabi tutulmuştur.

Fourier dönüşümlü kızılötesi (FTIR) spektroskopisi analizi

Öncelikle 40-100 mesh aralığında öğütülmüş yongalar, moulinex değirmeninde homojen odun unu haline getirildikten sonra fourier dönüşümlü kızılötesi (FTIR) spektroskopisi analizinde kullanılmıştır. Her bir örneğin 1:100 (w/w) oranında KBr ile preslenmesiyle üretilen peletlerin spekrumları oda sıcaklığında gerçekleştirilen FTIR analizi sonucunda kaydedilmiştir. Analizlerde kullanılan cihaz Perkin Elmer BX FTIR spektrometredir.

TG/DTA (Termogravimetrik/diferansiyel termogravimetrik analiz)

Odun unu haline getirilmiş kontrol ve ısıl işlem görmüş yonga örneklerinin TGA analizleri, dakikada 10 ºC ısıtma hızında 25 ile 900 ºC aralığında azot ortamında yapılmıştır. Kullanılan termograf Perkin Elmer SII Diamond termal analiz cihazıdır.

Yongalevha üretimi

Kızılçamın, %3 rutubet derecesine getirilmiş kontrol ve ısıl işlem görmüş yongalarından üretilen levhaların deneysel tasarımı Çizelge 1'de gösterilmiştir. Yongalar, ayrı gruplar halinde levhaların hedef yoğunluğu 0.65 g/cm^3 olacak şekilde tartılmıştır. Kontrol ve ısıl işlem görmüş yongalardan üretilecek levhalar için yongalara tam kuru ağırlıklarının %10'u oranında üre formaldehit tutkalı ve %1'i oranında sertleştirici (%35 NH_4Cl) ilave edilmiş ve karıştırılmıştır. Tutkallanan yongalar 31 x 35 x 1.2 cm ebatlarındaki metal bir çerçeve içerisine ahşap perdeleme yardımı ile serilmiştir. Metal çerçeve içerisindeki, hazırlanmış levha taslağı daha sonra 150 ±5ºC'deki sıcak preste 2.5-3 N/mm^2 basınç altında 5 dakika boyunca bekletilmiştir. Üretilen yongalevhaların kondisyonlanması 20ºC sıcaklık ve %65 rutubet derecesinde 30 gün süreyle klima odası ortamında yapılmıştır. Kontrol ve ısıl işlem görmüş yongalardan üretilen levhaların eğilmede elastikiyet modülü (EM) ve eğilme direnci (ED) TS EN 310 (1999),

yüzeye dik çekme direnci (YDÇD) TS EN 319 (1999), su alma (SA) ve kalınlığına şişme (KŞ) değerleri TS EN 317 (1999)'de belirtilen şekilde yapılmıştır.

Çizelge 1. Yongalevhaların deneysel tasarımı

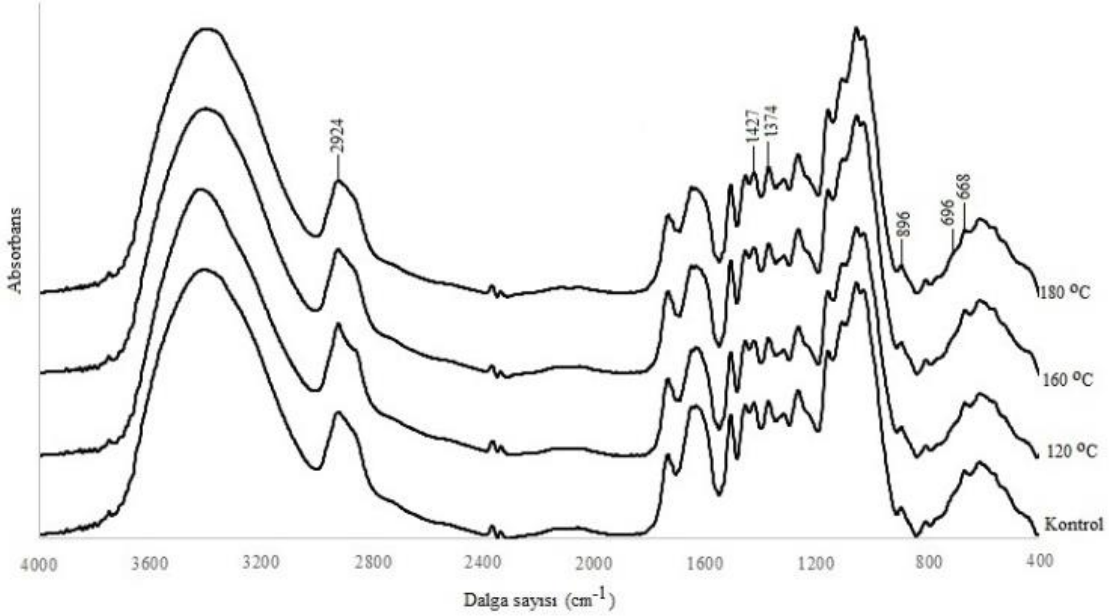
Levha tipi	Kullanılan kızılçam yongaları
A	İşlem görmemiş (kontrol)
B	120 ºC'de ısıl işlem görmüş
C	160 ºC'de ısıl işlem görmüş
D	180 ºC'de ısıl işlem görmüş

Yüzey pürüzlülüğü ölçümleri

Kontrol ve ısıl işlem görmüş kızılçam yongalarından üretilen levhaların yüzey pürüzlülüğü ölçümleri DIN 4768 (1990) standardına uygun olarak gerçekleştirilmiştir. Levhalardan 100x40 mm ebatlarında elde edilen örneklerde, iğne taramalı pürüzlülük aleti (Mitutuyo SJ 201) ile yüzey pürüzlülük ölçümleri yapılmıştır. Yüzey pürüzlülük aletinin iğne uç yarıçapı 0.5 mm^2, iğne uç açısı 90 derece, dalga boyu (λ) 2.5 mm ve ölçme hızı 0.5 mm/sn olarak programlanmıştır.

3. BULGULAR VE TARTIŞMA

Kontrol ve ısıl işlem görmüş kızılçam yongalarının FTIR spektrumları 4000 ile 400 cm^{-1} dalga sayıları arasında kaydedilmiştir (Şekil 1). 1430 ve 897 cm^{-1} civarındaki bandlar CH_2 bükülmesi ve anomerik CH_2 deformasyonunu temsil etmektedir (Kataoka ve Kondo, 1998). Spektrumlardaki A_{1430}/A_{897} ve A_{1370}/A_{2900} oranları selülozun kristallik indeksinin hesaplanmasında kullanılmıştır (Hassan vd., 2000). A_{1370}/A_{670} ve A_{1370}/A_{690} oranları selüloz 1'in selüloz 2'ye dönüşümünün göstergesi olarak kullanılabilmektedir (Hassan vd., 2000; Akerholm vd., 2004). 1370 cm^{-1} civarındaki band absorbans değeri 1370, 1335 ve 1315 cm^{-1} civarındaki CH bükülmesinin birleşimini, 670 cm^{-1} civarindaki band ise düzlem dışı C-OH bükülmesini ilgilendirmektedir (Evans vd., 1995).



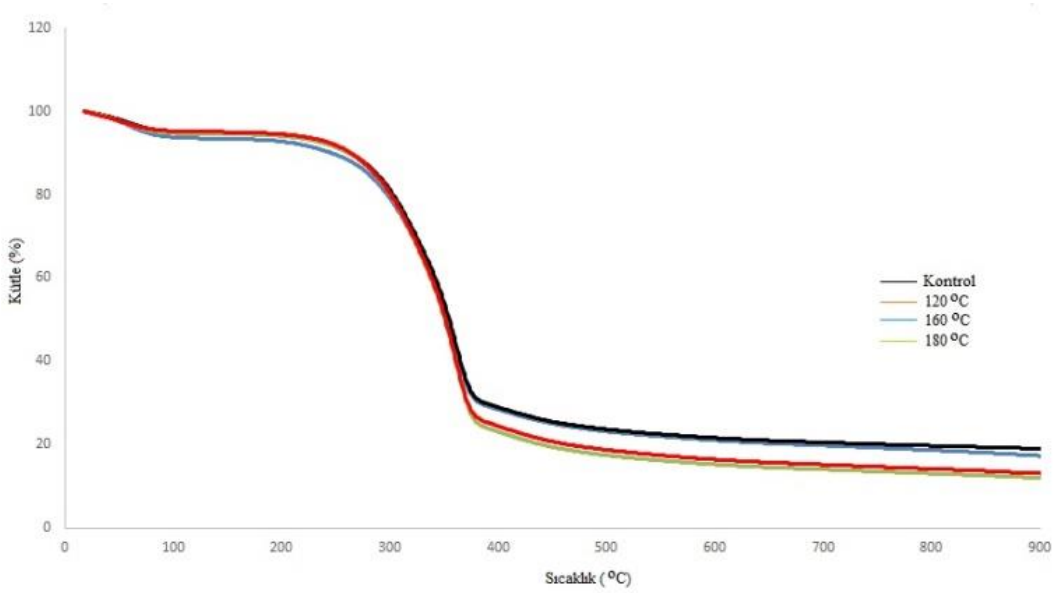
Şekil 1. Kontrol ve ısıl işlem görmüş kızılçam yongalarının FTIR spektrumları

Odunun ana kimyasal bileşenlerinden selüloz önemli düzeyde kristal yapı sergilerken, lignin ve hemiselülozlar amorf yapıya sahiptirler (Fengel ve Wegener, 1984). Ahşap malzemenin ısıl işleme tabi tutulması hücre çeperi bileşenlerinin modifiye olmasını sağlamaktadır. Isıl işlemden sırasıyla en fazla düzeyde hemiselülozlar, selüloz ve lignin etkilenmektedir. Isıl işlem sonucu materyalde holoselüloz oranında azalış görülürken, lignin oranında artış görülmektedir. Ayrıca, ısıl işlemin selülozun kristalit yapısını değiştirmediği ve selülozun relatif kristallik indeksinde herhangi bir etkiye sahip olmadığı çeşitli çalışmalarda belirtilmiştir (Yıldız ve Gümüşkaya, 2007; Ateş vd., 2009, 2010). Bu çalışmada, FTIR spektroskopik metot (Ateş vd., 2009, 2010) örneklerdeki kristallik indeksinin hesaplanmasında kullanılmıştır (Çizelge 2). Elde edilen sonuçlar, farklı sıcaklıklardaki ısıl işlem uygulamalarının kızılçam yongalarının selüloz kristallik indeksinde belirgin bir etkiye sahip olmadığını göstermiştir. Bu durum literatürle (Yıldız ve Gümüşkaya, 2007; Ateş vd., 2009, 2010) uyumluluk göstermektedir.

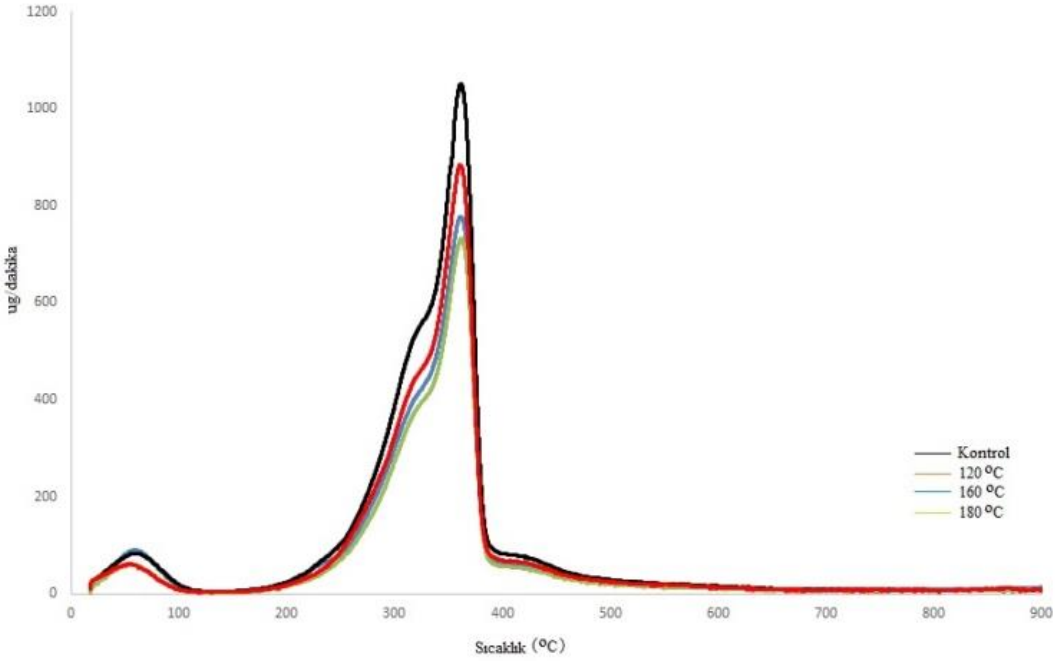
Çizelge 2. Kontrol ve ısıl işlem görmüş kızılçam yongalarının kristallik indeksi

Kristallik indeksi	Kontrol	120 ºC	160 ºC	180 ºC
$A_{1427/A896}$	3.85	3.91	3.93	3.95
$A_{1374/A2924}$	1.09	0.95	1.48	1.95
$A_{1374/A668}$	2.00	2.18	2.21	2.25
$A_{1374/A696}$	3.21	3.21	3.24	3.27

Kontrol ve ısıl işlem görmüş kızılçam yongalarının TGA ve DTG (diferansiyel termogravimetrik analiz) termogramları Şekil 2 ve 3'te gösterilmiştir.



Şekil 2. Kontrol ve ısıl işlem görmüş kızılçam yongalarının TGA termogramları



Şekil 3. Kontrol ve ısıl işlem görmüş kızılçam yongalarının DTG termogramları

Kontrol ve ısıl işlem görmüş kızılçam yongalarında esas bozunma 142 ºC'den itibaren gerçekleşmektedir. Bu sıcaklığa kadar suyun ve bir kısım ekstraktiflerin (Thurner ve Mann, 1981) numunelerden uzaklaştığı anlaşılmaktadır. Kontrol ve ısıl işlem görmüş kızılçam yongalarında esas bozunma 665 ºC'ye kadar devam etmiştir. Esas bozunma esnasında bitkisel biyoküylelerde hemiselülozlar, ekstraktiflerin kalanı, selüloz ve lignin (Thurner ve Mann, 1981; Meszaros vd., 2007) bozunmaya uğramaktadır. Özellikle DTG sonuçlarında, kontrol numunesine kıyasla ısıl işlem görmüş numuneler için ısıl işlem uygulamasının sıcaklığının artırılmasına bağlı olarak, esas bozunma bölgesinde 210 ºC'den itibaren kütle kaybının giderek azaldığı görülmüştür. Bu durum ısıl işlemin özellikle numunelerde hemiselüloz daha ilerisinde selülozda kayba neden olduğunu ortaya koymaktadır. Ayrıca, ısıl işlem görmüş numunelerin daha yüksek termal stabiliteye sahip olduklarını göstermektedir. TGA ve DTG sonuçlarının literatürle (Kandem, 2002; Hill, 2006; Martinka vd., 2014; Zang vd., 2019; Bürüç vd., 2019) aynı doğrultuda olduğu görülmektedir.

Kontrol ve ısıl işlem görmüş kızılçam yongalarından üretilen levhaların fiziksel özellikleri Çizelge 3'te verilmiştir. Yongalara uygulanan ısıl işlemin sıcaklık derecesi artırıldıkça üretilen levhaların SA ve KŞ değerlerinin kontrol grubuna kıyasla sürekli düştüğü kaydedilmiştir.

