World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:5, No:8, 2011

Evaluation of Guaiacol and Syringol Emission upon Wood Pyrolysis for some Fast Growing Species

Sherif S. Z. Hindi

International Science Index, Materials and Metallurgical Engineering Vol:5, No:8, 2011 waset.org/Publication/7020

***Abstract*—**Wood pyrolysis for *Casuarina glauca*, *Casuarina cunninghamiana*, *Eucalyptus camaldulensis*, *Eucalyptus microtheca* was made at 450°C with 2.5°C/min. in a flowing N_2-atmosphere. The *Eucalyptus* genus wood gave higher values of specific gravity, ash , total extractives, lignin, N_2-liquid trap distillate (NLTD) and water trap distillate (WSP) than those for *Casuarina* genus. The GHC of NLTD was higher for *Casuarina* genus than that for *Eucalyptus* genus with the highest value for *Casuarina cunninghamiana*. Guiacol, 4-ethyl-2-methoxyphenol and syringol were observed in the NLTD of all the four wood species reflecting their parent hardwood lignin origin. *Eucalyptus camaldulensis* wood had the highest lignin content (28.89%) and was pyrolyzed to the highest values of phenolics (73.01%), guaiacol (11.2%) and syringol (32.28%) contents in methylene chloride fraction (MCF) of NLTD. Accordingly, recoveries of syringol and guaiacol may become economically attractive from *Eucalyptus camaldulensis.*

***Keywords*—**Wood; Pyrolysis; Guaiacol; Syringol

As an option for mitigating the threat of global warming, the utilization of biomass for energy and/or chemical recoveries is under consideration for today's society [1]. Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Wood and other forms of biomass are one of the main renewable energy resources available that give heat and power, biomass represents the only source of liquid, solid and gaseous fuels. Wood and other biomass can be treated in a number of different ways to provide such fuels. In general such methods are divided into biological (anaerobic digestion and fermentation) and thermal [2]. Thermochemical processes, especially pyrolysis, are the most common route for converting the biomass to energy and chemicals feedstock. Along with guaiacol, syringol and its derivates are characteristic products of pyrolysis of lignin [1]. As such, syringol is an important component of wood smoke. In preparation of food by smoking, syringol is the main chemical responsible for the smoky aroma, while guaiacol contributes mainly to taste. Further, Assessment of the chemical components in smoke from biomass burning is important for both accidental and planned fires and with respect to both environmental impact and health hazards [3].The pyrolysis behavior of biomass has been widely investigated, which depends on the three main components, *i.e*. cellulose, hemicellulose and lignin [4]. Lignin units are divided into three types, guaiacyl(4-hydroxy-3-methoxyphenyl), syringyl (3, 5-dimethoxy-4-hydroxyphenyl) and *p*-hydroxy-phenyl [5]-[6]. Lignin thermally decomposes over a broad temperature range, because various oxygen functional groups from its structure have different thermal stabilities, their scission occurring at different temperatures [7].Wood lignin undergoes in three consecutive stages, corresponding to the evaporation of water, the formation of primary volatiles and the subsequent release of small molecular gases. The main pyrolysis sections and the maximum weight loss rates are quite different for different wood species. Phenols are the main volatile products, in addition to alcohols, aldehydes, acids, and so on. As the main gaseous products, CO, CO_2 and CH_4 are released out greatly [8].The semivolatile mono cyclic methoxyphenols are emitted as gases, and quantitative proportions have been reported from controlled analytical pyrolysis of wood and pulp [9]. At ambient temperatures, the methoxyphenols tend to condense, and they are present in extracts of smoke aerosols together with non-volatile compounds [10]. Small amounts of the most volatile methoxyphenols remain gaseous in smoke from different forest biomass materials [11].It was found that the guaiacol-type and syringol-type compounds as the primary products of lignin pyrolysis are predominant in bio-oil, acting as the significant precursors for the formation of the derivatives such as the phenol-, cresol- and catechol-types. Further, The methoxy group (-OCH(3)) is suggested to work as an important source for the formation of the small volatile species (CO, CO_2 and CH_4) through the relevant free radical coupling reactions [12].Only minute amounts of material, mostly guaiacol or syringol, were released at either 200 or 300 ^oC. Upon increase of the temperature to 400 ^oC, the hardwood lignin was found to release substantial amounts of phenols, and at 500 ^oC, a maximum in the release of material was found. No loss of material could be detected at 700 ^oC or higher, however. For the hardwood lignins, the dominant products were of similar types with syringol, 4-methylsyringol and 4-vinylsyringol constituting about 60 % of the mixture at either 500 or 600 ^oC. In addition, substantial amounts of guaiacol and 4-methylguaiacol were present at 600 ^oC [13].The pyrolysis of milled wood lignin generated a higher yield of bio-oil, mainly composed of phenols, guaiacols, syringols and catechols, and a less yield of char. In addition, guaiacol and

