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Investigation of Polycyclic Aromatic Hydrocarbons (PAHs) and Methoxyphenols (MPs) from Laboratory Scale Thermaloxidation of Waste Wood Samples

Atık Ahşap Örneklerinin Laboratuvar Ölçekli Isıloksidasyonu Sonucu Oluşan Polisiklik Aromatik Hidrokarbonların (PAHlar) ve Metoksifenollerin (MFler) Araştırılması

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Abstract

In the present study, Polycyclic Aromatic Hydrocarbons (PAHs) and Methoxyphenols (MPs)emitted from the low temperature oxidation of the waste wood samples were identified in thelaboratory scale small burning system. Four types of waste wood includinguntreated hardwood (HW), untreated softwood (SW), treated roof material (RM) and treated window frame (WF) were examined during the experiments. XAD-2 adsorbent tubes were used for sampling of the gaseous combustion products. After extraction of the sample tubes, extracts were analyzed by using the Hewlett Packard 6890 GC coupled with Agilent 5971 Mass Selective (MS) Detector.

The relative average contributions of the naphthalene, acenaphthylene and retene in hardwood samples were found higher than those measured in softwood. On the contrary, the relative average contribution of the phenanthrene, anthracene, fluoranthene, benzo(a)anthracene, chrysene and benzo(b)fluoranthene to the total PAH concentration in softwood samples were obtained higher as compared to hardwood sample. Syringol, 4-methyl syringol, 4 methyl guaiacol, eugenol, properlysyringol, 4-ethylsyringol, syringylacetone and iso-eugenol were found to be most abundant compounds in the hardwood samples. On the other hand, the most observed compounds in the softwood samples were 4-methylguacicol, iso-eugenol, eugenol and vanillin.

Keywords: Biomass, Waste wood, PAHs, Methoxy Phenols, Thermal oxidation, GC-MS

Öz

Bu çalışmada, atık ahşap örneklerinin düşük sıcaklıkta oksidasyonu sonucu oluşan Polisiklik Aromatik Hidrokarbonlar (PAHlar) ve Metoksifenoller (MPler) laboratuvar ölçekli küçük bir yanma sisteminde ölçülmüştür. Deneyler sırasında dört çeşit ahşap malzeme kullanılmıştır; kimyasal maddeyle işlem görmemiş sert kereste (HW), kimyasal maddeyle işlem görmemiş ibreli kereste (SW), işlenmiş ahşap çatı malzemesi (RM) ve işlenmiş ahşap pencere çerçevesi (WF). Gaz halindeki yanma örneklerinin toplanması için XAD-2 adsorbent tüpleri kullanılmıştır. Toplanan örnekler ekstre edildikten sonra, ekstreler Agilent 5971 Kütle Seçici (MS) detektörü bağlanmış Hewlett Packard 6890 Gaz Kromatografisi (GK) ile analiz edilmiştir.

Naftalin, asenaftilen ve retenin sert kerestedeki toplam PAH konsantrasyonuna katkıları ibreli kerestedeki ölçülen değerlerinden daha yüksek olarak bulunmuştur. Buna karşılık ibreli kereste örneklerindeki phenantrene, antrasen, fluoranthene, benzo(a) antrasen, chrysene ve benyo(b)fluoranthene'in toplam PAH konsantrayonuna ortalama katkıları sert keresteye kıyaslan daha yüksek olarak bulunmuştur. Syringol, 4-metil syringol, 4-metil guaiacol, eugenol, propyl syringol, 4-etil syringol, syringylaceton ve iso-eugenol sert kereste örneklerinde en çok bulunan bileşiklerdir. Diğer taraftan, 4-methylguaiacol, iso-eugenol, guaiacol, eugenol ve vanilin ise ibreli kereste örneklerinde en çok bulunan bileşiklerdir.