Çizelge 3. Kontrol ve ısıl işlem görmüş kızılçam yongalarından üretilen levhaların fiziksel özellikleri

Levha Tipi	SA-2 saat	SA-24 saat	KŞ-2 saat	KŞ-24 saat
A	113.51 (3.10)[1] a[2]	119.90 (4.04) a	56.28 (1.73) a	63.08 (1.10) a
B	98.40 (2.06) b	110.23 (3.45) b	46.58 (1.32) b	54.77 (1.03) b
C	92.70 (1.25) c	105.01 (2.05) c	40.37 (1.84) c	46.37 (1.43) c
D	87.71 (1.26) d	101.23 (0.45) d	38.56 (0.93) c	44.47 (1.29) c

1: Standart sapma, 2: Duncan testine göre her sütundaki homojen gruplar. SA-2, 24 ve KŞ-2, 24 saat için $p<0.001$ şeklindedir.

Odundaki, holoselülozu oluşturan selüloz ve hemiselülozlar molekül yapılarında yüksek miktarda -OH grubu içermelerinden kaynaklı olarak hidrofilik bir özellik ortaya koymaktadırlar (Fengel ve Wegener, 1984). Özellikle materyaldeki ısıl işlemden kaynaklanan holoselüloz kaybının (Ateş vd. 2009; 2010) serbest -OH gruplarının miktarını azaltması nedeniyle su alma ve kalınlığına şişme değerlerinde azalmaya sebep olduğu anlaşılmaktadır.

Kontrol ve ısıl işlem görmüş kızılçam yongalarından üretilen levhaların mekanik özellikleri Çizelge 4'de sunulmuştur. Yongalara uygulanan ısıl işlemin sıcaklık derecesi artırıldıkça üretilen levhaların ED, EM ve YDÇD değerlerinin kontrol grubuna göre sürekli azaldığı görülmüştür.

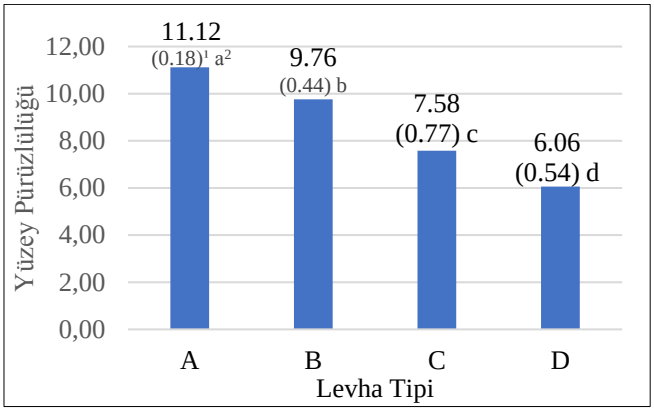
Çizelge 4. Kontrol ve ısıl işlem görmüş kızılçam yongalarından üretilen levhaların mekanik özellikleri

Levha Tipi	ED (N/mm^2)	EM (N/mm^2)	YDÇD (N/mm^2)
A	8.05(0.61)[1] a[2]	1664(121) a	0.26(0.01) a
B	6.43(0.78) b	1331(91) b	0.23(0.01) b
C	4.39(0.68) c	1227(82) c	0.22(0.01) c
D	4.06(0.69) c	1080(64) d	0.10(0.02) d

1: Standart sapma, 2: Duncan testine göre her sütundaki homojen gruplar. ED ve EM ve YDÇD için p<0.001 şeklindedir.

Özellikle, holoselüloz (selüloz ve hemiselüloz) ve lignin odundaki polar -OH gruplarının kaynağını oluşturmaktadır. Polar -OH grupları, polar yapıştırıcı polimerlerle hidrojen bağlarının oluşmasında etkili olmaktadır (Aydın, 2004). Dolayısıyla, ısıl işlem sebebiyle holoselüloz miktarında görülen düşüşün (Ateş vd., 2009; 2010) materyaldeki reaktif -OH gruplarının miktarında (Ndazi vd., 2007a, 2007b) azalmaya neden olmasının, üretilen levhaların mekanik özelliklerini zayıflatacağını göstermiştir.

Kontrol ve ısıl işlem görmüş kızılçam yongalarından üretilen levhaların yüzey pürüzlülük değerleri (Ra) Şekil 4'de gösterilmiştir.



1: Standart sapma, 2: Duncan testi homojen grupları. Ra için $p<0.001$ bulunmuştur.

Şekil 4. Kontrol ve ısıl işlem görmüş kızılçam yongalarından üretilen levhaların yüzey pürüzlülük değerleri (Ra)

Kızılçam yongalarına uygulanan ısıl işlemin sıcaklık derecesi yükseltildikçe üretilen levhaların yüzey pürüzlülük değerlerinde kontrol grubuna göre sürekli düşüş tespit edilmiştir. Isıl işlem uygulamasının materyalin hücre yapısında öncelikle hemiselülozlar ve devamında selülozda bozunmaya sebep olduğu ve söz konusu bozunmanın ısıl işlem sıcaklık derecesinin yükseltilmesiyle hızlandığı ve arttığı TGA ve DTG analizi sonucu elde edilen termogramlardan anlaşılmaktadır. Yüzey pürüzlülüğü üzerine çok fazla sayıda faktörün etkili olduğu bilinmektedir. Bunlar içerisinde yıllık halka yapısı, genç odun, olgun odun, yoğunluk, hücre yapısı gibi faktörler sayılabilir (Liu vd., 1998; Aydın ve Çolakoğlu, 2005; Temiz vd., 2005; Dündar vd., 2008; Karagöz vd., 2011; İstek vd., 2012; Baysal vd., 2014, Güler ve Beram, 2018; Güler, 2019). Çalışmada elde edilen, ısıl işlemin materyalde yarattığı bozunma sebebiyle gerçekleşen ve ısıl işlem sıcaklık derecesinin artırılmasıyla üretilen levhalarda sürekli düşüş gösteren yüzey pürüzlülük değerlerine ait sonuçların literatürle (Ünsal ve Ayrılmış, 2005; Korkut vd., 2008; Özcan vd., 2012; Özdemir, 2016) uyumluluk içesinde olduğu görülmektedir.

4. SONUÇ VE ÖNERİLER

120, 160 ve 180 ^oC'lerde ısıl işlem görmüş kızılçam yongalarının FTIR spekroskopik ve termal özellikleri incelenmiş, devamında yongalardan elde edilen levhaların fiziksel, mekanik ve yüzey özellikleri değerlendirilmiştir. FTIR sonuçlarına göre, numunelerin kristallik indeksinde ısıl işlemden kaynaklı önemli bir değişmenin gerçekleşmediği görülmüştür. Termal bozunma eğrilerindeki esas bozunma aşamasında ısıl işlem görmüş yongalarda kontrol yongalarına göre daha az madde kaybı meydana geldiği ve termal stabilitenin arttığı gözlenmiştir. Bununla birlikte, TGA ve DTG sonuçlarına göre ısıl işlem sıcaklık derecesinin artışıyla yongalarda önemli düzeyde holoselüloz kaybı gerçekleştiği anlaşılmıştır. Buna bağlı olarak, elde edilen sonuçlarda levhaların su alma ve kalınlığına şişme değerlerinin yongalara uygulanan ısıl işlem sıcaklık artışına bağlı olarak sürekli düştüğü belirlenmiştir. Buna göre, ısıl işlem uygulanmış

yongalardan üretilen levhaların daha az su absorbe ettiği görülmüştür.

Isıl işlem ile yongaların kimyasal bileşimde gerçekleşen değişimler nedeniyle üretilen levhaların eğilme direnci, eğilmede elastikiyet modülü ve yüzeye dik çekme değerlerinde yongalara uygulanan ısıl işlem sıcaklığı arttıkça azalma gözlenmiştir. Mekanik özelliklere ait en yüksek değerler kontrol yongalarından elde edilen levhalarda görülmüştür. Bu nedenle ısıl işlem görmüş yongalardan üretilen levhaların yük taşıma amaçlı kullanılmaması gerektiği önerilebilir.

Isıl işlemin yongalarda yarattığı hücresel bozunma sebebiyle gerçekleşen ve ısıl işlem sıcaklık derecesinin artırılmasıyla üretilen levhalarda sürekli düşüş gösteren yüzey pürüzlülük değerlerine ulaşılmıştır.

Sonuçlardan da anlaşılacağı üzere ısıl işlem görmüş yongalardan üretilen levhaların fiziksel özelliklerinde genel olarak gelişme sağlanırken, mekanik özelliklerinde zayıflama kaydedilmiştir. Bu nedenle, ısıl işlem görmüş yongalardan üretilen levhaların dekorasyon amaçlı ve nemli ortamlarda, yani malzemede fiziksel özellik beklenen ve kısmen yanmaya dayanıklı yapılarda kullanılması önerilebilir.

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Bilge International Journal of Science and Technology Research

ISSN: 2651-401X
e-ISSN: 2651-4028
2020, Volume: 4, Issue: 1, 21-26
Received: 30.10.2019; Accepted: 17.02.2020
DOI: 10.30516/bilgesci.640084

Grafen Takviyeli PS Kompozitlerinin Yapısal, Isıl ve Mekanik Özelliklerinin İncelenmesi

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Özet: Günümüzde nanopartikül takviyeli kompozitlerin endüstriyel kullanımı giderek artmaktadır. Kullanılan nanopartikül takviyeleri ile kompozitin birçok özellliğinde iyileşme sağlanabilmiştir ve bu durum onları birçok alanda tercih sebebi yapmaktadır. Nanopartiküllerle üretilen kompozit malzemeler diğer yöntemlerle üretilen malzemelere göre daha fonksiyonel ve üstün özelliklere sahiptir. Kompozitlerin kullanıldığı alanlardan biri de yalıtım malzemeleridir. Eklenen farklı takviyelerle bu malzemelerin özellikleri geliştirilmektedir. Bu çalışmada polistiren matris içerisine farklı ağırlık oranlarında 30 µm parçacık boyutlu grafen takviyesi ile kompozit üretilmiştir. Saf polistirene ağırlıkça %0,1, 0,2 ve 0,3 oranlarında nano takviyeler eklenmiş ve plastik enjeksiyon yöntemiyle malzemeler üretilmiştir. Malzemelerin üretim aşamasında kristal polistirenler eritilip nano takviyelerle birleştirilip kalıplara dökülerek üretilmiştir. Birleştirme esnasında malzemelerin homojen dağılımı için 80 Rpm hızında 10 dakika boyunca karıştırılmıştır. Üretilen kompozit malzemelere mikroyapı karakterizasyonu için SEM analizi, mekanik ve ısıl özelliklerin belirlenmesi için sertlik, çekme ve TGA analizi yapılmıştır. Malzemelerin molekül yapıları incelendiğinde ise takviye malzemesinin saf polistirenin mikroyapısında anlamlı ölçüde değişikliğe sebep olmadığı görülmüştür. Çekme testlerinde grafen takviyeli kompozitler malzemenin yüzde uzamasını ortalama %1,3 arttırmıştur. Polistiren matris içerisine takviye edilen grafen partikülleri tane sınırları boyunca gerilme yığılmasına neden olduğundan, saf polistirene göre maksimum kopma dayanımı değerinde yaklaşık %30 oranında azalmaya neden olmuştur. Yapılan çalışmalarda grafen yapıda değişime neden olmamakla birlikte birçok özellikte anlamlı oranda iyileşme sağlamıştır.

Anahtar kelimeler: Nanokompozit, grafen, plastik enjeksiyon, mekanik özellikler.

Investigation of Structural, Thermal and Mechanical Properties related to Graphene Reinforced PS Composites

Abstract: Nowadays, the industrial use of nanoparticle reinforced composites is increasing. With the nanoparticle reinforcements used, many properties of the composites may be improved and this makes them preferred in many areas. Composite materials produced with nanoparticles have more functional and superior properties than the materials produced by other methods. One of the areas where composites are used is insulation materials. The properties of these materials are improved by the addition of different reinforcements. In this study, 30 µm particle size graphene reinforcement was produced in polystrene matrix with different weight ratios.Nano reinforcements of 0.1, 0.2 and 0.3% were added to pure polystyrene and materials were produced by plastic injection method. In the production stage of the materials, crystal polystyrene was melted and combined with nanoparticles and poured into molds. For homogeneous distribution of materials during jointing. Stirred at 80 rpm for 10 minutes. The materials produced are plate-shaped. SEM analysis for microstructure characterization of composite materials, tensile strength, hardness and TGA analysis were performed to determine mechanical and thermal properties. When the molecular structure of the materials were examined, it was seen that the reinforcing material did not cause any change in the microstructure of pure polystyren. In tensile tests, graphene doped composites increased the average percent elongation of the material by 1.3%. Since the graphene particles reinforced into the polystyrene matrix cause stress build-up along the grain boundaries, the maximum breaking strength value was reduced by about

30% compared to pure polystyrene. Although graphene did not cause changes in the studies, it has improved significantly in many features.

Keywords: Nanocomposites, graphene, plastic injection, mechanical properties.

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Citation: Gündoğan, K., Karağaç, A. (2020). Grafen Takviyeli PS Kompozitlerinin Yapisal, Isil ve Mekanik Özelliklerinin İncelenmesi. Bilge International Journal of Science and Technology Research, 4 (1): 21-26.

1. GİRİŞ

Uygarlık tarihi boyunca malzemenin ne kadar önemli olduğunu anlamak için tarih çağları olarak ifade edilen taş devri, tunç devri, demir devri gibi dönemleri gözlemleyerek anlayabiliriz. Bu malzemeler günümüz koşulunda geçmişe göre yaşamımızda ve bununla birlikte ekonomide daha fazla önem kazanmıştır (Ateş, 2011).

Kompozit malzemeler, eski çağlardan beri mevcuttur. Mısırda M.Ö. 3000 yıllarında arkeologlar lamine edilmiş tahta tabakalar bulmuşlardır. Yine Ortadoğu'da daha fazla eğilme dayanımı elde etmek amacıyla ok yayları üst üste konulan malzemelerle faklı lif yönleri oluşturularak kompozit yapılmıştır. Bina yapımı için çamur içine karıştırılan saman çöpleri ile yapılan kerpiç te bir kompozit malzemedir Çinliler ve Japonlar, daha çok darbe sönümleme direncini arttırmak için metal ve işlem görmüş derinin bir araya getirilmesi ile ok yayı gövdesi yapmışlardır. Modern kompozit malzemeler ise II. Dünya Savaşı döneminde başlamış ve özellikle askeri kullanım amaçları için geliştirilmiştir (Karademir, 2013).

Kompozit malzemeler uzun zamandır teknolojik problemleri çözmek için kullanıldı. Ancak 1970' li yıllarda polimerik takviyeli kompozitlerin keşfedilmesiyle endüstri sektörünün dikkatini çekmeye başlamıştır. Bundan sonra kompozir malzemeler çok sık tercih edilen mühendislik uygulamalarından biri haline gelmiştir ve otomotiv, uçak, spor, petrol sanayinde sıklıkla kullanılmaya başlanmıştır. Evrensel pazarda hafif malzeme tercih edilmesi kompozitin pazar payını arttırmıştır. Kompozit malzemeler çelik, alüminyum gibi malzemelerin yerine geçmeye ve daha iyi performans göstermeye başlamıştır (Ersoy, 2005).

Polistiren yaygın olarak kullanılan bir plastik türüdür. Kolay işlenmesi ve uçuculuğu sayesinde kâğıt, tahta ve metallerin yerini almıştır.

Kristalize polistiren sağlam ve şeffaf bir malzemedir. Polimerin yoğunluğu 1,06 gr/cm3 gerilme dayanımı 8000 psi, yumuşama noktası 106o C, darbe dayanımı 0,2-0,5 ft.1b/inç, uzaması % 3, esneklik modülü 450000 psi'dir. Bu özellikler molekül ağırlığına ve kullanılan katkılara bağlı olarak değişir. Ancak genel maksatlı polistirenin UV ışığına, bazı kimyasal maddelere ve yiyeceklere karşı dayanıklılığı azdır. 106oC gibi bir düşük yumuşama sıcaklığı da yaygın olarak kullanımını engeller (Dreijers ve Medne, 2006).