Dr. Sherif S. Z. Hindi is with Faculty of Meteorology, Environment and Arid Land Agriculture with the Department of Arid Land Agriculture and the Manager of Agricultural Research Center, King Abdul-Aziz University, Jeddah, Saudi Arabia (shindi@kau.edu.sa).

International Science Index, Materials and Metallurgical Engineering Vol:5, No:8, 2011 waset.org/Publication/7020

syringol were the typical products from G-lignin and S-lignin, probably attributed to the easier cleavage of the aryl-alkyl linkage in the side chain compared with the C-OCH_3 bond in the benzene ring [1]. Pyrolysis of raw maple wood produced 67 wt% of condensable liquid products (or bio-oils) that were a mixture of compounds including sugars, water, phenolics, aldehydes, and acids. pyrolysis of the lignin residue produced only 44.8 wt% of bio-oil that mostly composed of phenolics such as guaiacol and syringol compounds [14]. The pyrolytic condensates of about 53.9%, including 8% reaction water, was obtained upon pyrolysis of birch wood. The steam-distilled fractions of pyrolytic oil were found to be chemically and thermally stable when subjected to further purification processes. The syringol-rich fraction was separated and purified with a purity of about 92.3% [15].Wood, twigs, bark and needles from the conifers Norway spruce and Scots pine emitted twelve reported 2-methoxyphenols in similar proportions. Grass, heather and birchwood released the same 2-methoxyphenols as well as 2,6-dimethoxyphenols which are characteristic of angiosperms [3]. The lignin of vascular plants decomposes to fuel-specific methoxyphenols from biomass burning. Qualitative gas chromatographic and mass spectrometric data for 36 methoxyphenols from wood burning were recently presented [16].The purpose of this study was to determine and characterize the amounts of methoxyphenols released, especially guaiacol and syringol, as well as the NLTD yielded from the four wood species upon the pyrolysis process.

Materials and Methods

Branches of four Egyptian hardwood species, namely *Casuarina glauca* Sieb., *Casuarina cunninghamiana* Miq., *Eucatyptus camaldulensis* Dehn., and *Eucalyptus microtheca* F.V.M were used in the present study. Three trees were selected from each species from the same location. The ages of the selected trees and the specified branches were about 15 and 8 years old, respectively. The diameter outside bark of the selected trees ranged from 30-45 cm. From each of the selected trees, one of the primary branches was selected. Accordingly, three branches were selected from each species. The diameter outside bark of the selected branches ranged from 15-20 cm. Each of the selected branches was cut at height of 10 cm above its base at about 140-170 cm above ground level. From each isolated branch, one disc of about 30 cm along the grain was cut, converted into meal after discarding both the pith and outer- zone wood and sieved for wood determinations and pyrolysis process. The pyrolysis runs were carried out with a bench scale reactor (Fig. 1) which consists of an electric tube furnace (carbolite furnace modle MTF 12/338) controlled by a microprocessor temperature programmer with an error of ±5°C with an accuracy of 1°C and heating rate of 0.01°C/min., digital thermometer with a chromel alumel thermocouple (type K with an error of ±1°C), nitrogen regulator system consisted of a regulator and a flowmeter with an accuracy of ±2% of the full scale and the reactor body made up of Pyrex glass that consists of the samples tube (with outer diameter of 2.8 cm) and the train of traps. This train is consisted of two connected traps: The first one is immersed in covered Dewar flask filled with liquid nitrogen and the second one is simply a water scrubber, held at room temperature.