Anahtar Kelimeler: Biyokütle, Atık ahşap, PAH, Metoksifenol, Isıl oksidasyon, GK-MS

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1. Introduction

Wood is used in different fields such as making electricity poles, telephone poles and production of wood based panels, furniture and construction material as well as fuel. During the production of wood based products or after the service life of these products, great amounts of waste wood are generated as by product. Therefore, "waste wood" term not only includes the residual wood from industry, but also used wood.

Depending on the production processes or usage purposes, these wastes will contain a variety of contaminants. Wood is protected from the attack of decay fungi, harmful insects, or marine borers by applying chemical preservatives. Thus, some wood preservatives such as oil borne, waterborne and creosote solutions are used for the production of the structural composites and wood based panels. Therefore, it can be stated that to supply necessary protection, different type of preservatives and chemicals are used during the production of wood based products (Ibach 1999).

Toxic emissions during combustion of biomass are very low (Demirbas 2003). However, combustion of the waste wood may cause environmental risks due to their chemical contents (Samaras et al. 2001). Accordingly, combustion of treated wood may result in release of toxic organics to the atmosphere such as metals, PCDD, PCDF and PAHs (Samaras et al. 2001, Barri et al. 2001).

In the present study, a laboratory scale small burning system was used to identify organic compounds originated from the low temperature thermal oxidation of the waste wood samples including HW, SW, RM and WF.

2. Material and Methods

2.1. Sampling

Approximate and proximate analysis results of the waste wood samplesused during the study are given in Table 1.5 wood pieces (cut in 1.5×2 cm dimensions, 7.17 ± 2.1 g) were used in each experiment and each set was repeated at least three times. DESAGA GS 312 model pump was used during the experiments. Flow rate was selected as 2 L/min. Orbo-43 tubes (Supelco) filled with XAD-2 were used for the collection of PAHs and MPs. Schematic diagram of the small burning system is given in Figure 1.

After ignition of the wood pieces in the burner; gas samples were collected into the tubes by using pump during the whole thermal oxidation period. At the end of the collection of the samples, caps were used and tubes were stored in the refrigerator at +4 °C.NIOSH method 5515 was followed and toluene was used during the extraction of collected samples.

2.2. Analysis of the Samples

Extracted samples were analyzed by using the Hewlett Packard 6890 GC coupled with an Agilent 5971 Mass Selective (MS) Detector. The GC conditions were as follows: A 30 m long fused silica capillary column Agilent J and W DB-5MS (250um X 0.25um X 0.25 mm); carrier gas He with 1 ml/min flowrate; splitless injection; injection temperature, 250 °C. The GC oven was heated following program; start at 80 °C and stay for 1 min, with 7 °C/min ramp reach 180 °C and stay constant for 1 min, then with 12 °C/min ramp reach 240 °C and finally with 20 °C/min ramp reach 300 °C and stay 10 min. The MS conditions were as follows: Dwell time per ion, 20 msec;

 Table 1. Approximate and proximate analysis results of the samples

	HW	SW	RM	WF
Moisture (%)	6.35	7.14	6.77	6.11
Volatile matter (%)	76.6	76.9	76.4	75.3
Ash (%)	1.94	0.42	0.34	0.77
Fixed Carbon (%)	15.1	15.5	16.5	17.8
C (%)	45.3	46.4	46.9	45.5
H (%)	7.96	8.87	8.14	8.87
N (%)	<0.3	<0.3	5.36	2.70
S (mg/kg)	< 0.3	< 0.3	< 0.3	< 0.3



Figure 1. Schematic representation of the small burning system.

solvent delay, 5 min; transfer line temperature 280 °C; electron impact ionization (EI) mode; ionization energy, 70 eV; The electron multiplier voltage (EMV) offset, 400 V. During the analysis MS was operated in full scan mode. An isotope labeled a PAH standard including 16 perdeuterated PAHs shown in US EPA priority list was used and internal standard addition method was followed for the quantification of the target PAHs. Each compound was identified based on its Retention Time (RT) and molecular ion fragments (m/z). Measured PAHs and their retention times are given in Table 2.

