JOURNAL OF THE FACULTY OF FORESTRY ISTANBUL UNIVERSITY
İSTANBUL ÜNİVERSİTESİ ORMAN FAKÜLTESİ DERGİSİ
ISSN: 0535-8418 e-ISSN: 1309-6257

Online available at / Çevrimiçi erişim
http://dergipark.gov.tr/jffiu - http://dx.doi.org/10.17099/jffiu.292273

Research Article / Araştırma Makalesi

Thermal behavior of *Liquidambar orientalis* mill wood before and after extraction processes

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Received (Geliş): 14.02.2017 - **Revised (Düzeltme):** 06.04.2017 - **Accepted (Kabul):** 25.04.2017

Abstract: The effect of extractives on the thermal behavior of *Liquidambar orientalis* Mill. (storax) wood is studied using thermogravimetric analysis (TGA). To evaluate the effects of polar and apolar extractives on the thermal behavior of wood, sawdust samples from the heartwood of *L. orientalis* are extracted with either cold water (48 h), hot water (48 h), or ethanol/toluene (1:2 v/v) (6 h) prior to thermal analysis. Thermogravimetry (TG) curves show that polar and apolar extractives promote char formation, increase the amount of residue, and improve the thermal behavior of *L. orientalis* wood. In addition, derivative thermogravimetry (DTG) curves demonstrate that thermal degradation of un-extracted and cold water-extracted wood samples occurs in a single step, while a two-step degradation pattern is seen for hot water- and ethanol/toluene-extracted wood samples. It is also observed that first degradation reactions in hot water and ethanol/toluene-extracted wood samples occur faster than those in unextracted and cold water-extracted wood samples. Although there are approximately half the number of extracted apolar compounds compared to polar compounds, the removal of both types of compounds affect the thermal properties of *L. orientalis* wood to the same degree. It is thus deduced that apolar extractives significantly affect the thermal behavior of *L. orientalis* wood.

Keywords: Wood extractives, thermogravimetric analysis, *Liquidambar orientalis*, storax wood, thermal degradation, natural fire retardants

Ekstraksiyon işlemleri öncesi ve sonrası *Liquidambar orientalis* mill. odununun termal davranışı

Özet: *Liquidambar orientalis* Mill. odununun termal davranışı üzerine ekstraktif maddelerin etkisi termogravimetrik analiz (TGA) yöntemiyle incelenmiştir. L. orientalis öz odunundan elde edilen öğütülmüş odun unu örnekleri termal analizler öncesinde polar ve apolar ekstraktiflerin odunun termal davranışı üzerine etkisinin araştırılması amacıyla soğuk su (48 s), sıcak su (48 s) ve etanol/toluen (1:2 v/v) (6 s) ekstraksiyonlarına tabi tutulmuştur. Termogravimetri (TG) eğrileri polar ve apolar ekstraktiflerin kömürleşmiş tabaka oluşumunu desteklediğini, kalıntı madde miktarını artırdığını ve *L. orientalis* odunun termal davranışını iyileştirdiğini göstermiştir. Türevsel termogravimetri (DTG) eğrileri ise ekstraksiyon işlemi uygulanmamış ve soğuk su ile ekstraksiyonuna tabi tutulmuş odun unu örneklerinde termal bozulmanın tek aşamada gerçekleşirken sıcak su ve etanol/toluen ekstraksiyonuna tabi tutulmuş örneklerde termal bozulmanın iki aşamada gerçekleştiği tespit edilmiştir. Ayrıca, sıcak su ve etanol/toluen ekstraksiyonuna tabi tutulmuş örneklerde ilk termal bozulma reaksiyonlarının ekstraksiyon işlemi uygulanmamış ve soğuk su ile ekstraksiyonuna tabi tutulmuş odun unu örneklerine göre daha hızlı olduğu tespit edilmiştir. Ekstrakte edilen apolar bileşiklerin miktarı polar bileşiklerin yaklaşık yarısı kadar olmasına rağmen apolar bileşiklerin ekstraksiyonunun *L. orientalis* odununun termal özellikleri üzerine polar bileşikler ile aynı seviyede etkilediği tespit edilmiştir. Bu durum, *L. orientalis* odununun apolar ekstraktiflerinin odunun termal davranışını önemli derecede etkileyebildiğini ortaya koymaktadır.