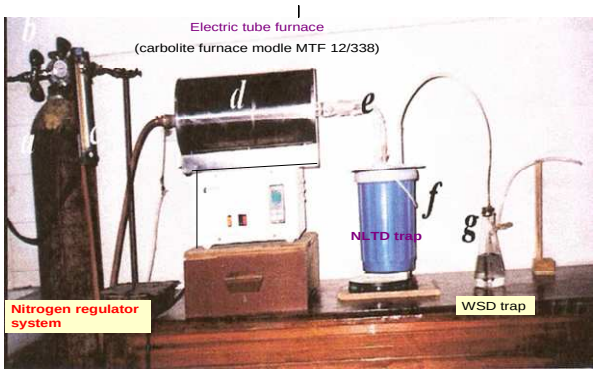


Fig. 1 he apparatus used for pyrolysis of the ten wood species

Before starting a pyrolysis run, the samples were centered in the tube furnace with the chromel-alumel thermocouple of the digital thermometer. Nitrogen flow was introduced at 354 ml/minute until a steady gas flow was obtained, increased to 825 ml/minutes for 10 minutes and re-adjusted at 354 ml/minute for the duration of the pyrolysis run. The cover of the Dewar flask was raised only while the liquid nitrogen was being poured. Then, after five minutes of pouring, the liquid nitrogen trap was connected to the water scrubber trap. However, this period is long enough for the nitrogen gas inside the reaction body to approach, relatively, its original state after addition of N_2-liquid to prevent a back suction that force water to move inversely from the water scrubber toward the pipe attached to N_2-liquid trap where the water freezes and plug it. This can prevent the nitrogen gas to pass through it increasing the pressure inside it and explores the glassy reactor. At the beginning of the run, the furnace was switched on and the temperature program was set on the desired maximum final temperature (MFT) of 450°C with a heating rate (HR) of 2.5°C/min., starting from a room temperature. After the MFT was reached, the heating system was shut off and the samples were allowed to cool to 100°C with maintenance of nitrogen flow at 354 ml/minute. Isolation of the methylene chloride fraction from the NLTD was performed according to the procedure suggested by [17]. Two mini glass columns, having an internal diameter of about 1.5 cm and 20 cm long each, were used for each sample. For column chromatography fractionation, initially, about one gram of air-dry NLTD was transferred to the first column filled with 6g of activated anhydrous sodium sulphate to dehydrate the sample and/or retain part of the tar pitch. The methylene chloride extract (MCE) was added to the second column filled with 9g of activated neutral aluminium oxide to retain the remaining pitch tar and additional fractionation of the extract. The extract obtained by methylene chloride/ n-hexane mixture (95:5 V/V) from the second column was concentrated, quantitatively redissolved in methylene chloride to a volume of about 15ml and stored at 0°C for chromatographic analysis. During eluting the second column containing the pyrolytic distillate sample with either n-hexane or methylene chloride, consecutive

International Science Index, Materials and Metallurgical Engineering Vol:5, No:8, 2011 waset.org/Publication/7020