An authentic standard was used for retene and 7 points calibration curve was prepared for the quantification of retene. Internal Standard addition method was followed during the calibration process and Fluoranthene-d was used as an internal standard for the quantification of the retene. Standards used for the analysis of MPs were purchased from Sigma-Aldrich (Steinheim, Germany). Stock solutions of each methoxyphenols were prepared taking about 20 mg of each compound mixed with 100 ml toluene. By using a certain amounts of these stock solutions, a standard mix solution was prepared (10 ng/ ul of each methoxyphenols).

Methoxyphenols were also identified based on their retention time and molecular ion fragments. 6 points calibration curves were prepared for each compound and integrated area of each compound was compared with the integrated area of corresponding internal standard for quantification. For this purpose, perdeuterated PAH standard (1 ng/µl) was added into each sample and Fluoranthene-d10 (m/z 212) and Pyrene-d10 (m/z 212) were used for the quantification of the methoxyphenols because the highest correlation coefficients during the calibration process were obtained with these two perdeuterated PAHs. The quantification of the rest seven MPs was performed by using the response factors of the closely related authentic standards. Retention Time (RT), quantification mass fragments (m/z values) and calibration equations of these target organics with R² are given in Table 3.

Target Compounds	RT (min)	m/z	ISTDs	m/z
Naphthalene (Nap)	5.5	128	Naphthalene-d8	136
Acenaphtylene (Acy)	12.62	152	Acenaphthene-d8	160
Acenaphthene (Ace)	13.1	154	Acenaphthylene-d10	164
Fluorene (Fl)	14.96	166	Fluorene-d10	176
Phenanthrene (Phe)	18.46	178	Phenanthrene-d10	188
Anthracene (An)	18.64	178	Anthracene-d10	188
Fluoranthene (Flut)	21.93	202	Fluoranthene-d10	212
Pyrene (Pyr)	22.45	202	Pyrene-d10	212
Retene	23.18	219, 234	y=0.6007x and R ² =0.994	
Benzo[a]anthracene (BaA9	24.82	228	Benzo[a]anthracene-d12	240
Chrysene (Chr)	24.89	228	Chrysene-d12	240
Benzo[b]fluoranthene (BbF)	27.06	252	Benzo[b]fluoranthene-d12	264
Benzo[k]fluoranthene(BkF)	27.13	252	Benzo[k]fluoranthene-d12	264
Bnezo[j] fluoranthene	27.17	252		
Benzo(e)pyrene	27.43	252		
Benzo[<i>a</i>]pyrene (BaP)	27.9	252	Benzo[a]pyrene-d12	264
Perylene	28.17	252		
Dibenzo[<i>a</i> , <i>h</i>]anthracene(DBA)	31.34	278.1	Dibenzo[<i>a</i> , <i>h</i>]anthracene-d14	292
Indeno[1,2,3,-cd]pyrene (IP)	31.38	276.1	Indeno[1,2,3,-cd]pyrene-d12	288
Benzo[<i>ghi</i>]perylene (BghiP)	32.40	276.1	Benzo[ghi]perylene-d12	288