Anahtar kelimeler: Odun ekstraktiflerin, termogravimetrik analiz, Liquidambar orientalis, sığla odunu, termal bozulma, doğal yangın geciktiriciler

Cite (Atıf) : Terzi, E. 2017. Thermal behavior of *Liquidambar orientalis* mill wood before and after extraction processes. *Journal of the Faculty of Forestry Istanbul University* 67(2): 150-156. DOI: 10.17099/jffiu.292273.

1. INTRODUCTION

Wood may have different thermal degradation profiles depending on its chemical composition. Since cellulose is a thermally stable polymer, the hemicelluloses and lignin are degraded before cellulose during thermal degradation. Different types of wood extractives, on the other hand, can promote or demote of thermal degradation of wood and have an effect on thermal behavior of wood material. Some extractives, however, do not pose any significant impact on the thermal behavior of wood material. Mészáros et al. (2007) compared extracted and un-extracted *Robinia pseudoacacia* woods and found that extracted wood showed slight differences in the thermal behavior compared to the un-extracted wood. According to Várhegyi et al. (2004), the removal of extractives from *Castenea sativa* wood caused a decrease in the fixed carbon content, a decrease in char yield and a displacement of the entire TG curve towards higher temperatures. Compared with *C. sativa* the effects of extractions were less for beech wood. Shebani et al. (2008) founded that the removal of extractives from *Quercus alba, Pinus radiata*, *Eucalyptus grandis* and *Acacia cyclops* woods TG and DTG curves shifted to higher temperatures and the final amount of residue (char) decreased in all wood species.

The aim of the recent study was to investigate the effect of extractives on the thermal behavior of heartwood extractives of *Liquidambar orientalis* Mill. (storax) wood. *L. orientalis* trees are ecologically and economically important in Turkey due to balsam content in their barks, which is mainly used in cosmetics and pharmaceutical industry (Öztürk et al. 2008), even though the number of *L. orientalis* trees have been declined seriously in the country (Alan and Kaya 2003). In recent years, however, various attempts regarding the protection of *L. orientalis* trees, the formation of new plantations, the regeneration of ecosystem in *L. orientalis* forests, the formation of novel management plans for balsam production, *etc.* have been made by The Turkish Government. Since *L. orientalis* wood has very limited usage as a construction material, such as for furniture, veneer production, ornamental and decoration goods, *etc.* (Bozkurt et al. 1989; Doğu et al. 2002), no detailed investigations have been made on its various properties. Recently, a series of studies were performed to evaluate the resistance of *L. orientalis* wood and balsam and its main constituents against wood decay, mold fungi, termite and insects, along with its chemical properties (Kartal et al. 2012; Terzi et al. 2012). In this study, thermogravimetric analysis (TGA) curves were used to quantify the weight loss and thermal degradation steps and to compare the thermal behavior of wood before and after different extraction procedures that removed different types of extractives. Knowledge about thermal effect of wood extractives on wood might be useful to improve natural fire retardants for wood products.

2. MATERIAL AND METHODS

2.1 Heartwood Sawdust

One *Liquidambar orientalis* Mill. tree was obtained from Muğla, Turkey. Since chemical properties can vary according to the position (from the top to the bottom trunk) in the heartwood from which an item of wood is taken, heartwood portions from the trees to be used in the study was cut from a disk (20 cm thick) obtained at breast height (1.3 m above ground level) of the tree. Heartwood portions were cut from the center area of heartwood discs since properties can change from the heartwood boundary towards the pith. The heartwood portions chosen were free of knots or any visible concentration of resins, and showed no visible evidence of infection by mold, stain, or wood-destroying fungi. The heartwood portions of *L. orientalis* was ground in the Richter mill and screened through 40 to 80-mesh sieve to obtain sawdust samples.