Genel amaçlı ve darbeye dayanıklı türler enjeksiyon kalıplama veya ekstruzyon metodları ile işlenirler. Enjeksiyon sıcaklığı 380-400 F arasında değişir. Erime akışları çok farklı aralıklarda olan ve farklı sahalarda kullanılabilen PS'ler mevcuttur. Bu ürünün sertliği ve işleme kolaylığı yüksek veya alçak basınç prosesi ile köpük üretiminde kullanımını kolaylaştırmaktadır. Genel amaçlı ve darbeye dayanıklı türlerden levha, profil ve boru imal edilebilmektedir. Kristal polistiren darbeye dayanıklı türle birlikte ekstrüzyonuyla, parlaklığı iyi olan levhalar elde edilir. Ayrıca polistirenin diğer maddelerle de karıştırılarak işlenmesi mümkündür (Medne vd., 2010).

Grafen, keşfinden bu zamana kadar fiziksel ve kimyasal özellikleri sebebiyle oldukça dikkat çekmiştir. Grafen çelikten 40 kat daha güçlüdür ve grafitin bir tek katmanından oluşmaktadır. Grafenin sadece 0,42 nm kalınlığında olduğunu düşünürsek bunun oldukça etkileyici olduğunu görebiliriz. Grafenin elektron taşıma özellikleri inanılmazdır. Bu özelliklerinden biri, bir elektrik akımının ışık hızına yaklaşan hızda akmasına izin veren yüksek bir taşıyıcı konsantrasyonu olmasıdır. Yani elektrik akımını ileten taşıyıcı elektronların ışık hızına yakın hızlarda malzeme içinde hareket etmesiyle elektrik akımı da diğer bilindik malzeme malzemelerden daha hızlı bir biçimde iletilmektedir. Bunun sonucunda da daha hızlı bilgisayarlar, performansı yüksek elektronik aygıtlar üretilebilecektir (Chen vd., 2003). Oda sıcaklığında, grafende herhangi bir saçılma olmadan elektronlar uzun mesafelerde hareket edebilir. Bu nedenle grafen, çoğu malzemeye göre daha iyi elektriksel özellik gösterir. Bu üstün özelliklere sahip olan grafen kompozit materyaller için takviye olarak kullanılmaktadır. Polimer matrisli kompozitler de takviye olarak kullanılan grafen birçok önemli uygulamada büyük bir atılım göstermiştir (Dikin vd., 2007).

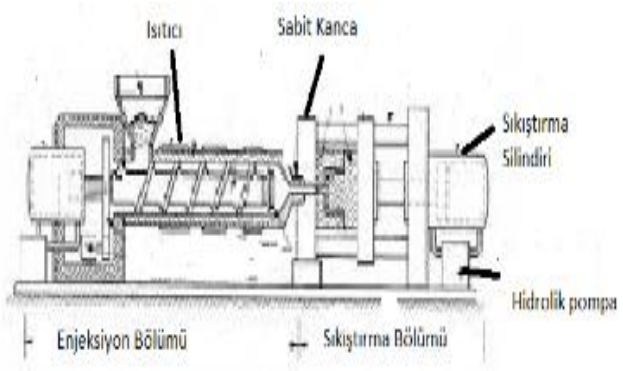
Grafen 2004 yılında Nobel ödüllü Andre Geim ve Kostya Novoselov tarafından keşfedilmiştir. Grafen sp2 bağlı karbonun mono tabakasıdır. Bir bal peteğine benzer kafes içerisinde atom dizisidir. Grafen, mekaniksel, elektriksel ve termal özellikleri sayesinde polimerlerde dikkat çeken takviye partikülü olmuştur. Grafenin polimerlerde dolgu maddesi olarak kullanılması matrisin mekanik ve elektrik iletkenliği arttırması yanında elektrokimyasal performansını da arttırmıştır (Nieto ve Boesl, 2015; Qiu vd., 2017; Wei ve Qu, 2012; Liem ve Choy, 2013; Balandin vd., 2008; Bustillos vd., 2017, Khan vd., 2015). özellikle enerji uygulamalarında grafen takviyeli kompozitlerde yapılan

çalışmalar çok iyi sonuçlar gösteriştir (Novoselov vd., 2004). Bununla birlikte grafen tabakalarının toplanması ve dağılımındaki eşitsizlikler grafenin tam potansiyel verimliliğini etkilemiştir. Bunun yanı sıra yüksek temas direnci muazzam sayıda ana tabakaya bağlanmasını sağlar (Shi vd., 2014). Tüm dezavantajlarına rağmen grafen takviyeli kompozitler birçok uygulamada çok başarılı sonuçlar göstermiştir.

2. MATERYAL VE YÖNTEM

Bu çalışmada saf kristalize polistiren kullanılmıştır. Takviye malzemesi olarak 30 µm parçacık boyutunda grafen kullanılmıştır. Deneysel çalışmalarda polistirene %0,1, 0,2, 0,3 oranlarında grafen nanopartikülleri takviye edilerek, plastik enjeksiyon cihazında 50x75 mm ebatında 5 mm kalınlığında kompozit plakalar üretilmiştir.

İlk olarak kristalize haldeki polistiren silindir hazne içerisinde 230 ºC sıcaklıkta eritilmiştir. Daha sonra grafen ağırlıkça %0.1, %0.2 ve %0.3 oranlarında eklenerek eriyik homojen hale getirilmek için 80 rpm hızda 10 dakika boyunca silindir içerisinde sürekli karıştırılmıştır ve plastik enjeksiyon yöntemiyle kalıba döküm işlemi gerçekleştirilmiştir. Kalıp içerisinde oda sıcaklığında doğal soğuma ile test numuneleri elde edilmiştir. Üretilen plaka şeklindeki kompozit malzemelere TGA, SEM, sertlik ve çekme analizleri uygulanmıştır.

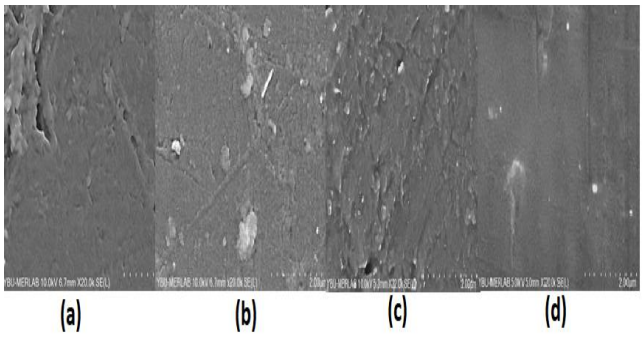


Şekil 1. Plastik enjeksiyon cihazının şematik gösterimi (Khan vd., 2015).

3. TARTIŞMA VE SONUÇLAR

Yapılan deneyler sonucunda elde edilen veriler yorumlanmış ve grafikler üzerinden gösterilmiştir.

Saf polistiren in SEM görüntüleri incelendiğinde literatüre uyumlu bir görüntü olduğu ve homojen bir dağılım görülmüştür.



Şekil 2. (a) saf polistiren, (b)% 0,1 Grafen, (c) % 0,2 Grafen, (d) % 0,3 Grafen SEM analiz sonucu.

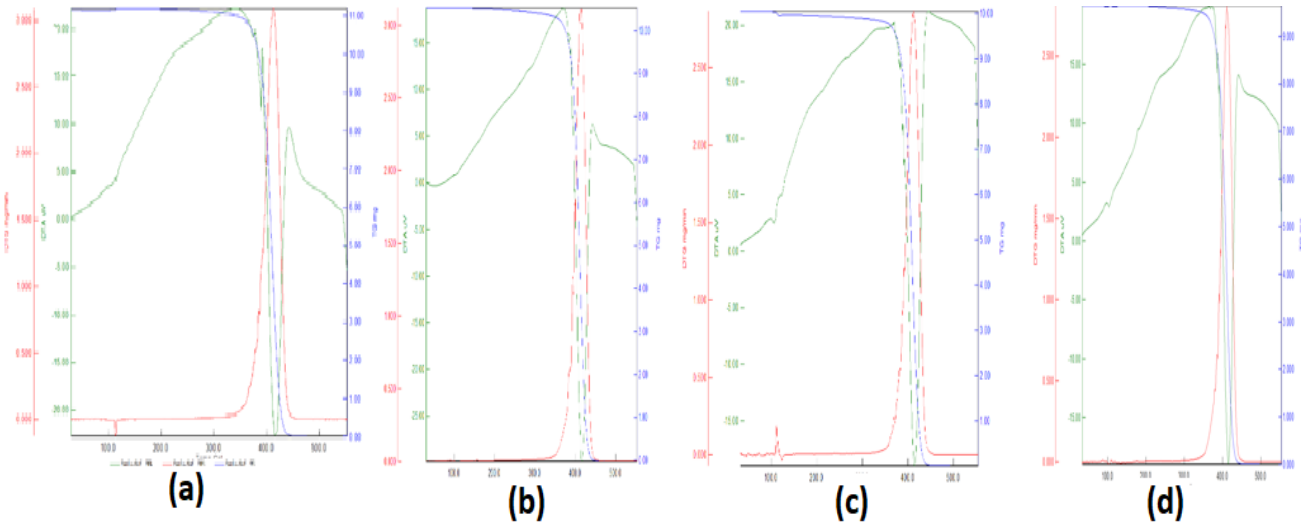
% 0,1 grafen takviyeli kompozitlerin SEM görüntüsü incelendiğinde numune yüzeyinde bir toplanma görülmemiştir. Tüm yüzey alanına dağılmış çok sayıda küçük beyaz noktaların olduğu gözlemlenmiştir.

%0.2 grafen takviyeli numunelerin yüzeyi incelendiğinde ise yüzey alanına dağılmış olan beyaz noktacıkların daha küçük ve daha fazla yayılmış oldukları görülmektedir. Buradaki yapı % 0.1 grafen takviyeli kompozite göre daha katmanlı bir görüntü vermektedir.

% 0,3 grafen takviyeli kompozitlerin SEM görüntüsü incelendğinde diğer iki görüntüye göre takviye malzemesinin oldukça homojen bir dağılım yaptığı açıkça görülmektedir. Ayrıca safsızlık yüzdesi en düşük bu ağırlık oranındaki kompozit malzemededir.

Termogravimetrik analiz (TGA), Bir örneğin kütlesinde artan sıcaklık sonucu meydana gelen ağırlık değişimlerini kantitatif olarak veren bir tekniktir. Bir maddenin dehidrasyonu veya bozunması sırasındaki ağırlık değişimlerini zamana veya sıcaklığa bağlı olarak gözlemek mümkündür. Ağırlık değişimi yüksek sıcaklıklarda fiziksel veya kimyasal bağların kopması sonucunda meydana gelmektedir. Kütlenin veya kütle yüzdesinin zamana karşı grafiği termogram veya termal bozunma eğrisi olarak adlandırılır (Soria-Verdugo vd., 2015).

Grafikte TGA eğrisine bakıldığı zaman saf polistirenin bozunma sıcaklığı 380 ºC olarak okunmuştur. Bu değer literatür sonuçları ile örtüşmektedir.



Şekil 3. (a) saf polistiren,(b) %0,1 Grafen, (c) %0,2 Grafen, (d) %0,3 Grafen takviyeli TGA sonuçları.

Şekil 3'te sunulan TGA eğrisinde ise %0,1 grafen takviyeli kompozitlerin bozunma sıcaklığının 382ºC ye çıktığı görülmüştür. Düşük ağırlık oranlarında grafen eklenmesi bile malzemenin bozunma sıcaklığına olumlu katkı yapmıştır.

Grafiğe bakıldığında %0,2 grafen takviyeli kompozitlerin bozunma sıcaklığı 384ºC olarak okunmuştur. Grafen takviyeli kompozitlerde ağırlık oranları arttıkça kompozit malzemenin bozunma sıcaklığı da doğru orantılı olarak yükselmektedir.

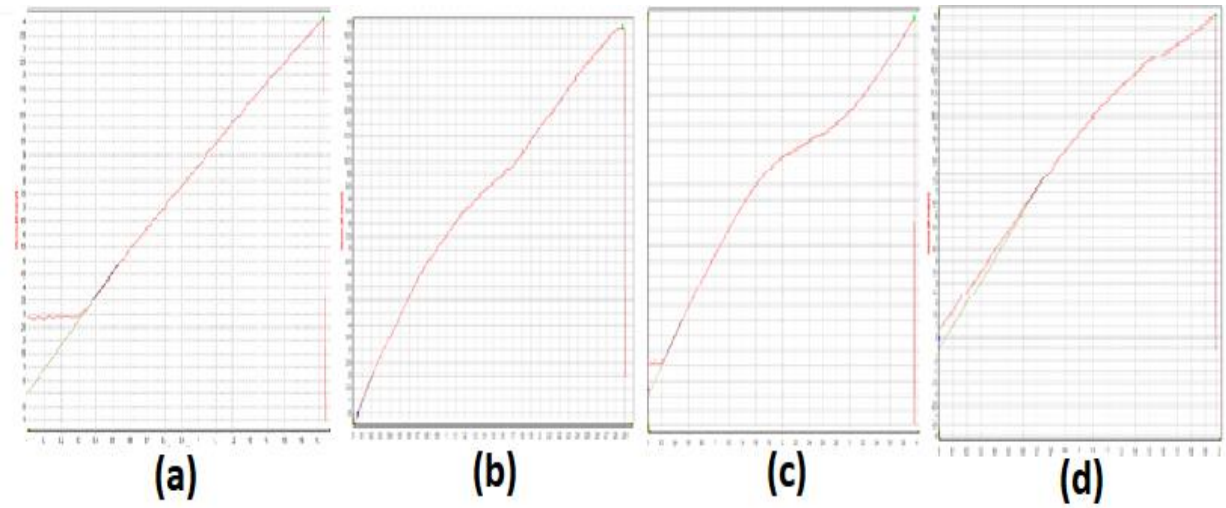
0,3 % grafen takviyeli kompozitlerde ise beklenildiği gibi malzemenın bozunma sıcaklığı artmıştır. Genel anlamda değerlendirildiğinde grafen katkısı kompozitlerin bozunma sıcaklığını olumlu etkilemiştir.

Yapılan TGA analizlerinde saf PS ve % 0,1, 0.2, 0,3 takviyeli grafen kompozit numunelerin bozunma sıcaklıkları incelenmiştir. Grafiklere bakıldığında grafen takviye malzemesinde PS polimerinin bozunma sıcaklığına olumlu etki yapmıştır. Özellikle %0,3 grafen takviyeli kompozitler PS polimerinin bozunma sıcaklığına anlamlı katkı sağlamıştır.

Tablo 1. Numunelerin bozunma sıcaklıkları.

NUMUNE	BOZUNMA SICAKLIĞI
Saf Polistiren	380ºC
% 0,1 Grafen	382ºC
%0,2 Grafen	384ºC
% 0,3 Grafen	386ºC

Grafen takviyeli kompozitlerde sıcaklık değişimi olmasının nedeni bu iki malzemenin yüksek ısıl kararlılığa sahip olmasıdır. Grafen sahip olduğu ısıl kararlılık sayesinde malzemenşn de kararlılığını arttırarak bozunma sıcaklığını yükseltmiştir. Yüzde ağırlık oranları arttıkça ısıl kararlılık artmakta ve bozunma sıcaklığında iyileşme görülmektedir.



Şekil 4. (a) saf polistiren,(b) %0,1 Grafen, (c) %0,2 Grafen, (d) %0,3 Grafen katkılı kompozitlerin çekme testi sonuçları.

Yukarıdaki grafiğe göre %0,1 grafen takviyeli kompozitlerde maksimum yüzde uzaması %2,9 iken maksimum kopa dayanımı 15,75 N/mm^2 dir.

Yukardaki grafiğe göre %0,2 grafen takviyeli kompozitlerde maksimum yüzde uzaması %3,96 ya yükselmiştir. Maksimum kopma dayanımı ise uzama ile doğru orantılı olarak 25,180 N/mm^2 ye yükselmiştir. %0,3 grafen takviyeli kompozitlerde ise, diğer katkı oranlarına göre değerlerde düşüş meydana gelmiştir.