 Table 2. Measured PAHs in this study

	Compounds	RT (min)	m/z	Equation	R ²	Selected ISTD
1	Guaiacol	5.74	109,124,81	y = 0.6038x	0.9987	Fluoranthene-d
2	4-methylguaiacol	7.55	138,123,95	y = 0.5601x	0.9982	Fluoranthene-d
3	2-allyl-6-methoxyphenol	8.9	148,133,91	y = 0.4792x	0.9999	Fluoranthene-d
4	4-ethyl-guaiacol	9.132	137,152,122	y = 0.7628x	0.9999	Fluoranthene-d
5	Eugenol	10.66	154,139,96	y = 0.1918x	0.9999	Pyrene-d
6	Syringol	10.54	164,149,131,103	y = 0.2294x	0.9998	Pyrene-d
7	4-propylguaiacol	10.85	137,166,122	y = 0.7564x	0.9989	Fluoranthene-d
8	Vanilin	11.55	152,81,109	y = 0.2696x	0.9999	Fluoranthene-d
9	4-methyl,2.6- dimethoxyphenol	12.33	168,153,125	y = 0.2115x	0.999	Pyrene-d
10	Acetovanilin	13.147	151,166,123	y = 0.6668x	0.9995	Fluoranthene-d
11	Guacylacetone	13.736	137,122	y = 0.6668x	0.9995	Fluoranthene-d
12	4-allylsyringol	14.734	194,91,119	y = 0.4721x	0.9981	Fluoranthene-d
13	Syringealdehyde	15.128	182,111,96	y = 0.5622x	0.9996	Pyrene-d
14	Coniferaldhyde	16.283	178,135	y = 0.1688x	0.9959	Pyrene-d
15	Sinapaldehyde	17.568	208,165,137	y = 0.1612x	0.9968	Pyrene-d
16	Acetosyringone	17.677	181,196,153,	y = 0.2717x	0.9993	Pyrene-d
17	4-ethylsyringol	20.960	167,182,60,168	Acetovanilin was used for the quantification		
18	Syringylacetone	18.046	167,210,181	Coniferaldhyde was used for the quantification		
19	propionylsyringol	18.899	181,210,153	Coniferaldhyde was used for the quantification		
20	Propylsyringol	15.203	167,196,123	4-allylsyringol was used for the quantification		
21	Properylsyringol	17.018	194,91,179	Acetosyringone was used for the quantification		
22	Iso-eugenol	12.440	164,149,77	4-methyl,2,6-dimethoxyphenolwas used		olwas used
23	4-vinylguaciol	9.855	150,135,77,107	4-ethyl-guaiacol was used for the quantification		

Table 3. Analytical properties of the target methoxyphenols

2.3. Quality Assurance and Quality Control of the XAD Tubes

Blank values of the 17 PAHs and 23 MPs were examined and all values were found below the detection limit except naphthalene (0.58±0.55 ng). Two tubes were serially connected to see whether there is any breakthrough or not. Collected 6 tubes were analyzed for 17 PAHs and 23 MPs and any breakthrough could not be observed for the target compounds.

Percent recovery rates of the PAHs were calculated by using a syringe standard (BiPhenyl-d10) into the standard. A prepared 100 μ l mixture (perdeuterated PAH standard+ BiPhenyl) was directly injected into GC-MS three times for this calculation. The ratio of the each PAH to Biphenyl was calculated. Then, PAH mixture was injected into four XAD tubes. Before injection into GC-MS, 100 μ l BiPhenyl-d10 was added into extract and sample was concentrated to 100 μ l under the mild nitrogen stream and the ratio of the each PAH to BiPhenyl was calculated and by using this ratio Recovery Rates of the each compound was calculated. Recovery Rates of the target compounds were found between 89% for Benzo(a)anthracene and 104% for Phenanthrene.

3. Results and Discussion

The measured PAH concentrations of the burned wood samples are given in Table 4. The highest concentrations were detected for lower molecular weight PAHs such as naphthalene. The partitioning of the PAHs between

Compounds	HW	SW	RM	WF
	avg±stdv	avg± stdv	avg± stdv	avg± stdv
Napthalene	24.60±5.79	35.91±1.91	42.27±7.42	28.68±23.12
Acenaphtylene	2.91±0.59	6.35±0.76	7.59±1.83	6.43±5.25
Acenaphtene	-	-	-	-
Fluorene	2.96±0.49	3.88±0.18	5.77±1.58	3.71±2.95
Phenanthrene	7.42±0.87	6.14±0.97	10.92±2.26	7.67±5.97
Anthracene	1.35±0.31	1.14±0.19	2.06±0.47	1.26±1.03
Fluoanthene	1.74±0.36	1.57±0.06	1.87±0.09	1.93±1.53
Pyrene	1.59±0.28	1.40±0.14	2.00±0.41	1.64±1.31
Benzo(a)anthracene	0.51±0.37	0.41±0.03	-	0.47±0.18
Chrysene	0.57±0.42	0.23±0.01	-	0.39±0.06
Benzo(b)fluoranthene	0.35±0.37	0.09±0.01	-	-
Benzo(k)fluoranthene	0.11±0.10	-	-	-
Benzo(a)pyrene	0.27±0.18	-	-	-
Dibenzo(a,h)anthracene	-	-	-	-
Indeno (1,2,3-cd) pyrene	-	-	-	-
Benzo(g,h,i)perylene	_	-	-	-
Retene	0.57±0.29	2.41±0.40 9.39±1.1		1.20±0.73
Total	44.95	59.52	81.80	53.38