2.3 Extraction Processes

Sawdust samples were extracted with either cold water (48 h), hot water (48 h) or ethanol/toluene (1:2 v/v) (6 h) in accordance with the Technical Association of the Pulp and Paper Industry (TAPPI) standards TAPPI T 207 cm-99 (TAPPI, 1999a) and TAPPI T 204 cm-97 (TAPPI, 1999b).

2.4 Thermal Analyses

Thermal degradations of extracted and un-extracted-wood sawdust samples were carried out by using Perkin Elmer Diamond Thermal Analysis Instrument (Perkin Elmer Diamond TG/DTA), which was calibrated using the melting points of indium (T_m=156.6°C) and tin (T_m=231.9°C) under the same conditions as the sample. The analyses were performed at a heating rate of 10°C/min. in an atmosphere of nitrogen that had a constant flow rate of 100 ml/min. The sawdust samples (~5 mg) were allowed to settle in standard alumina crucibles and heated up to 800°C.

3. RESULTS AND DISCUSSION

3.1 Solubility of Heartwood of *L. orientalis*

Table / Tablo 1 gives solubilities of the heartwood samples of *L. orientalis* by cold water, hot water and ethanol/toluene. Higher solubilities were obtained by hot water extraction in comparison with those by cold water and ethanol/toluene extractions.

Table 1. Solubility of *L. orientalis* heartwood samples
Tablo 1. *L. orientalis* öz odununun çözünürlüğü

Solubility Type	**Solubility (%)**
Ethanol/toluene solubility	2.66
Cold water solubility	1.36
Hot water solubility	5.80

3.2 Thermal Behavior of Extracted and Un-extracted *L. orientalis* Wood Samples

Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves were obtained from thermal analysis (Figures / Şekil 1 and 2). The initial thermal degradation temperature (T_i), the maximum thermal degradation temperature (T_m), the final thermal degradation (T_f) and the amount of char residue were obtained from TG and DTG curves summarized in Table / Tablo 2. TG and DTG curves were used to determine thermal behavior of extracted and un-extracted sawdust samples. All curves showed around 7 to 8% weight loss because of the evaporation of water, which was not evaluated in order to explain the thermal behavior of the wood samples as described in Reaction Step 1 (Table / Tablo 2). The weight loss rate increased above 200°C for all wood samples. Main weight losses were observed between 200°C and 400°C for un-extracted and cold water-extracted wood samples, in which the weight losses were approximately 69 and 75%, respectively. This phase was observed to be Reaction Step 2. In contrast, the main weight losses continued until the temperature of 500°C for ethanol/toluene- and hot water-extracted wood samples. These wood samples exhibited a loss of about 89 and 90%, respectively, during Reaction Steps 2 and 3. Main weight losses can be attributed to the degradation of cellulose, the hemicelluloses and lignin. The TG curves obtained from thermal analysis showed that the extracted wood samples had lower residue (char yield) than the un-extracted sawdust sample at 800°C. The residue yield can be used to explain thermal stability of the wood and higher thermal stability gives rise to a higher amount of residue after thermal degradation. Hot water and ethanol/toluene extractions caused a decrease in thermal stability of *L. orientalis* wood because of its lower residual yield.

In the case of the extraction of wood samples with hot water and ethanol/toluene, the TG and DTG curves shifted to lower temperatures. This can be attributed to a reduction in thermal stability, which can be supported by decreasing the amount of residue at 800°C. This validation is necessary because some treatments can shift the curves of TG and DTG for wood samples to a higher temperature while the amount of residue increases (Hirata et al., 1991; Terzi et al., 2009). Ethanol/toluene as an organic solvent can dissolve apolar extractives, such as waxes, fats, resins, some gums, *etc.* On the other hand, hot water and cold water as an inorganic solvent can dissolve polar extractives, such as tannins, gums, starches, *etc.* (Shebani et al., 2008). Results showed that polar and apolar extractives of *L. orientalis* promote char formation, increased the amount of residue and improved thermal stability of *L. orientalis* wood. This observation could be attributed to how char formation acts as an insulation layer against thermal degradation (Le Van, 1989; Marcovich and Villar, 2003).