Yapılan çekme testi sonuçlarına göre; saf polistirene eklenen takviye grafen partiküllerinden en olumlu katkıyı %0,2 kütle oranında takviye edilen grafen yapmıştır. Grafen katkılı kompozitlerde maksimum uzama ve maksimum kopma değerleri saf polistirene oranla belirgin bir şekilde iyileşmiştir.

Numunelerimize yapılan sertlik testi sonuçları Tablo 2 de gösterilmiştir.

Tablo 2. Saf polistiren ve grafen katkılı numunelerin sertlik deneyi sonuçları.

%0,1 GRAFEN	98,1
%0,2 GRAFEN	97
%0,3 GRAFEN	95
SAF POLİSTİREN	97,1

Yapılan sertlik deneylerine göre grafen nanopartikül takviyesinde malzemenin sertlik değeri önce artmış daha sonra azalmaya başlamıştır. Nanotakviyelerin ağırlık oranları arttıkça malzemenin sertlik değerinde azalma gözlenmiştir. En yüksek sertlik değeri %0,1 grafen katkılı kompozit örneğinde elde edilmiştir.

Yapılan bu çalışmada saf polistiren polimerine grafen nanopartikül takviyeleri sırasıyla % 0,1, %0,2 ve %0,3 ağırlık oranlarında eklenerek plastik enjeksiyon yöntemiyle plaka şeklinde numuneler üretilmiştir. Elde edilen kompozit numunelerine TGA, SEM, AFM, çekme testi ve sertlik analizi yapılmıştır. Malzemelerin ısıl özellikleri incelendiğinde eklenen takviyelerin polstirenin özelliklerine belirgin bir etki yapmadığı görülmüştür. Yapılan mekanik testlerde ise nanotakviyelerin kompozitlerin mekanik özelliklerine olumlu etki yaptığı görülmüştür. Mekanik testler sonuçlarında görülen bu olumlu etkilerin sebebi tanecikle matris arasındaki ara yüzey etkileşimidir.

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Bilge International Journal of Science and Technology Research

ISSN: 2651-401X
e-ISSN: 2651-4028

2020, Volume: 4, Issue: 1, 27-30
Received: 29.01.2020; Accepted: 09.03.2020
DOI: 10.30516/bilgesci.688845

Hydrodistillation of *Nigella Sativa* Seed and Analysis of Thymoquinone with HPLC and GC-MS

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Abstract: *N. sativa* seeds, commonly known as black seeds, are used for headaches in traditional medicine by many Asian, Middle Eastern and Far Eastern countries. It is used to treat cough, abdominal pain, diarrhea, asthma, rheumatism and other diseases. The seeds contain both fixed and essential oils, proteins, alkaloids and saponin. Much of the biological activity of the seeds has been caused to be due to thymoquinone, the major component of the essential oil, but which is also present in the fixed oil**.** The essential oil of black cumin seeds, *Nigella sativa* L., was tested for a possible antioxidant activity**.** In our study, it was aimed to increase the yield of essential oil in hydrodistillation of black seed oil in the presence of surfactant (Tween 80). While traces of essential oil were obtained in hydrodistillation of black seed seeds under similar conditions, 2.1% essential oil was obtained in the presence of surfactant. In this study, we also measured the amount of thymoquinone compound in aromatic water. The proportion of thymoquinone passing into the aromatic water show that it is necessary to consume the correct amount of water and essential oil, which is significantly measurable by GC MS and HPLC. We used HPLC for the determination of the amount of thymoquinone in aromatic water, and GC-MS was used in the analysis of Nigella essential oil components. According to the results of analysis, thymoquinone was found to be 790 ± 12 ppm in aromatic water and 45.78% in essential oil. Sufficient analytic work was performed with this method and the results were reported in the study.

Keywords: *Nigella Sativa*, thymoquinone, hydrodistillation, GC-MS, HPLC.

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Citation: Erdoğan, Ü., Yılmazer, M., Erbaş, S. (2020). Hydrodistillation of Nigella Sativa Seed and Analysis of Thymoquinone with HPLC and GC-MS. Bilge International Journal of Science and Technology Research, 4 (1): 27-30.

1. INTRODUCTION

Nigella sativa L., which is a member of the Ranunculaceae (Ranunculaceae) family, grows in South West Asia, Europe, North Africa and Turkey regions (Aljabre et al. 2015). It is a 20-30 cm long flowering plant. Sensitive flowers have 5-10 leaves and the colors are usually yellow, white, pink, pale blue or pale purple (Güzelsoy et al. 2018). Black colored seeds are flat, oblong, angular and juvenile. Seeds are 0.2 cm long and 0.1 cm wide (Forouzanfar et al. 2014). Black seed seeds, commonly known as black seeds, are headaches in traditional medicine by many Asian, Middle Eastern and Far Eastern countries (Salem 2005). It is used to treat cough, abdominal pain, diarrhea, asthma, rheumatism and other diseases (Al-Haj et al. 2010). Corek seed has high nutritional value and contains various active chemical components. Mainly saturated / unsaturated fixed oils (31.0-35.5 %), essential oils (0.40-0.45%), carbohydrates (33.0-34.0%), proteins (16.0-19.9%), amino acids, alkaloids, tannins, saponins, fibers, minerals (calcium, zinc, phosphate), vitamins (ascorbic acid, thiamine, niacin, pyridoxine and folic acid) (El-Tahir and Bakeet 2006). The main compounds of black seed are essential oil and fixed oil (Kiralan 2014). Black seed essential oil, anti-inflammatory, antimicrobial, anticancer (Bourgou et al. 2010; Harzallah et al. 2011) and has antioxidant activity (Burits and Bucar 2000). Thymoquinone, which is the main constituent of both essential oil and essential oil, inhibits nonenzymatic lipid peroxidation in liposomes (Houghton et al. 1995). According to GC-MS results of the main components of black seed essential oil; p-simene (32.02%), α-thujen (2.4%), α-pinene (1.48%), β-pinene (1.72%), carvacrol (10.38%), thymol (2.32%) and thymoquinone (23.25%)

reported (Sultan et al. 2009). Thymoquinone (2-isopropyl-5-methyl-1,4-benzoquinone) (Figure 1) is the main bioactive component of the essential oil of the medicinal plant *Nigella sativa* (Black seed) (Odeh et al. 2012).

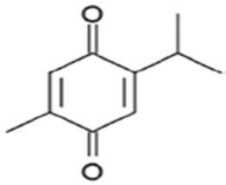

Figure 1. Chemical structure of Thymoquinone.

In the literature, it has been determined that thymoquinone (TQ) has promising antitumor properties against in vitro types such as human colorectal cancer cell (GaliMuhtasib et al. 2004), myeloblastic leukemia cells (El-Mahdy et al. 2005), prostate cancer (Kaseb et al. 2007), pancreatic adenocarcinoma ((Worthen et al. 1998) and breast adenocarcinoma (Shoieb et al. 2003).

2. MATERIAL AND METHOD

2.1. Plant Material

N. sativa seeds were collected from Turkey Isparta region. After harvesting, all seeds were kept in the dark at +4 ºC until extraction.

2.2. Chemicals

Thymoquinone (2-isopropyl-5-methyl-1,4-benzoquinone) (HPLC,98%) and Tween 80 Sigma Aldrich (Sigma–Aldrich GmbH, Sternheim, Germany) were purchased. All solvents and reagents are of HPLC purity and were purchased from Sigma-Aldrich and Merck (MerckKGaA, Darmstadt, Germany).

2.3. Essential oil extraction

The extraction procedure of the essential oil is as follows; The extract (fixed oil) obtained from the *N. sativa* seeds by cold press method was applied hydrodistillation using Clevenger type apparatus (Isparta University of Applied Sciences-Industrial Crops Laboratory). 50 g of the fixed oil obtained by the cold press method was dissolved in 500 mL of water which contains 10% of Tween 80 (5g) according to oil weight and the final volume was completed to 1 L. 50 grams of fixed oil in 1 L of water ,was hydrodistilled for 2.5 hours. The essential oil obtained with dark yellow color and pungent odor was dried with anhydrous sodium sulfate and kept in the dark at +4 ºC until use. Aromatic water, along with essential oil from hydrodistilation products, was also collected for future analysis.

2.4. HPLC analysis of thymoquinone

The thymoquinone analysis of the black seed aromatic water was performed according to the modified HPLC method of developed by Selin et al**.** (2017).

For quantity analysis; standard thymoquinone solutions were prepared at concentrations of 62.5 125, 250, 500 and 1000 ppm. The areas of all these concentrations were used for calibration (r^2=0.9995). Aromatic water was injected directly. Samples, a diode detector (DAD detector (Lambdamax = 278nm), an auto sampler (SIL – 10AD vp), a vacuum degasser (DGU-14A), system controlled (SCL-10Avp) and a pump (LC-10ADvp). Chromatographic separations were carried out on AgilentEclipse XDB-C18 column (250x4.60 mm, 5 µm) The column temperature was 30 ºC. 3% acetic acid, Methanol (50:50) was selected as mobile phase and the flow rate was 0.8. The injection volume is 20µL for each sample and standard The analysis time is 30 minutes and the detection wavelength is set to 278 nm for thymoquinone.

2.5. Essential oil components analysis with GC-MS

Essential oil analysis of volatile components were performed on a Shimadzu GCMS-QP2010 SE (Japan) model with Support Rx-5Sil MS capillary column (30 m x 0.25 mm, film thickness 0.25 µm). GC analysis were performed under the following conditions. Carrier gas 1mL / min. helium with flow. The split ratio is 1:10. After 1 minute at 60 ºC, the temperature program reaches 250 ºC with an increase of 4ºC per minute and was kept at 250 ºC for 15 minutes. The mass spectra were taken at 70 eV. 970 microlitre hexan is added over 30 microliters of pure essential oil. 1 microliter is injected from the capped vial.
Identification of components with mass spectra data according to mass library was used NIST, WILEY also thymoquinone reference standart was used. % areas of essential oil showed that thymoquinone was the major volatile component.

3. RESULTS AND DISCUSSION

Fixed oil obtained from *N. sativa* seeds by cold press had a green color, pungent aromatic odor. From the fixed oil, dark yellow, pungent essential oil was obtained by hydrodistillation method according to the above method. In conventional hydrodistilation methods, plant materials such as leaves, flowers, seeds, roots and so on are used. In our study fixed oil obtained from *N. Sativa* seeds was dissolved in water with Tween 80 surfactant and then hydrodistillation was performed. The purpose of using Tween 80 is to minimize the problems in the fixed oil-water mixture during hydrodistillation and to ensure a homogeneous mixture of constant oil and water. In similar conditions, a trace of essential oil was obtained in the hydrodistilation of black seed oil without surfactant. On the other hand 2.1% essential oil was obtained from the fixed oil obtained from the *N. Sativa* seed and collected for analysis in aromatic water. In a similar study, yellow essential oil was obtained by hydrodistilation method from fixed oil obtained by hexane extraction (Nickavar et al. 2003).
The main pharmacologically active compound in the structure of *N. Sativa* essential oil is thymoquinone. Determination of thymoquinone content in aromatic water according to HPLC method was performed as above. Standard, aromatic water chromatograms are given in Figure 2, Figure 3 respectively. The amounts of

thymoquinone in the investigated sample are also given in Table 1.

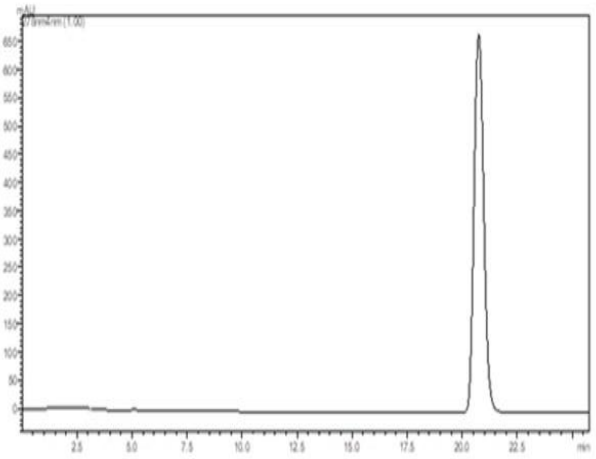

Figure 2. HPLC chromatogram of Thymoquinone standard.

Table 1. Concentration of thymoquinone in aromatic water

Sample	Amount (ppm)
Aromatic water	790 ±12

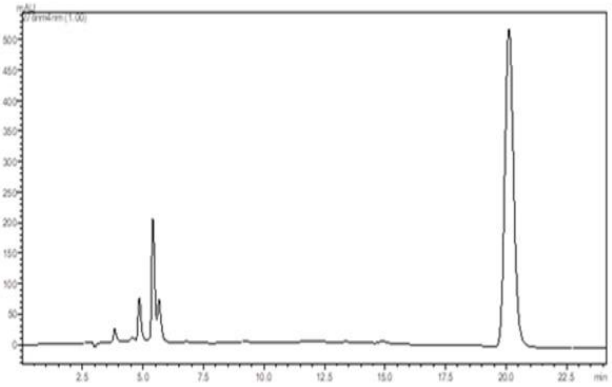

Figure 3. HPLC chromatogram of *N. Sativa* aromatic water.

Thymoquinone was determined by HPLC analysis of the aromatic water. In a similar study, 10 different black seed seeds and oil obtained from herbal extracts from Ankara were examined by HPLC according to the amount of thymoquinone they contain (Selin et al. 2017). Due to the presence of thymoquinone in aromatic water is likely. Solubility studies showed that thymoquinone had the same solubility in commonly used solvents such as 0.1N HCl and PBS (pH 5; 7.4 and 9.0) (Goyal et al. 2017) thought to be used.

The components of *N. sativa* essential oil obtained by hydrodistillation were investigated by GC-MS. 20 components were identified in essential oil (Table 2).

Table 2. GC MS % total percentage of *Nigella Sativa* L. seed essentail oil results

Peak#	R.I	Compound Name	Area%
1	927.8	a-Thujene	6.50
2	936.1	a-Pinene	1.50
3	977.7	ß- Pinene	1.94
4	1011.3	3-Carene	5.51
5	1024.3	p-Cymene	29.45
6	1029.5	Limonene	1.61
7	1030	ß- Phellandrene	0.97
8	1031	1,8-Cineole	0.05
9	1059.7	γ-Terpinene	0.20
10	1086.9	Terpinolene	0.11
11	1098	Sabinene hydrate, trans-	0.96
12	1127.5	p-Mentha-2,8-dien-1-ol, trans-	0.51
13	1177.1	Terpinen-4-ol	0.82
14	1218.3	ß- Cyclocitral	1.07
15	1249	Thymoquinone	45.78
16	1300.4	Carvacrol	0.44
17	1317	2,4-Decadienal, (2E,4E)-	0.05
18	1347	a-Terpinyl acetate	0.07
19	1352	a -Longipinene	0.34
20	1406.8	Longifolene	1.54

The main components were thymoquinone (45.78%), p-Cymene (29.45%), a- Thujone (6.5%), 3- Carene (5.51%), respectively. In a similar study, GC-MS analysis of 7 different black seed essential oils revealed that the main components were thymoquinone (30% - 48%), p- cymene (7% –15%), carvacrol (6% –12%), Terpinen-4-ol (2%-7%), t-anethol (1% –4%) and longifolene (1% –8%) (Burits and Bucar 2000).

4. CONCLUSIONS

In our study, 2.1% essential oil was obtained in hydrodistilation of black seed oil in the presence of surfactant (Tween 80). We used HPLC for the determination of the amount of thymoquinone in aromatic water, and GC-MS was used in the analysis of Nigella essential oil components. According to the analysis results thymoquinone was dedected 790±12 ppm in aromatic water and 45.78% in essential oil.

In this original study, especially; It has been shown that Thymoquinone can be dissolved in aromatic water by distillation method. According to its benefits of Thymoquinone , this water can be used as drinking or other applications such as food and cosmetic. There are not much data for water solubility of Thymoquinone. With this study, we think that aromatic water can be contributed by the food, cosmetic and drug industry.