Table 4. Average PAH concentrations of the wood samples as $\mu g/m^3$

gas and particulate phase is directly related with the vapor pressure of each compound. Thus, although lower molecular weights PAHs (2-3 rings) are detected in the gas phase, higher molecular ones (4-6 rings) are mainly detected in the particle phase. In the literature, although the particle phase wood smoke emissions change between 5.1 and 32000 mg/kg, vapor phase wood smoke emissions vary from 43.4 and 355mg/kg (Bari 2009). Consequently, particle phase PAHs either not detected or very low concentrationswere obtained from the collected gas samples in the present study.

The highest PAH concentrations were observed for green coloredroof waste wood. The green color of the roof waste wood is also indicator of the chemical treatment because green color is caused by chemical reactions take place between the chemicals and wood. Copper is mostly used as a wood preservative and it supplies a green color on the wood (Ibach 1999).To protect wood from attack of insects and fungi, chemical treatment is applied to natural wood. Probably, due to this chemical treatment, higher PAH concentrations were obtained when roof waste wood was burned.

Consequently, except that the roof waste wood, similar total concentrations were obtained as a result of the thermal oxidation of hardwood, softwood and window frame. As MP emissions of the samples were examined (Table 5), both roof waste wood and window frame were also identified as softwood because syringol and its derivatives could not be detected in the extracts of these samples (Schauer et al. 2001). Moreover, good correlations (R²) were obtained between PAH concentrations of softwood and window frame (0.92) and also between softwood and roof waste wood (0.97). However, this value was found to be 0.77 between softwood and hardwood samples. Therefore, there must be some differences between hardwood and softwood samples. The contribution of the measured average PAH concentrations to the total PAH concentrations for the waste wood samples are given in Figure 2.

The predominant PAHs detected in the softwood emissions were found to be naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene and small contributions of benzo(a)anthracene, chrysene and benzo(b)fluoranthene. The predominant PAHs in the hardwood emissions were also measured to be naphthalene, acenaphthylene, fluorine, phenanthrene, anthracene, fluoranthene and small contributions of benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene. Moreover, the relative average contributions of the naphthalene, acenaphthylene and retene in hardwood sample were calculated higher than those measured in softwood. On the contrary, the relative average contributions of the phenanthrene, anthracene, fluoranthene, benzo(a) anthracene, chrysene and benzo(b)fluoranthene in softwood samples were obtained higher as compared to hardwood samples.

Wood smoke is composed of many complex organic compounds. Methoxyphenols are mainly emitted as a result of pyrolysis of lignin. These compounds are assumed to be wood smoke markers (Bari 2009). The volatilities of the MPs also varyfrom relatively volatile (such as guaiacol) to exclusively particle phase (such as sinapaldehyde).

According to the literature, emission rates of the MPs change from 1200 to 1500 mg/kg wood burned in the