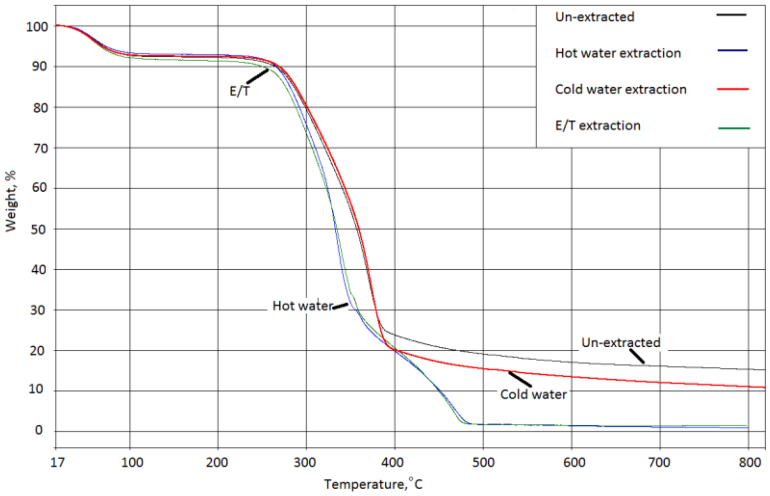

Figure 1. TG curves of extracted and un-extracted sawdust samples
Şekil 1. Ekstrakte edilmiş ve edilmemiş odun örneklerinin TG eğrileri

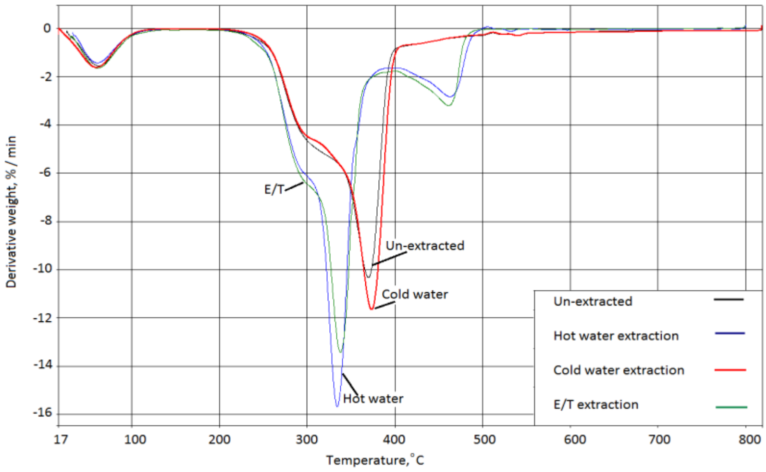

Figure 2. DTG curves of extracted and un-extracted sawdust samples
Şekil 2. Ekstrakte edilmiş ve edilmemiş odun örneklerinin DTG eğrileri

Table / Tablo 2 shows the reaction steps, reaction temperatures and amount of residues at 800°C of un-extracted and extracted wood samples. T_i is the initial temperature at which degradation starts. T_m is the maximum thermal degradation temperature, which produces the most parallel point to the axis on the TG curve and shows peaks in the DTG curves. T_f is the final thermal degradation temperature, above which does not appear as shoulders or peaks in the TG and DTG curves within its reaction step. The first degradation event was observed at about 240°C for un-extracted and cold water-extracted wood samples and at about 208°C and 230°C for hot water- and ethanol/toluene-extracted wood samples, respectively.