ACKNOWLEDGEMENTS

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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Bilge International Journal of Science and Technology Research

ISSN: 2651-401X
e-ISSN: 2651-4028

2020, Volume: 4, Issue: 1, 31-42
Received: 07.09.2019; Accepted: 20.03.2020
DOI: 10.30516/bilgesci.616818

A Tool Development for Test Case Based Code Optimization in Java

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Abstract: Java has been a popular programming language since its first stable release in 1996 because of its platform independence. Along with its popularity Java has been a focus of performance studies since its debut. Developments in hardware has unbelievably advanced the performance of the devices that run Java and thus software performance has lost its popularity until the release of Android OS and rapid increase in mobile device ownership Java language usage has increased once again. Mobile devices having far less system resources compared to personal computers had re-brought software performance studies into the spotlight. However mobile devices have gone into a fast-paced development like all other information technologies and this brought down the need for software performance studies, again. Also, worth mentioning that development of new Java Virtual Machine (JVM) versions has made the specialized compiler studies, which may threaten the platform independency, obsolete except for specific situations. Today it is not enough to consider code optimization solely in terms of performance improvement. Much broader vision is needed like software development processes such as Maintainability, code readability, improving cooperation in multi-programmer projects, software quality assurance.

In this study, white box testing approach is adopted as the software testing technique and static code analysis method is selected to ensure line coverage. A new software (JPA) has been developed based on a currently used testing tool (PMD) to improve the user experience.

Keywords: Java, code optimization, PMD, static code analysis.

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Citation: Taymaz, T., Birant, K. U. (2020). A Tool Development for Test Case Based Code Optimization in Java. Bilge International Journal of Science and Technology Research, 4 (1): 31-42.

1. INTRODUCTION

Rose flower is seen as a symbol of purity, beauty, love and Java programming language is a general-purpose, concurrent, class based, object-oriented language which allows application developers to write programs that can run on any platform; either online or on different types of devices (Gosling et al., 2018). Java compiler converts the source code to bytecode, which then can be executed on any operating system using JVM (Java Virtual Machine). Independence from operating systems provides flexibility and simplicity, which has considerably increased the popularity to this programming language since the release of version 1.0 in 1996. However, being flexible can also lead the developers to a non-focused implementation and in turn might make some applications to be less efficient than other platform dependent programming languages, which brings out a need for performance improvement applications for Java.

While performance studies have been conducted, starting with the first version of Java programming language with projects such as High Performance Java (HPJAVA) and The Ninja Project, these studies have discontinued due to Java Development Kit (JDK) updates and due to the fact that developments in computer hardware have rendered these studies redundant. (Carpenter et al.,1997; Moreira et al., 2001). Nevertheless, performance studies for Java came back into focus again with the announcement of the Android operating system in 2008.

Android operating system is based on an open-source distribution of Linux operating system. Programmers can

develop Java-based applications and deploy them on Android devices (Hall & Anderson 2009). There has been a steady growth from the start in the numbers of the applications that were developed for Android OS because Java was already a popular and well-known programming language when Android OS was commercially released in 2008. Today, Android OS is the most popular operating system for all devices surpassing even Microsoft Windows, given in Figure 1.

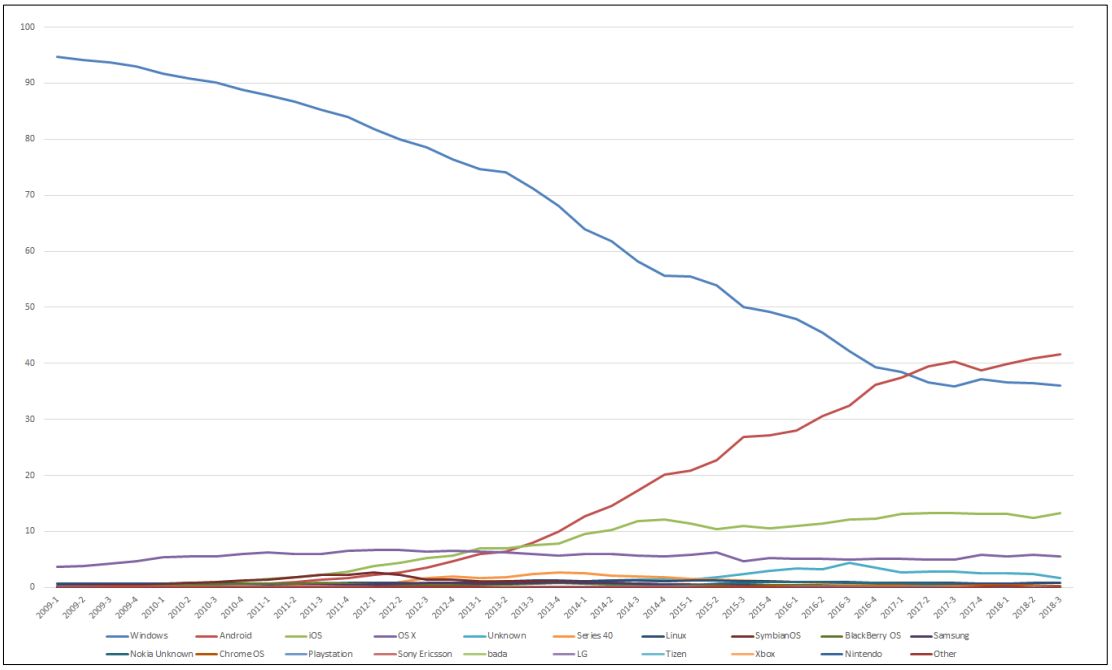

Figure 1. Operating system market share worldwide (Statcounter, n.d.)

2. Material and Method

2.1 What is code optimization

A definition that most programmers will agree is that the main purpose of code optimization is to increase the quality of the code in terms of time and space without affecting the output result of the code (Bajwa et al., 2016).

The terms time and space lead to a common perception of code optimization as only the performance increase; in a wider perspective, optimization may also mean an improvement in other aspects as defined below.

Code optimization is the process of modifying source code to improve code quality and efficiency. For instance, a program can be optimized so that it runs faster, or works with less memory storage or other resources, or consumes less power, or can be more readable to facilitate maintenance and updating (Bajwa et al., 2016; Johnson 2008; Lins, 2017; Palaniappan, 2016).

Code optimization can be performed at levels such as design level, algorithms and data structures, source code level, build level, compile level, assembly level and run time (Lins, 2017). In general, higher optimization levels have a greater impact and are more difficult to change later in a project, so they require a complete rewrite if they need to be changed. For this reason, optimization generally proceeds from higher to lower levels. Larger gains can be achieved at higher levels with less effort, then gains get smaller and require more effort as levels go lower. However, this is not always the case, in some cases the performance of the program may show tremendous increases in performance with small changes made at lower levels. Therefore, it is not possible to foresee whether the time and effort required are worth the performance increase, not to mention the unforeseen errors that may occur. Because of this unpredictability, the changes made for optimization can be abandoned, partially abandoned or postponed to a later date, depending on the size and complexity of the project.

Assuming the code optimization only as performance enhancements would compromise the stability of the program. Because such an approach would be ignoring the concept of code quality as in debugging, maintenance efforts and design process of later versions.

2.2 When to optimize?

Choosing the right programming language and platform in the design phase will be the most basic start for optimization. The right architecture selection is also made at this beginning stage since it can be very challenging to change later. In general, it will be even more difficult to change the data structure than the algorithm because the data structure assumption and its performance assumption will be used throughout the entire program. For the sake of improving performance, adding new codes and changing

source code may reduce readability. This can result in serious complications in maintaining and debugging the program. Therefore, optimization for performance improvement is better to be left to the end of the development phase.

Premature optimization is the (so-called) improvement effort in an immature system. The following quote is about premature optimization from Donald Knuth: "The real problem is that programmers have spent far too much time worrying about efficiency in the wrong places and at the wrong times; premature optimization is the root of all evil (or at least most of it) in programming."(Knuth, 1974).

Indisputably that was a different time when mainframes and punch cards were common and CPU processing cycles were also scarce. With advancing technology, innovations such as much higher CPU processing cycles have emerged, still premature optimization has become a controversial issue.

Nowadays, programs can be quickly distributed over the Internet and the codes are updated if necessary, afterwards. A classic example of this would be a start-up that spends a lot of time trying to figure out how to scale their software to handle millions of users. This may seem like a valid concern to be considered. But it makes more sense to worry about processing millions of users, after making sure that at least 100 users like this product and want to use it. If the product is coded in an easy to maintain, the necessary optimizations are easily taken care of (Watson, 2017).

Developments in compilers made some optimizing operations unnecessary, such as bitwise shift and mask used to divide or multiply a positive integer expression by two, because the compiler performs these operations automatically when compiling the code. As a result, ease of maintenance by writing readable code has come to the fore once again.

Before starting optimization, it would be more useful to prepare a report of the program code including suggestions in source code level and then apply the selected suggestions and re-report including a comparison between the multiple versions previously tested by the user.

2.3 Optimizing Java source code

In order to understand Java code optimization, it is necessary to explain the technology behind the Java programming language and the development of this technology. In other programming languages the compiler generates machine code for a particular system. But in the Java programming language, the compiler generates its own alternative format, which is called bytecode, for Java Virtual Machine (JVM) instead of the machine language. JVM is an abstract computing machine and provides Java programming language hardware and platform independence.

Just-In-Time (JIT) compiler improves the performance of Java applications at run time and it is a component of JVM. JVM loads the class files at program runs time. The class files determine the meaning of each bytecode and make the appropriate calculation. For comparing to a native application, additional processor and memory usage during interpretation may cost Java application extra time. However, as JIT completes the compilation, the application reaches its peak performance approaches the performance of a native application.

In Java programming language, to make performance improvements, codes can be refactored, or settings can be adjusted on the compiler, and even a new compiler can be designed to generate bytecode for JVM. However, in this study, instead of these options, it was aimed to create a report by examining the source code with static code analysis and to increase the optimization by increasing the code quality depending on this report. The main reasons for this are listed below.

Java is a language licensed by General Public License developed by Oracle and is regularly updated. With these updates, there is also an increase in performance.

The execution speed of Java code is highly dynamic and fundamentally depends on the underlying Java Virtual Machine. An old piece of Java code may well execute faster on a more recent JVM, even without recompiling Java source code (Evans et al., 2018). Combining this fact with the possibility that refactoring may not sufficiently improve the software performance, refactoring approach was not pursued in this research. Although there may be optimizations that can still be applied for special circumstances and unforeseen cases in the future, they cannot be generalized and may not be expected for the same performance increase in the upcoming Java versions.

JDK compilers can be customized to create a more efficient bytecode for JVM. Additionally, new programming languages such as Scala and Kotlin have been developed and are available as alternatives, which can also work with JVM. Scala combines object-oriented and functional programming in one concise, high-level language. Scala's static types help avoid bugs in complex applications, and its JVM and JavaScript runtimes let you build high-performance systems with easy access to huge ecosystems of libraries (Scala n.d.). Kotlin is a statically typed programming language that runs on Java Virtual Machine and can also be compiled to JavaScript source code or use LLVM compiler infrastructure (Kotlin n.d.).

Considering the above-mentioned information, working to optimize the software at the source code level appears much more promising than just increasing the performance for current runtime version. Additionally, leaving the final decision to the programmer by producing reports provides flexibility for the programmer who may have specific needs or specific requirements. For this purpose, statement coverage, a White-Box Test technique, is implemented in this study.

2.4 Software testing

Software testing is used to expose defects and errors in the software. Principal benefits that can be gained by testing are software quality assurance, reliability estimation of software, validation and verification. Software testing is a key component of software quality assurance and represents a refinement of specification, design and coding (Khan & Khan, 2012).

The primary purpose of the software test is to verify the quality of the software system, another purpose is to determine the integrity and accuracy of the software and ultimately reveal undiscovered errors. Software testing ensures an effective performance of the application (Singh & Kazi, 2016).

Software can be tested with box approach. There are essentially two types of the "box" approach: black box testing and white box testing. The combination of said approaches is called grey box testing. Figure 2. shows the "box" approaches in software testing.

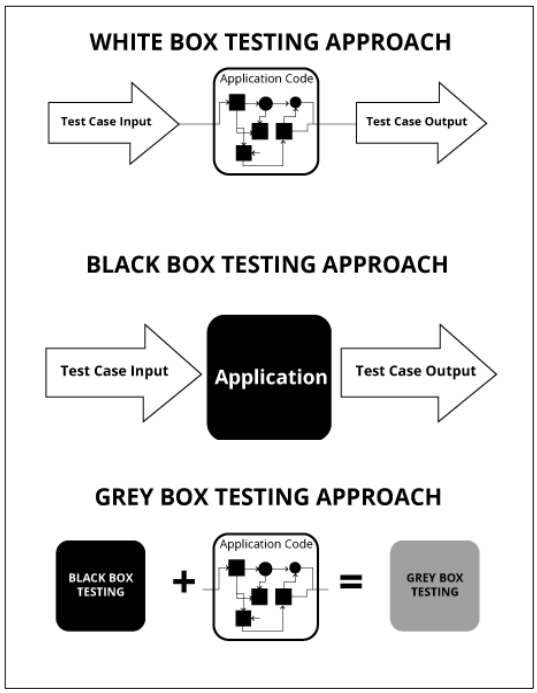

Figure 2. Software testing "Box" approaches (Invensis, n.d.)

White box testing deals entirely with the code structure. Both the source code and the compiled code of the project are tested. Unlike white box testing, black box approach, allows testing to be performed without any requirement of inside knowledge of the code structure or design of the project. The comparison of the input and output can obviously only test if the functional requirements of the system are met or not. Grey box testing, as previously stated, is a combination of white-box testing and black-box testing approaches. Although Grey box testing depend on some inside knowledge of the code structure, it is actually platform and language independent. The reason behind this is; it is essentially a black box test modified according to the main data structures and algorithm of the application but not the details of the code. (Sawant et al., 2012; Jovanović, 2009).

Black box testing doesn't need any knowledge of the internal structure or coding in the program, and more importantly doesn't give any conclusions or suggestions about it either. Similarly, grey box testing doesn't require that the tester have access to the entire source code and again limited to boundary values and interfaces between program modules. White box testing is preferred in this study because it is focused on the code and would give more meaningful results pertaining to the code structures (Jovanović, 2009).

2.4.1 White box testing

White box testing is sometimes referred to as clear box testing, glass box testing, transparent box testing due to its access to the codes and algorithms or structural testing because of its focus on internal structure or working of a software, rather than its functionality (Karnavel & Santhoshkumar, 2013).

Performing white box testing technique follows a step by step approach and tries to verify each program statement even the comments. White box testing enables performance of data processing and calculations correctness tests, software qualification tests, maintainability tests and reusability tests. The implementation of white box testing is based on controlling the data processing for each test case which in turn raises the issue of coverage of a huge number of possible processing paths and the numerous lines of code. This adversity has given rise to two approaches called "Path coverage" and "Statement coverage". Path coverage is to check whether all possible routes are applied along a certain part of the code. Statement coverage, also known as line coverage, is verifying whether each statement in the program is executed or not (Galin, 2004).

In a software structure, different paths are created by conditional expressions such as IF - ELSE, DO - WHILE. Path testing attempts to provide the full scope analysis of a program by testing all possible paths. Therefore, "path test's completeness" is defined as the percentage of program paths carried out during the test. The concept of path testing is not practical in most cases because of the vast resources needed for its performance. Because of this predicament, statement coverage has been developed as an alternative. In statement coverage, test cases leave most of the possible paths untested however requires far fewer test cases to cover all paths compared to path coverage. As an alternative to creating multiple test cases to cover all paths, static code analysis is a viable solution, or even better, using a tool to automate static code analysis (Galin, 2004).