samples were taken by a capillary glass tube, just from beneath the column trap, to determine the presence of aromatic hydrocarbons by thin layer chromatography (TLC) technique. After air-drying, the spots on the TLC plates were detected under UV lamp to 254 nm which allowed the aromatic hydrocarbons in both the sample and the reference to become visible in the form of light blue spots. Hence, the efficiency of the separation at a certain time was evaluated.Identification of the chemical constituents of MCF from the N_2-Liquid trap distillate was made using HB5890 gas liquid chromatograph (GLC) coupled with HB5890B series mass spectrometer (MS) at Central Lab. Unit in High Institute of Public Health, Alexandria, Egypt. The gas chromatograph was equipped with a splitless injector adjusted at 280°C, and a flame ionization detector (FID) held at 300°C using helium as a carrier gas. Samples were separated on a capillary column (30m long, and 0.25 mm internal diameter) HP-5 (Avondale, PA, USA) of 0.25 μm flim thickness. The temperature of the gas chromatograph column was programmed from 80°C to 100°C at a HR of 15°C/minute, and then increased to a MFT of 310°C at a HR of 5°C/minute, holding the MFT for a residence time of 10 minutes. The temperature of ion source in the mass spectrometer was held at 200°C. All mass spectra were recorded in the electron impact ionization made at 70 electron volts. The mass spectrometer was scanned from m/z 40 to 410 at a rate of two scans per second. Peaks areas were automatically calculated by an integrator. Interpretation the resultant mass spectra was made based on published mass spectra [9]. standards solutions, a computerized library searching program, and by studying the fragmentation pattern of such compound resulted from mass spectrometry analysis. Concentration of such constituent was calculated based on whole peak areas for a detected compounds in a MCF.

Results and Discussion

The wood properties determined and summarized in Table 1 indicate that the four species differed significantly and the differences due to genus are more visible than those due to species. The *Eucalyptus* genus had higher values of specific gravity (SG) of wood, ash , total extractives (TE) and lignin contents of wood than those for *Casuarina* genus.

TABLE I
MEAN VALUES[1,2] FOR SPECIFIC GRAVITY (SG), ASH, TOTAL EXTRACTIVES (TE) AND LIGNIN CONTENTS OF WOOD OF THE FOUR SPECIES

Species	SG[3]	Ash[4] %	TE[4] %	Lignin[4] %
Casuarina glauca	0.62^{B}	1.19^{A}	12.2^{CD}	27.71^{AB}
Casuarina cunninghamiana	0.51^{C}	1.01^{B}	13.81^{C}	25.61^{B}
Genus[3] mean	0.56^{b}	1.10^{a}	13.02^{b}	26.66^{b}
Eucalyptus camaldulensis	0.56^{B}	0.78^{CD}	16.94^{AB}	28.89^{A}
Eucalyptus microtheca	0.79^{A}	0.89^{C}	17.64^{A}	27.80^{AB}
Genus mean	0.678^{a}	0.84^{b}	17.29^{a}	28.35^{a}

[1] Means with the same letter are not differed significantly at 5%.
[2] Based on oven-dry weight and green volume.
[3] As percentage of oven-dry Wood Weight.

The mean values of yield of NLTD and WSP presented at Table II indicate that the quantities obtained from *Eucalyptus* genus were higher than those from *Casuarina* genus. On the other hand, the GHC of NLTD was found to be higher for *Casuarina* genus than that for *Eucalyptus* species with the highest value for *Casuarina cunninghamiana*. However, the obtained distillates can be used as a good source for energy due to their contents of calorific value approaching to those for parent wood.

TABLE II
MEAN VALUES[1] OF YIELD AND GROSS HEAT OF COMBUSTION (GHC) OF N_2-LIQUID TRAP DISTILLATE (NLTD) AND YIELD OF WATER SCRUBBER DISTILLATE (WSD) PRODUCED FROM THE PYROLYZED WOOD

Species[2]	Yield of NLTD[3] %	Yield of WSP[3] %	GHC of NLTD[1] %
Casuarina glauca	25.20^{C}	0.61^{B}	4108^{B}
Casuarina cunninghamiana	28.54^{B}	0.54^{B}	4735^{A}
Genus[3] mean	26.87^{b}	0.58^{b}	4421^{a}
Eucalyptus camaldulensis	29.47^{A}	1.52^{A}	3658^{C}
Eucalyptus microtheca	29.52^{A}	1.78^{A}	3819^{C}
Genus mean	29.495^{a}	1.65^{a}	3739^{b}

[1]Mean with the same letter are not differed significantly at 5%. [2]Capital letters for comparing means between species.
[3]Small letters for comparing means between genus's.