Compounds	SW	HW	RM	FM
	avg±stdv	avg±stdv	avg±stdv	avg±stdv
Guaiacol	1094.68±610.17	137.34±35.85	1603.45±504.5	948.86±632
4-methylguaiacol	3147.70±1468.89	479.85±131.37	3597±1039.34	1587.17±1108.25
2-allyl-6-methoxyphenol	-	-	-	-
4-ethyl-guaiacol	687.48±334.94	144.07±58.92	968.35±273.37	524.88±359.2
Eugenol	1080.29±389.70	367.93±123.66	1612.28±285.38	1198.94±867.1
Syringol	-	1946.42±815.91	-	-
4-propylguaiacol	265.39±98.72	37.13±8.83	402.20±108.56	182.17±127
Vanilin	1092.49±313.77	220.59±60.36	1524.63±269.62	1339.02±930.8
4-methyl,2,6-dimethoxyphenol	-	2421.58±883.63	-	-
Acetovanilin	293.72±59.88	119.38±31.99	1424.74±1674.71	274.95±197.2
Guacylacetone	83.94±23.27	-	150.78±44.88	98.10±79.4
4-allylsyringol	-	250.07±28.41	-	-
Syringealdehyde	-	193.63±58.29	-	-
Coniferaldhyde	535.05±266.36	278.05±50.14	990.31±365.69	571.53±708.8
Sinapaldehyde	-	118.52±127.09	-	-
Acetosyringone	-	241.82±58.37	-	-
4-ethylsyringol	-	525.79±187.95	-	-
Syringylacetone	-	488.32±316.93	-	-
Propionylsyringol	-	204.96±79.39	-	-
Propylsyringol	-	134.42±72.31	-	-
Properylsyringol	-	548.51±301.58	-	-
iso-eugenol	2407.48±797.08	487.08±261.49	3961.95±995.91	2794.47±2331.8
4-vinylguaiacol	691.73±84.84	151.62±46.08	1028.48±273.49	710.19±580.7
Total	11379.96	9497.08	17264.17	10230.27

Table 5. Average MPs concentrations of the wood samples as $\mu g/m^3$

vapor phase. However, emission rates of the MPs vary between 28 and 1000 mg/kg wood burned in particle phase (Bari 2009). In the present study, average MP concentrations are in the range of 84-3147 μ g/m³, 37-1946 μ g/m³, 150-3961 μ g/m³ and 98-2794 μ g/m³ for the softwood, hardwood, roof wood and window frame samples, respectively (Table 5). Syringol and its derivatives are mainly emitted from the hardwood samples (Schauer 2001).No compounds related with syringol could be observed in softwood samples however syringol and its derivatives were highly detected in hardwood samples as shown in Table 5. Moreover, the relative average contribution of the syringol and 4-methyl-syringol to the total MPs were found to be 20 and 25%, respectively. However, guaiacol and its derivatives were found in both hardwood and softwood samples. But the emission rates of guaiacol show difference between hardwood and softwood (Schiefer





Figure 2. The contribution of the average PAH concentrations to the total PAH concentrations (relative %).



2001). Similar result was also observed in this study and the relative average contribution of the guaiacol in the hardwood sample was found to be 1%. Whereas, the relative average contribution of the guaiacol to the total MPs were found to be 10% for the softwood (Figure 3).

As measured average MP concentrations are taken into consideration, the correlationsbetween softwood and hardwood, window frame and roof waste wood are 0.006, 0.82 and 0.93, respectively. Therefore, the profile of the MPs emitted from the thermal oxidation of softwood and hardwood was found very different then each other (p<.05). Consequently, PAH profiles of the waste wood samples were found to be more similar as compared to profile of the MPs.

In the present study, syringol, 4-methyl syringol, 4 methyl guaiacol, eugenol, properlysyringol, 4-ethylsyringol, syringylacetone and iso-eugenol were most abundant MPs detected duringthermal oxidation of hardwood. On the other hand, the most observed compounds were 4-methylguacicol, iso-eugenol, guaiacol, eugenol and vanillin during the thermal oxidation of softwood. Consequently, taking these results into consideration, it can be said that MPs can be utilized as wood marker to identify the wood type by using wood burning emissions (Bari 2009).

4. Conclusion

The highest PAH and MP concentrations were obtained for the treated roof waste wood samples. Therefore, if treated wood samples are burned in an uncontrolled manner, they will emit higher amounts of pollutants into the atmosphere as compared to natural wood. Moreover, due to differences in the MP concentrations of the hardwood and softwood samples, MPs can be used as wood marker to identify the wood type during the source profile studies.

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