2.5 Static code analysis

Static code analysis, also called static analysis, is the method of examining the program codes without the actual execution. Static analysis can be considered a code review process. Code reviewing is one of the oldest and safest

methods for detecting errors in the source. It suggests reading the source code carefully and make suggestions on how to improve it. This process is used to locate existing errors and pieces of code that may cause future errors. Code review process is useful, because programmers are more easily to notice others' mistakes than their own. The most important problem in this process is the need for periodical meetings of programmers to review each new code, or re-review a code after the proposed changes are applied. When programmers review large pieces of code at a time, they lose their attention quickly, so they need to rest regularly. Otherwise, code review will not help. This is a serious problem because of its immense cost in man hours. Automation of static analysis, i.e. static code analysis tools would be a good solution to reduce this cost (Ayewah et al., 2008).

2.5.1 Static code analysis tools

Static code analysis tools examine the source code of programs and give suggestions to the programmer as to which parts of the code to reconsider. These tools may not replace a code review by a team of programmers, but the benefit/cost ratio makes the use of static analysis a very good option. Static code analysis tools are very successful in detecting errors in programs and providing code formatting suggestions. One of the main advantages of static analysis is that it allows the cost of eliminating errors in the software to be greatly reduced. This is mainly because this analysis can be performed at the coding stage. Fixing an error at the testing stage costs about ten times more compared to development stages, as shown in Table 1. Static analysis can be performed in construction, system test and post-release phases.

Table 1. Average cost of fixing defects based on when they're introduced and detected (McConnell, 2014)

	Time Detected				
Time Introduced	Requirements	Architecture	Construction	System Test	Post-Release
Requirements	1	3	5 – 10	10	10 – 100
Architecture	-	1	10	15	25 – 100
Construction	**-**	**-**	**1**	**10**	**10 – 25**

Static analysis does not depend on the compiler used and the platform in which the compiled program is executed, thus making it possible to find hidden errors, such as undefined behavioral errors, that may occur even a few years after it was created or errors that may occur in different compilers and platforms. In addition, typos and other errors caused by Copy-Paste usage can be easily and quickly detected.

Static code analysis tools perform these operations according to the rules and standards of the programming language. There are a lot of commercial and free static code analysers. In a research, PMD was deemed to be the best static analysis tool for Java programming language (Abdallah & Al-Rifaee, 2017).

While most static analysis tools for Java programming langue, use SUN or Google standards, some tools such as PMD use developers approved rules in addition to SUN and Google standards. This makes PMD a multi-standard based tool to implement. In addition, PMD enables the development of tools through the APIs it provides. Therefore, PMD is used in this study.

2.6 How PMD works?

PMD is an open source, static code analysis tool with comprehensive configurable rule sets (Thomas et al., 2003). PMD supports Java, JavaScript, Salesforce.com Apex and Visualforce, PLSQL, Apache Velocity, XML, XSL languages (Nembhard et al., 2017).

In PMD, multiple rules or rulesets can be used together, or a custom ruleset can be created. For Java Programming Language, there are more than 280 rules which are defined in eight rulesets: Best Practices, Code Style, Design, Documentation, Error Prone, Multithreading, Performance and Security (PMD n.d.). Additionally, PMD users can execute custom analyses by developing new evaluative rules.

Instead of the source code itself, PMD uses abstract syntax trees (ASTs) created by a JavaCC parser from Java sources. The main loop of PMD then examines AST, visiting all registered rules related to specific AST structures. The rule scan then checks AST and report violations (Aderhold & Kochtchi, 2013). The following example, given in Figure 3., illustrates rule creating process for PMD and also illustrates inner workings of PMD.

```
class Example {
    void bar() {
        while (baz)
            buz.doSomething();
        }
}
```

Figure 3. Sample Java code

In PMD, rules are written as Java classes or XPath expression. It actually gets quite difficult to follow source code especially as it gets longer. This is mainly because it is difficult to tell where the curly braces belong. To be able to do this, it is necessary to determine the changes that happen in AST if "buz.doSomething()" clause had braces inserted as shown in Figure 4.

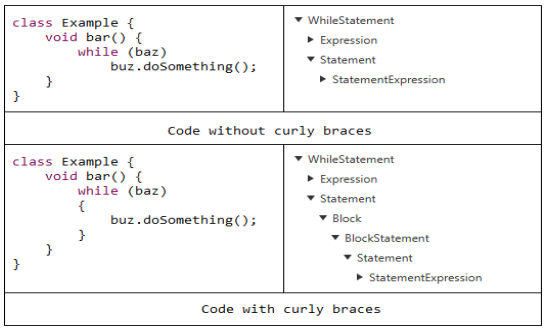

Figure 4. Different AST for sample code with-without curly braces

When the curly braces are added, AST nodes are formed with the names “Block” and “BlockStatement”. A rule violation can be detected by writing a rule that detects a "WhileStatement" declaration that is not followed by “Block”. This can be done with one of Java class or XPATH experission rule writing methods. To write a custom rule, a new java class needs to be created that is inherited from net.sourceforge.pmd.lang.java.rule.AbstractJavaRule. PMD works by creating AST and then traverses it recursively. By doing this, a rule can get a call back for any type it’s interested in. The rule that gets called whenever AST traversal finds a “WhileStatement” can be seen in Figure 5.

```
import net.sourceforge.pmd.lang.java.rule.*;
import net.sourceforge.pmd.lang.java.ast.*;
public class WhileLoopsMustUseBracesRule extends AbstractJavaRule {
    public Object visit(ASTWhileStatement node, Object data) {
        System.out.println("Avoid using 'while' statements without using curly braces");
        return data;
    }
}
```

Figure 5. WhileLoopsMustUseBracesRule java code

Once the rule class is written, PMD must be told of this. PMD needs a ruleset XML file to recognize the rule. “sampleCustomRule.xml” file can be seen in Figure 6. The elements and attributes of the file are explained below.

●name - The rule’s name.

●message - Message for report.

●class - Location of the rule class.

●description - A description of what this rule looks for.

●priority - There are five levels of priority in the PMD for the rules:

1. High priority. Code revision absolutely required.
2. Medium high priority. Code revision highly recommended.
3. Medium priority. Code revision recommended.
4. Medium low priority. Code revision optional.
5. Low priority. Code revision highly optional.

●example - A code fragment between CDATA tags to explain the rule violation.

```
<?xml version="1.0"?>
<ruleset name="Sample custom rules"
    xmlns="http://pmd.sourceforge.net/ruleset/2.0.0"
    xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance"
    xsi:schemaLocation="http://pmd.sourceforge.net/ruleset/2.0.0 https://pmd.sourceforge.io/ruleset_2_0_0.xsd">
  <rule name="WhileLoopsMustUseBracesRule"
      message="Avoid using 'while' statements without curly braces"
      class="WhileLoopsMustUseBracesRule">
    <description>
      Avoid using 'while' statements without using curly braces
    </description>
    <priority>3</priority>

    <example>
      <![CDATA[
        public void doSomething() {
          while (true)
          x++;
        }
      ]]>
    </example>
  </rule>
</ruleset>
```

Figure 6. SampleCustomRule.xml

To test the rule run PMD in command line by giving command:

pmd.bat -d “Path to Sample Code” -R “Path to sampleCustomRule.xml”

All findings obtained should be explained with figures and / or charts and avoided from unnecessary repetitions.

After running the command PMD prints “Avoid using ‘while’ statements without using curly braces”, as shown Figure7.

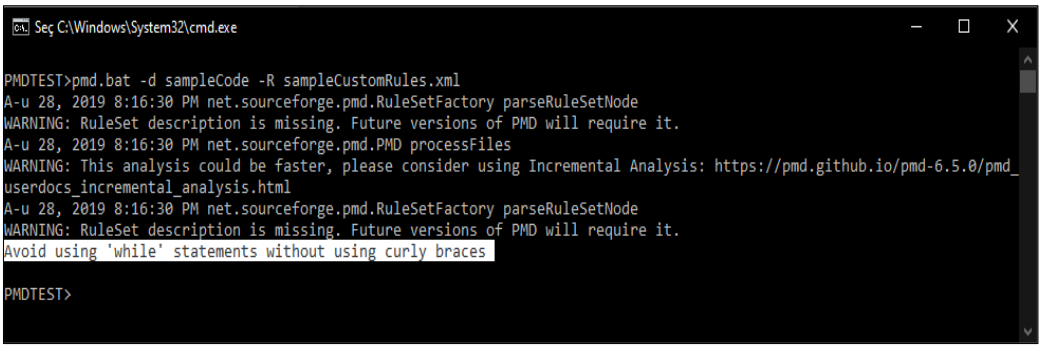

Figure 7. Output of running PMD with sample custom rule

After testing the rule, it is necessary to make changes to the rule class in order to include the rule in the reports to be prepared by PMD. However, since the aim is to explain how PMD works instead of preparing a custom rule for PMD, the continuation of the subject and/or preparing the rule with XPATH expressions will not be included here.

2.7 Operating PMD

PMD is distributed as a zip archive. The latest binary distribution can be downloaded from the releases page. In Windows operating system, to run PMD, unzip it in any directory and run the file "pmd.bat" under the "bin" folder with the required parameters from the command line. PMD does not have a graphical user interface. pmd.bat requires two arguments:

●-d <path>: Path to files of source code to analyse.
●-R <path>: The ruleset file. PMD uses xml configuration files.

Other arguments of PMD are optional. For instance, PMD displays the report on command line by default. But user can change this by giving "-r" argument with a path to a file in which the report output will be recorded. Full list of arguments can be found on PMD's documentation page.

3. RESULTS

3.1. Shortcomings of PMD and Java Project Analyser (JPA)

Although the generated report will be displayed on the command screen or stored in the name and type specified at each run, PMD will not operate if the parameters are missing or incorrect. Moreover, it will overwrite a previous existing report if the same name is given as a parameter again without warning. Another major difficulty with PMD is keeping track of the names of the rulesets. Most importantly it will not be able to compare the report files. Java Project Analyser (JPA) was developed to prevent these hurdles and improve the user experience in this study. Using JPA is considerably easier because it can be used via the graphical user interface after running the file named JPA.jar.

3.2. How JPA works

The following describes how JPA works with sample test codes. JPA is developed for this study and its main window can be seen in Figure 8.

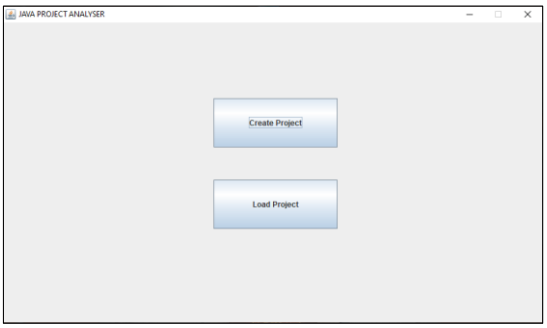

Figure 8. JPA main window

As shown in Figure 8, when JPA is first run, a window with two buttons is displayed. The first button can be used to create a new project for analysis, or the second button can be used to re-analyze an existing project or compare old analyses. To test with JPA, two source code files named "CodingHorror.java" and "StringHorror.java" are prepared in the "TestCodeFolder" folder and the codes are given in Figure9.

CodingHorror.java

```java
package testSrc;

public class CodingHorror {

    public static void main(String args[]) {

        //Violations for AvoidUsingShortType -Start-
        short doNotUseShort = 1;
        short shouldNotBeUsed = 2;
        //Violations for AvoidUsingShortType -End-
        doNotUseShort += shouldNotBeUsed;
        System.out.println("Short Variable 1 : " + shouldNotBeUsed);
        System.out.println("Short Variable 2 : " + doNotUseShort);

        //Violations for BooleanInstantiation -Start-
        Boolean bar = new Boolean("true");
        System.out.println("Boolean Variable 1 : " + bar);
        //Violations for BooleanInstantiation -End-

        Boolean buz = Boolean.FALSE;
        System.out.println("Boolean Variable 2 : " + buz);


        String s = StringHorror.retS();
        System.out.println("String Variable 1 : " + s);
        String t = Integer.toString(456);
        System.out.println("String Variable 2 : " + t);
    }
}
```

StringHorror.java

```java
package testSrc;

public class StringHorror {

    public static String retS() {

        //Violations for AddEmptyString -Start-
        String s = "" + 123;
        //Violations for AddEmptyString -End-
        return s;
    }
}
```

Figure 9. CodingHorror.java and StringHorror.java

These codes run successfully and are sent to the command screen. However, there are three violations in these codes, one high priority (1), one medium high priority (2) and one medium priority (3) in the performance ruleset of PMD. Explanations for these three violations are given in Figure 10.

Rule Name	Priority	Definition
AvoidUsingShortType	1. High	Using "short" data type is beneficial for memory. However, since JVM can only perform arithmetic operations for data types "int" and "long", it requires to convert "short" to "int" when processing the value, and converts the result back to "short". This would result for losing of performance when trying to get more memory gains.
BooleanInstantiation	2. Medium High	Avoid using "new Boolean()" object. It can be referenced "Boolean.TRUE" or "Boolean.FALSE" instead. Also, using "new Boolean()" object is deprecated since JDK 9.
AddEmptyString	3. Medium	It is better to use one of the type-specific "toString()" methods to convert variable types to "string" instead of aggregating them with empty string ("").

Figure 10. PMD violations in sample codes

To analyze the test code with JPA, select the folder with the "Create Project" button as in Figure 11.

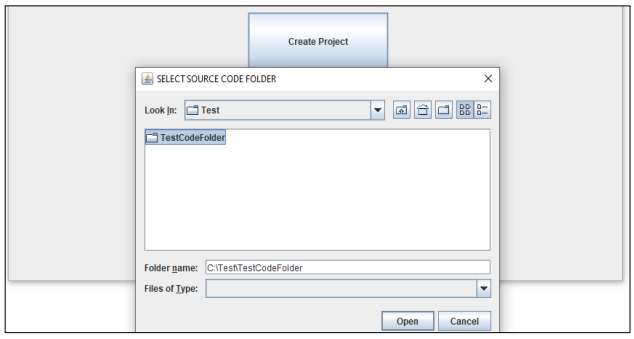

Figure 11. Selecting source code folder

After selecting the folder, ruleset(s) need to be selected to run analysis otherwise program will give error as shown Figure 12.

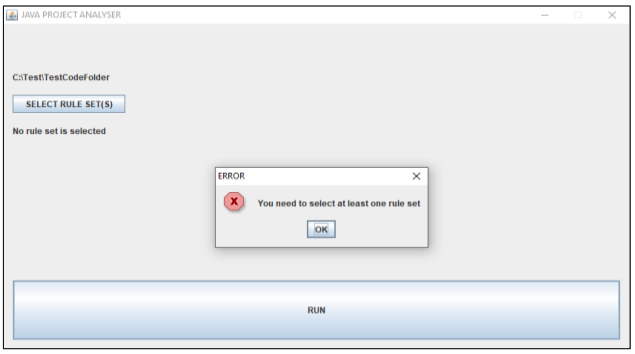

Figure 12. Error because ruleset(s) is not selected

"SELECT RULE SET(S)" button is used to select the ruleset(s). From the window that opens, the rulesets can be selected. For the test code "Performance" rule set was used, as in Figure 13.

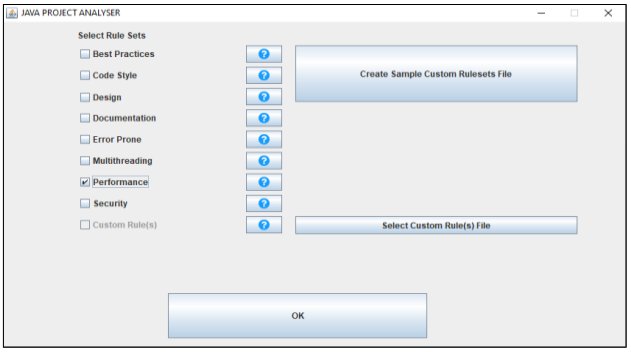

Figure 13. Ruleset(s) selection

Considering that this was just a demonstration and not a complete test, it was not necessary to use the entire performance ruleset for the test codes here. Since the example codes are known to contain three violations, "Custom Ruleset" file could be prepared in "xml" format as shown in Figure 14. and used at the rule selection shown in Figure 13.

```xml
<?xml version="1.0"?>

<ruleset name="Custom Rules"
    xmlns="http://pmd.sourceforge.net/ruleset/2.0.0"
    xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance"
    xsi:schemaLocation="http://pmd.sourceforge.net/ruleset/2.0.0 http://pmd.sourceforge.net/ruleset_2_0_0.xsd">

  <!-- Add AvoidUsingShortType,AvoidUsingShortType and AddEmptyString rules from Performance Rule Set -->
  <rule ref="category/java/performance.xml" />
    <exclude name="AvoidUsingShortType"/>
    <exclude name="AvoidUsingShortType"/>
    <exclude name="AddEmptyString"/>
  </rule>

</ruleset>
```

Figure 14. Custom ruleset xml file

After returning with "OK" button, selected rule sets are listed and with "RUN" button analysis starts. JPA uses PMD APIs to analyze the project and stores the generated report in SQLite database with the name ".AOP.db" in the same folder as test codes. To open the report, press the "OPEN REPORT" button as shown in Figure 15. The schema of the database is given in Figure 16.