The DTG curves showed that thermal degradation of un-extracted and cold water-extracted sawdust samples occurred in a single step (Reaction Step 2), while hot water- and ethanol/toluene-extracted sawdust samples occurred in two steps (Reaction Steps 2 and 3) (Table / Tablo 2). Reaction Step 2 was described as “the main degradation step.” It is clear in Figure 2 that the first reaction step related to the thermal degradation of wood samples continues up to around 330°C, 310°C, 300°C, and 310°C for un-extracted, cold water-, hot water- and ethanol/toluene-extracted sawdust samples, respectively. These temperatures produced the appearance of shoulders, which belong to degradation of the hemicelluloses (Orfao et al., 1999; Shebani et al., 2008; Gašparovič et al., 2009; Shen et al., 2009). Shoulder peaks can be observed, particularly with deciduous woods, due to decomposition of the hemicelluloses since the hemicelluloses in those types of woods have a different composition of polysaccharides and react faster than coniferous woods. This fast reaction causes this shoulder formation (Prins et al., 2006; Shen et al., 2009). After the shoulders, reactions continue until 401°C and 405°C for un-extracted and cold water-extracted sawdust samples, respectively, giving a peak at about 370°C which belongs to degradation of cellulose dominantly. After temperature levels of 401°C and 405°C for un-extracted and cold water-extracted wood samples, there are no peaks or shoulders, but weight losses continue due to degradation of the remaining lignin (Orfao et al., 1999; Shebani et al., 2008; Gašparovič et al., 2009; Shen et al., 2009).

Table 2. Thermal degradation temperature and amount of char residue of extracted and un-extracted sawdust samples
Tablo 2. Ekstrakte edilmiş ve edilmemiş odun örneklerinin termal degradasyon sıcaklıkları ve kalıntı kömür miktarı

Sawdust Type	**Reaction Steps**	**T_i [°C]**	**T_m [°C]**	**T_f [°C]**	**Char Residue at 800°C (%)**
Un-extracted	1	25.26	62.56	119.71	15
	2	241.23	371.43	401.81	
Cold-water-extracted	1	17.19	60.41	107.29	11
	2	243.53	374.65	405.41	
Hot-water-extracted	1	33.01	60.83	110.20	1.5
	2	229.80	334.80	379.30	
	3	379.30	462.74	502.38	
E/T-extracted	1	29.96	60.64	132.46	1.2
	2	208.46	338.84	400.20	
	3	400.20	462.26	519.43	

On the other hand, after the shoulders, reactions continue until about 380°C and 400°C for hot water-and ethanol/toluene-extracted sawdust samples, respectively, which belongs to the degradation of cellulose primarily. After 380°C and 400°C for hot water-and ethanol/toluene extracted-sawdust samples, a peak appears due to degradation of the remaining lignin unexpectedly. In general, DTG curves obtained from the thermal degradation of wood in an inert atmosphere do not yield a peak due to the thermal degradation of lignin. In contrast, DTG curves obtained from the thermal degradation of wood in an oxygen environment generally yield a peak due to the thermal degradation of lignin (Chauvette et al., 1985; Cordero et al., 1991; Orfao et al., 1999; Fang et al., 2006; Emandi et al., 2011; Niu et al., 2011).

4. CONCLUSIONS

In contrast to previous studies on the effect of extractives on the thermal properties for wood of various tree species, it is found that the extractives of *L. orientalis* wood increased the yield of char of *L. orientalis* wood (Várhegyi et al., 2004; Mészáros et al., 2007; Shebani et al., 2008). The extraction of the polar and apolar extractives caused a decrease in the thermal stability of *L. orientalis* wood. The cold water, hot water and E/T extracted-wood samples produced less char formation than un-extracted wood. On the other hand, it is known that tannins are effective in improving the fire resistance of wood as a natural fire retardant. Also, tannins could be used with boron and phosphorus to produce fire resistance wood (Tondi et al., 2012; González-Laredo et al., 2015).

In addition, thermal degradation started later for un-extracted wood than it did for hot water and E/T extracted wood samples. Despite the relatively low amounts of apolar comounds that could be extracted by E/T, which were about two times less than H/W extracted polar compounds, the removal of apolar compounds affected the thermal properties of *L. orientalis* wood to the same degree as the polar compounds.

Apolar extractives significantly improved the thermal stability of *L. oriantalis* wood. These extractives are also leach resistant potentially under wet conditions depending on their chemical structures. Apolar extractives of the *L. orientalis* wood could be further investigated individually.

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