As can be seen in Figure 17., the report can be reviewed together for all source code files or separately for each source code file.

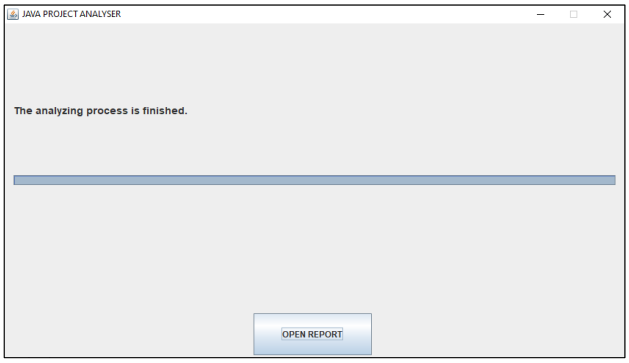

Figure 15. Post analysis confirmation screen

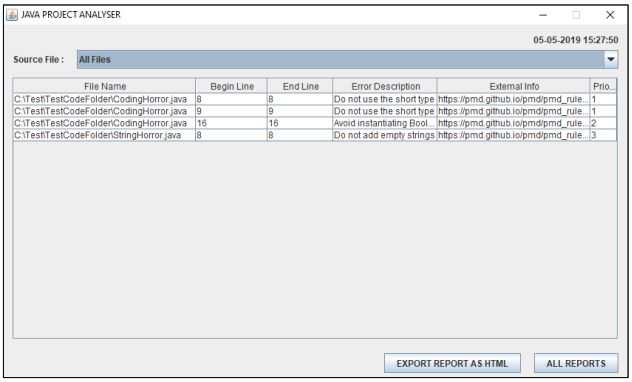

Figure 17. Generated report

"ALL REPORTS" button opens the window listing all the reports. In this window, the old reports can be viewed, the reports can be deleted or compared. At least two reports are needed for comparing or program gives error as expected shown in Figure 18.

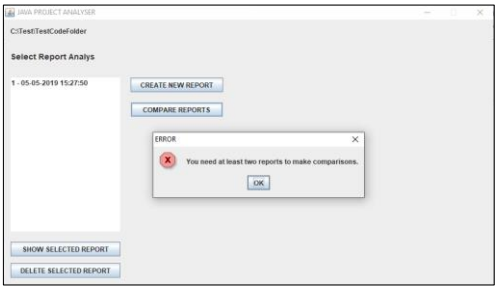

Figure 18. Error when try to compare reports

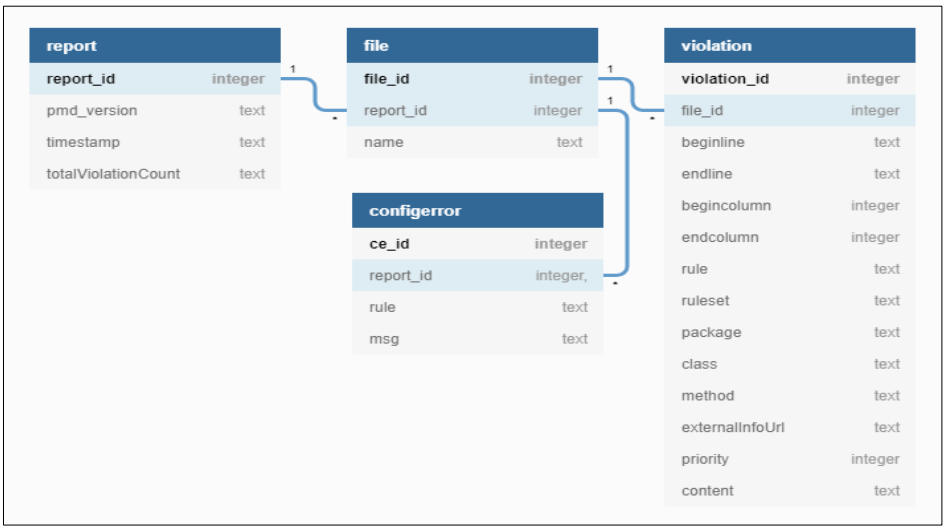

Figure 16. Database scheme for ".AOP.db"

Before creating new report, change the codes like in Figure 19. to eliminate violations. In order to ignore a violation and keep the code by PMD, just type "//NOPMD" at the end of that line if the violation consists of a single line. For multi-line violations there are several ways to ignore can be found on PMD documentation under "Suppressing Warnings" title.

In this example a single line suppression was typed in line 8 of the "StringHorror.java" source file, "short" variable type in lines 8 and 9 has been replaced with "int" in the source file "CodingHorror.java". Only the violation in line 16 remains.

CodingHorror.java

```
1  package testSrc;
2
3  public class CodingHorror {
4
5      public static void main(String args[]) {
6
7          //Violations for AvoidUsingShortType -Start-
8          int doNotUseShort = 1;
9          int shouldNotBeUsed = 2;
10         //Violations for AvoidUsingShortType -End-
11         doNotUseShort += shouldNotBeUsed;
12         System.out.println("Short Variable 1 : " + shouldNotBeUsed
13         System.out.println("Short Variable 2 : " + doNotUseShort);
14
15         //Violations for BooleanInstantiation -Start-
16         Boolean bar = new Boolean("true");
17         System.out.println("Boolean Variable 1 : " + bar);
18         //Violations for BooleanInstantiation -End-
19
20         Boolean buz = Boolean.FALSE;
21         System.out.println("Boolean Variable 2 : " + buz);
22
23
24         String s = StringHorror.retS();
25         System.out.println("String Variable 1 : " + s);
26         String t = Integer.toString(456);
27         System.out.println("String Variable 2 : " + t);
28     }
29 }
```

StringHorror.java

```
1  package testSrc;
2
3  public class StringHorror {
4
5      public static String retS() {
6
7          //Violations for AddEmptyString -Start-
8          String s = "" + 123; //NOPMD
9          //Violations for AddEmptyString -End-
10         return s;
11     }
12 }
```

Figure 19. Updated CodingHorror.java and StringHorror.java source code files

Figure 20 shows that only the "BooleanInstantiation" violation is reported when the analysis is performed again.

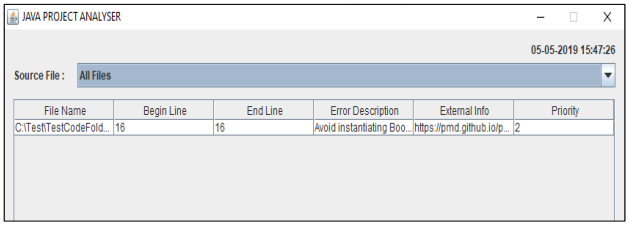

Figure 20. Generated report for updated codes

When comparing the two reports, as in Figure 21., only this violation is common.

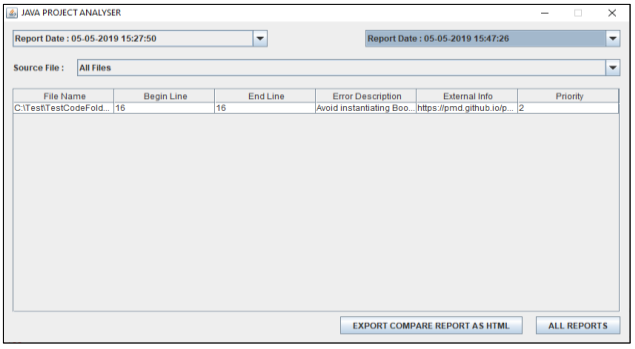

Figure 21. Comparison of reports

As in a single report view, the comparison of two reports can be exported as "html". Figure 22. shows the comparison of reports exported as "html".

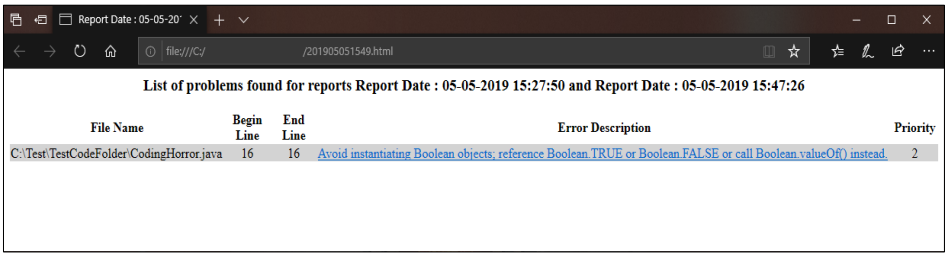

Figure 22. Comparison of reports exported as html

When reviewing reports in JPA, documentation page of a violation can be accessed from the column named "External Info". The same applies to the "Error Description" column when exporting the report as "html". The image of a sample documentation page for "BooleanInstantiation" violation that can be accessed through the link in the report in Figure 22. can be seen in Figure 23.

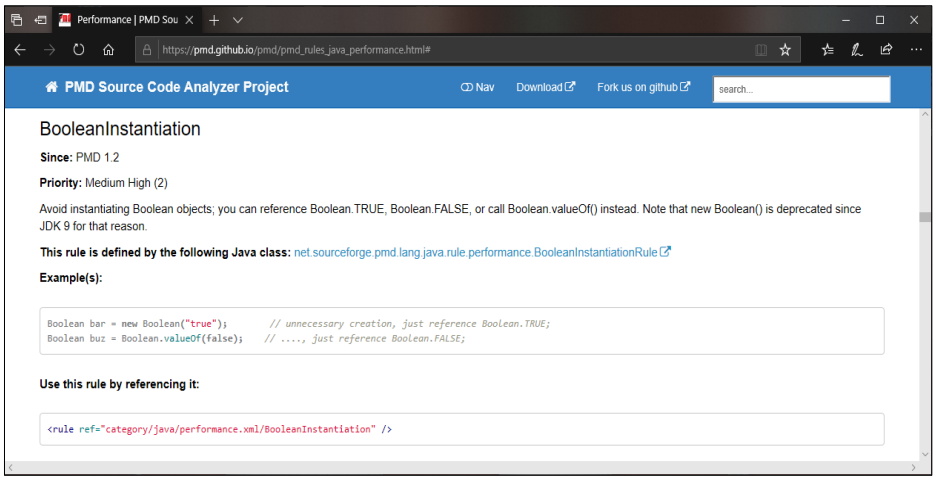

Figure 23. Documentation page for "BooleanInstantiation" violation

If a previously analyzed folder is selected as destination while creating a new project, it will notify user of the issue and ask whether to load the existing project or not, as shown in Figure 24. Similarly selecting an un-analyzed folder while loading a project will bring an appropriate notification, asking the user to create a new project or not as in Figure 25.

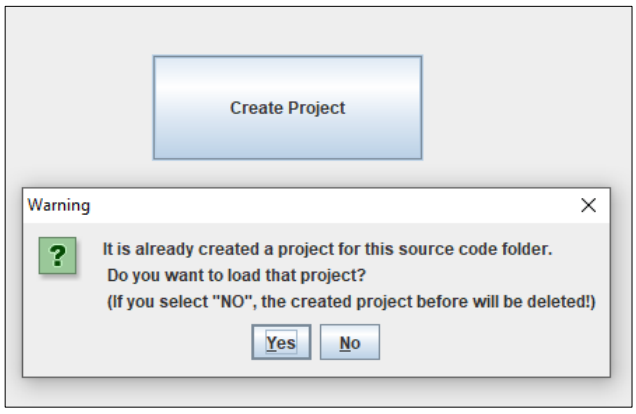

Figure 24. Warning for an already existing project where the new project is wanted to be created

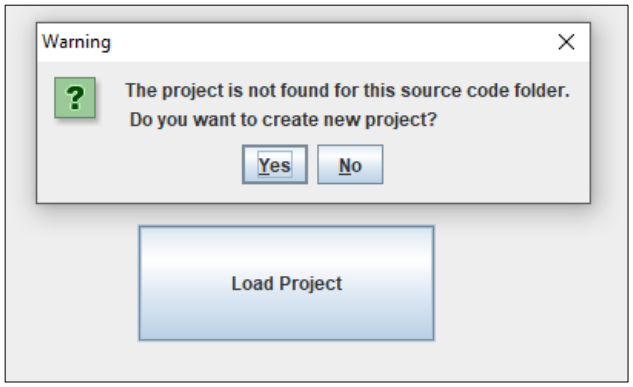

Figure 25. Warning for no existing project where the project is wanted to be loaded

4. DISCUSSION AND CONCLUSIONS

In this study, a platform independent tool is designed to perform static code analysis. The speed of execution of Java code is highly dynamic and fundamentally depends on Java Virtual Machine. An old piece of Java code may well

run faster on a more recent JVM, even without recompiling Java source code. Combining this fact with the possibility that refactoring may not sufficiently improve the software performance, software testing approach was preferred. It was decided to implement white box approach at source code level with statement coverage to optimize code. In order to cover all code lines, a tool has been developed based on PMD source code analyzer to perform static code analysis automatically and compare the analysis outputs.

Although PMD itself was a good starting point for static analysis there were obvious shortcomings to be improved. Plugins have been developed to integrate PMD source code analyzer into IDEs, Ant and Maven build tools by third parties. JPA, the tool built in this study, on the other hand has its own graphical interface and also can store and compare reports in its own database of projects. It has fundamentally been developed to improve the user experience in automating static code analysis. As a standalone program, JPA only needs source code for code analysis and does not require any IDEs or compilers. Since JPA keeps the reports methodically in a database form it can also be a useful tool in software testing development process.

This study provides detailed information about PMD source code analyzer and the tool built on PMD through its API's. Future studies may be done on automatic estimation for deciding which rulesets to use in code analysis using machine learning. Additionally, custom rule creation process may also be studied for improvement in the future. Furthermore, forthcoming updates and developments in PMD may inspire similar studies, or new ideas under new conditions that prevail at the time.

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Bilge International Journal of Science and Technology Research

ISSN: 2651-401X
e-ISSN: 2651-4028

2020, Volume: 4, Issue: 1, 43-47
Received: 21.02.2020; Accepted: 25.03.2020
DOI: 10.30516/bilgesci.692307

Comparison Of Time Consumption And Productivity During Beech Forest Felling And Processing In Two Different Working Conditions

Ylli Kortoci [1], Mirvjena Kortoci (Kellezi)*[1]

Abstract: This study was carried out in two countries, Italy and Albania. The aim of this research was to compare time consumption during felling and sorting works between two countries, considering the working conditions. The study was conducted in two utilization sites, one in each country, Monte Amiata site in Italy and Dardhe Xhyre in Albania. Field observation was used to determine the working conditions for each site. In Monte Amiata site it was noticed a delay working time of 40.13%, which is lower in comparison to Dardhe Xhyre, which was about 57.6%. Most of this time in both countries is an unavoidable delay time, respectively of 21.35% in Monte Amiata site and 36.93% in Dardhe Xhyre. Average productivity per gross hour in Monte Amiata is 3,480 m3 /h /team while in Dardhe Xhyre it is 3,610 m3 /h /team. Working conditions in Albania are worst compared with Italy, especially about accessibility and transport to the working place.

Keywords: Tree felling and sorting, working times, avoidable delay, unavoidable delay, productivity, working conditions.

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Citation: Kortoci, Y., Kortoci, M. (2020). Comparison of Time Consumption And Productivity During Beech Forest Felling And Processing in Two Different Working Conditions. Bilge International Journal of Science and Technology Research, 4 (1): 43-47.

1. INTRODUCTION

The distribution of forest species in Albania can be described as follows: beech accounts for about 21.6% of the surface; conifers, 19.6%; oaks 36.6% and 22.3% for other species. High forests represent approximately 45.5% of the total forest cover; coppice forests about 29.5%; shrubs, 25% (Kortoci and Kellezi, 2014). About 47% of the total timber volume comes from the use of beech forests, which is the main species in the Country. In terms of governance of beech forests, 90% of them are governed as high forest and only 10% as coppice. In Albania beech forests are generally located in marginal terrain where 70% of them belongs to the category of very rugged terrains (Kotro et.al. 1996).

Beech forests in Italy extend over 550,000 hectares; they can be governed as high forest or coppice. In Italy, the beech coppice (around 330,000 hectares), dominating the Alpine arc and the northern Apennines, has been widespread in relation to the growing demand for firewood and coal that has practically occurred up to half of the last century (Hofmann, 1991).

Time consumption of forest harvesting is studied for various reasons. The most typical task is to investigate the main factors affecting work productivity (Mousavi R., Naghdi R.).

The main factors which have influences on working times are the volume of logged trees, sorting type, the availability of suitable tools, the ability of workers and the efficiency of the organization and direction of the work. The working times increase while tree volume increases. Considerable reductions of working times can be achieved by sorting only the main assortments (Hippoliti and Piegai, 2000).

The objective of comparative studies is to compare two or several machines, working methods, etc, (Bergstrand, 1991).

The higher productivity suggest that forest workers are well motivated, properly trained and adequately remunerated (Ole-Meiludie & Fue).

Working without any breaks results in fatigue. This increases accidents, illness, discomfort and this reduce the productivity (Axelsson, 1998).

The aims of this study were to compare working times and productivity in felling and wood processing between two different working conditions, one in developed countries and the other one in developing countries.

2. MATERIALS AND METHODS

2.1. Study site

Monte Amiata has an elevation of 1680 meters above sea level. The climate of this area can be associated, within the temperate zone, with Mediterranean climates. Rainfall is on average more widespread around the reliefs. From a geomorphologic point of view, the territory of Tuscany region is generally very rough, hills and mountains represent 90% of the total area.

Beech is the dominant species of "Monte Amiata", and in this case it was managed as high forest. A few fir seedlings can be found sporadically distributed on the surface examined.

The apparent age of the forest was around 60-80 years old. The trees cut in this forest were old standards with a density of about 200 - 250 plants per hectare, a diameter greater than 60 cm, and average height of the trees varied between 20 - 25 m. This terrain is considered of the third class of slope (40-60%).

The maximum height above sea level in Dardhe Xhyre is 2253 meters, within continental climate conditions, which can be noticed in the fairly cold period of winter. In addition to cold temperatures, winter in this area is very humid, but summer is short, hot and very dry.

Beech is the dominant species also in Dardhe Xhyre, covering about 95% of the surface. The forest was about 100 years old, and clear cut of an area of 20 hectares was performed in this case. The diameter of plants was greater than 50 cm, and the height reached 20 - 25 m. The terrain was rough, with many holes and stones and it is considered of the third class of slope (40-60%).

This study examines forest logging and sorting by analyzing working phases, productivity, operators and machines safety in two different sites of beech forest.

The harvesting method applied in "Monte Amiata" is mixed by "cut to length" and "short wood system", this last for firewood production. The same harvesting method is used in Dardhe Xhyre.

2.2. Measurements and statistical analysis

In both the examined utilization sites, productivity data were collected, calculated and analyzed toward the applied methodologies. The equipments used for field data acquisition were an analogue chronometric table "Minerva", equipped with three chronometers with subdivisions per hundredth of a minute, a 40 cm “Haglof” caliper used for diameters measurement and a 25 m long self-rolling metric cord for distances. The distribution of times during the day has been estimated concerning each working phase and volume of harvested trees. "Working time" generally includes a whole series of items, but in the specific case only the following units have been taken into consideration: productive times, during which the workers and equipments are present in the workplace, accessory times subdivided into “service” and “preparation”, during which the workers and vehicles are present on the work area but do not perform functions directly finalized to the specific operation, operating times obtained by the sum of those mentioned before, non-operating times divided into various sub-items representing moments in which workers and equipments are physically stopped and not busy in any kind of jobs .

Hourly productivity was calculated on the basis of the working times and volume of material harvested, respectively average net hourly productivity based on the operating times, and average gross hourly productivity based on the total times. From these data, the respective daily productivity was then deduced referring to 8 gross hours.

For the determination of fresh density, three samples for each single plant positioned one at the base, one at mid-height and one at the top were taken on 10 plants. For each sample it was measured the fresh weight with bark, the two orthogonal diameters of each circle of wood and the thickness at the four external points. These values were used to calculate the volume.

The felling and bucking operation in Monte Amiata was performed by a single team of two workers. The division of work was as follows: the first operator, through the help of one "STIHL MS 660" chainsaw, cut down and bucked the trees, while the second one delimbed the felled stems and piled up the brushwood by using a "STIHL MS 362" chainsaw. While in Dardhe Xhyre the team was composed by two workers, the first one using a "STIHL MS 660" chainsaw performed the trees cutting down, bucking and delimbing of large branches, and the second operator helped by an ax, carried out the limbing of the small branches and piled up the brushwood.

During the felling and bucking phases, the following data were collected: approach time or the time for the team to approach the plant to be felled, notch time or the time needed by the chainsaw to make the directional notch on the plant to be cut, cutting time or the time it takes for the chainsaw to perform the felling cut, fall time or the time from the moment the plant starts to tilt until it reaches the ground, knockdown time that is the time it takes for the team to knock the plant down when it hungs up on the standing plants, unavoidable delay (dead) time, which are non-operational times used for breakfast, accidents or physiological needs, avoidable delay (dead) time, or non-operating times, when workers chatted, or had to lower the height of the stump, number of plants cut down, diameter of the felled plants, diameter in the middle and total length of a sample of plants, delimbing and bucking time of the plant.

Correlation and regression analysis have been performed to determine the dependence of working times from the breast height diameter of tree.

3. RESULTS

Wood density has been used to determine the weight after calculating volume of trees cut down.

Table 1. Fresh wood density in both study sites.

Harvest sites	Fresh wood density (g / cm^3)
Monte Amiata (fustaia)	1.007
Librazhdi	1,392

From the analysis of working times, a high percentage of delay times is present in both sites. This percentage in Monte Amiata is 40.13% while in Dardhe Xhyre it is almost 57.6% mainly due to the very scarce road accessibility in Albania. Most of these times are unavoidable delay time, 21.35% in Monte Amiata and 36.93% in Dardhe Xhyre, while about the time spent in total work phases, the biggest part belongs to tree bucking, 45% in Monte Amiata because of the diameter of trees, and 33% in Albania.

Table 2. Total values of the working times of felling, bucking and delimbing phases in both study sites.

Working times	Monte Amiata	Dardhe Xhyre
Gross Total Time (min)	1225,92	223,13
Net Total Time (min)	995,68	176,99
Total delay (dead) times	492,01	128,54
Avoidable delay times	230,24	46,14
Unavoidable delay times	261,77	82,4

For each sub-phase of work, the average net time and its standard deviation were determined, trying to highlight how much the bucking time affects the average cutting time per plant.

Table 3. Average felling and sorting (bucking and delimbing) times and standard deviation for tree divided into phases in both study sites.

Average times	Monte Amiata		Dardhe Xhyre	
	Per tree (min)	Standard deviation	Per tree (min)	Standard deviation
Passage time	1,54	0,78	2,46	0,32
Notch time	2,15	0,70	0,70	0,21
Cutting time	1,47	0,79	2,01	0,99
Bucking and delimbing	13,86	7,08	13,05	4,52
Avoidable delay time	5,48	6,90	7,69	4,52
Unavoidable delay time	6,23	6,10	13,73	14,56
Total net time	28,25		31,95	
Total gross time	30,73		39,64	

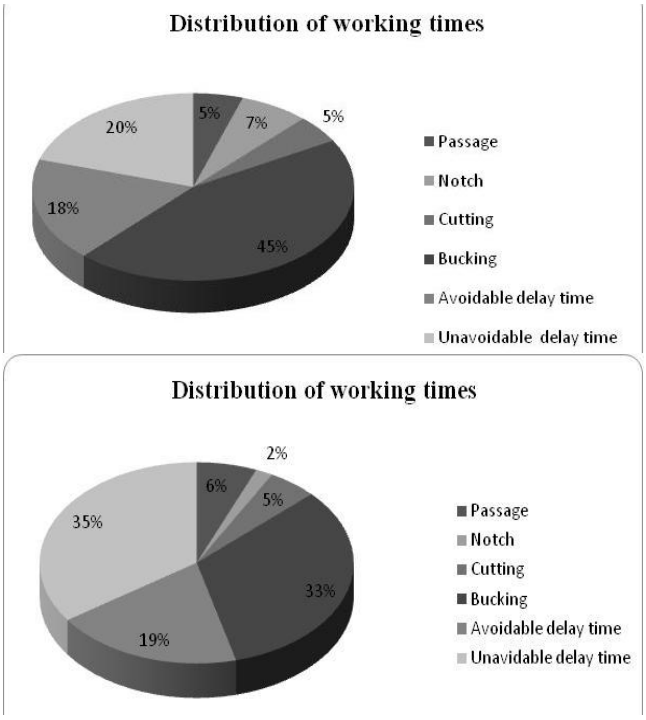

Figure 1. Percentage distribution of total working times respectively in Monte Amiata and Dardhe Xhyre.

It is obvious in both situations that bucking time has the biggest percentage (respectively 45% and 33%) of the total working time spent.

During the felling, tree diameters were measured and then the correlation with the respective felling times was made, as shown in the following graph.

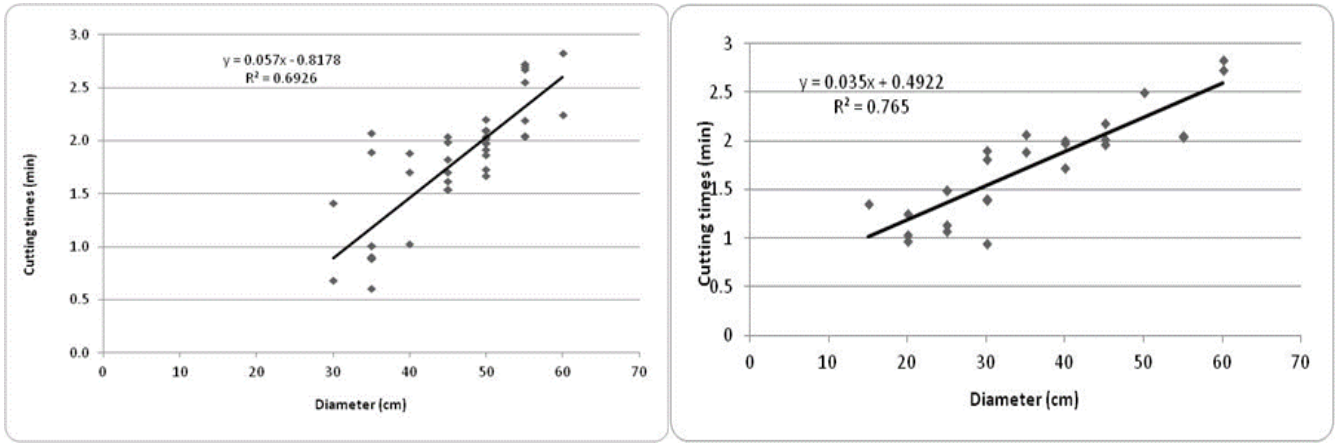

Figure 2. Correlation between diameter of cut trees and felling times respectively in Monte Amiata and Dardhe Xhyre.

There is a significant positive linear correlation between the diameter and working times in both cases.

Productivity was calculated both per team and per worker, considering the working day made up of 8 gross hours. The volume cut down in Monte Amiata was 73.477 m3, corresponding to a weight of 73.9 t. The volume cut down in Dardhe Xhyre was 13.42 m3, corresponding to a weight of 17.83 t.

It has to be stressed that a working day in Albania lasts only 4 hours because the workers need 3-4 hours to reach the working place. The real productivity is nearly the half of the potential productivity.

Table 4. Real gross and net productivity calculated per hour and per team in meter cube and in tons for both study sites.

Productivity	Monte Amiata	Dardhe Xhyre
Gross hourly average productivity (m^3/h/team)	3,480	3,610
Hourly average production net of ADT (m^3/h/team)	4,430	4,550
Gross hourly average productivity (t/ h/team)	3,50	4,79
Hourly average production net of ADT (t/ h/team)	4,46	6,04
Gross daily average productivity (m^3/day/team)	27,840	14,440
Gross daily average productivity (t/day/team)	28,00	19,16
Daily average productivity net of ADT (m^3/day/team)	35,440	18,200
Daily average productivity net of ADT (t/day/team)	35,68	24,16

In Albanian case potential productivity is calculated for both team and workers, taking into account a composite workday of 8 gross hours.

Table 5. Potential gross and net productivity calculated per hour and per team in meter cube and in tons for Dardhe Xhyre considering the day work of 8 hours.

Productivity	Dardhe Xhyre
Gross hourly average productivity (m^3/h/team)	3,610
Hourly average production net of ADT (m^3/h/team)	4,550
Gross hourly average productivity (t/ h/team)	4,79
Hourly average production net of ADT (t/ h/team)	6,04
Gross daily average productivity (m^3/day/team)	28,880
Gross daily average productivity (t/day/team)	38,32
Daily average productivity net of ADT (m^3/day/team)	36,400
Daily average productivity net of ADT (t/day/team)	48,32

A very important aspect to be stressed is that in both cases the security during work performance is almost inexistent, even though it is very important to be respected.

4. DISCUSSION AND CONCLUSIONS

The main purpose of this study was to compare beech forest harvesting, felling and processing, between Italy and Albania.

In Albania the road infrastructure is very scarce and not very present. The time needed for workers to reach the workplace was excessive (3-4 hours).

The productivity was almost the same in both areas because workers in Albania, taking into account the time spent to reach the working place, worked harder and with very limited breaks to compensate the time lost. According to this, the avoidable delay times are lower in Albania than in Italy. The unavoidable delay times were mostly due to the poor preparation of the workers and the lack of organization both in Italy and in Albania.

In Albania the beech is the most important forest species and, given the quality of its wood, it represents a great economic potential for the forest sector and for the whole Country. To ensure that the supply chains related to this species (timber and firewood) can develop, creating then new job opportunities, it is a first priority to ensure that operators,

often inexperienced, are informed about the principles of beech forestry. In fact, it is necessary that silvicultural treatments are carried out in the correct way and through the right working times to ensure the development of the stands and their safeguard.

Studies about these problems in Albania are almost inexistent.

To reduce the non-productive times due to the movement of workers, temporary shelters in the forest with beds and kitchen could be built, so that they can stay there from Monday to Friday without having to move for 3 - 4 hours.

(Halilovic et. al. 2017) reports unavoidable delay time is 30.79%, and avoidable delay time is 2.09% in his research about felling and processing work times. Tree cutting as a work operation participates with 8.46% in total time, that is a little bit higher comparing to our study, where cutting operation takes 5% of total work time.

(Halilovic et. al. 2017) reports that "Moving from tree to tree" operation takes a share of 7.58% of total time comparing to our study results where "Passage" occupied 5-6% of total work time.

ACKNOWLEDGEMENTS

We are grateful to Kole Sinani entrepreneur of the harvesting company of Dardhe Xhyre forest and Universita degli Studi della Tuscia for allowing us to conduct this field experiment on their lands.

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