It can be seen from Table 1 that lignin content of wood (LCW) ranged between 25.61 and 28.89% for *Casuarina cunninghamiana* and *Eucalyptus camaldulensis* , respectively. Further, the phenolics content produced from the same species differed between 38 and 73.01%, respectively (Table 3). The presence of syringol and guaiacol and their yield in all MCF from the four species reflects their origin from lignin (Table 3). Generally, *Eucalyptus* genus produced higher condensate yields (29.49%) than that for *Casuarina* genus, (26.87%). The condensate product of *Eucalyptus* genus had higher contents of guaiacol and syringol than those for *Casuarina* genus due to their difference in the LCW of the parent wood. Accordingly, species with high LCW such as *Eucalyptus* genus produces more guaiacol and syringol than those with lower LCW like *Casuarina* genus (Tables 1 and 3). This is confirmed by that Cellulose generated more acids, aldehydes, alcohols, ketones and saccharides during pyrolysis, while MWL produced more guaiacols, syringols, catechols and phenols [1].

TABLE III
MEAN VALUES[1] OF CONDENSATE YIELD (CY) AND PHENOLIC CONTENT (PC), GUAIACOL CONTENT (GC) AND SYRINGOL CONTENT (SC) PROBABLY PRESENT IN METHYLENE CHLORIDE FRACTION (MCF) OF THE CONDENSATE PRODUCED FROM THE FOUR WOOD SPECIES

Species[2]	CY	MCF		
	%	PC %	GC %	SC %
Casuarina glauca	25.2^{B}	47.6^{BC}	8.4^{C}	23.6^{C}
Casuarina cunninghamiana	28.5^{AB}	38.0^{C}	6.3^{D}	20.6^{D}
Genus[3] mean	26.9^{b}	42.8^{b}	7.4^{b}	22.1^{b}
Eucalyptus camaldulensis	29.5^{A}	73.0^{A}	11.2^{A}	32.3^{A}
Eucalyptus microtheca	29.5^{A}	55.3^{B}	9.5^{B}	28.3^{B}
Genus mean	29.5^{a}	64.1^{a}	10.4^{a}	30.3^{a}

[1] mean with the same letter are not differed significantly at 5%.
[2]Capital letters for comparing means between species.
[3]Small letters for comparing means between genus's.

The spectra of phenolic compounds detected for the MCF of NLTD of the four wood species show the typical features of those detected upon thermal degradation of lignocellulosic materials tested by other researchers. The data of retention times, molecular weights, formulas and yields of the detected phenols in the NLTD of the four wood species were presented in Table 4. Seven phenolic compounds were detected all over the four species evaluated excluding those with minor peaks or traces. It is clear that guiacol, 4-ethyl-2-methoxyphenol and syringol were observed in all NLTD's of the four wood species reflecting their parent hardwood lignin origin [1]. The NLTD of *Eucalyptus camaldulensis* had the highest contents of guiacol and syringol (11.2% and 32.28%, respectively) among the species studied. In addition, the NLTD of *Casuarina glauca* contained the highest value of 4-Ethyl-2-methoxyphenol (7.3%).

TABLE IV
IMPORTANT PHENOLIC COMPOUNDS PROBABLY PRESENT IN METHYLENE CHLORIDE FRACTION (MCF) OF N_2-LIQUID TRAP DISTILLATE (NLTD)

Compound	RT (min.)	Yield[a], %			
		Casuarina glauca	*Casuarina cunninghamiana*	*Eucalyptus camaldulensis*	*Eucalyptus microtheca*
M- or P-Cresol.	4.46	-	-	1.7	7.1
Guaiacol.	4.66	8.4	6.3	11.2	9.5
4-Methoxy-2-methylphenol	6	-	5.5	-	-
2-Methoxy-4-methylphenol.	6.51	8.3	-	6.6	8.3

[1]Based on total areas of the identified peaks.

The properties of parent wood (Table 1) affect the thermal degradation products (Tables 2-4). It has been reported that the differences in wood species mainly result in different degradation rates for lignin, as well as for the early stages of hemicellulose degradation. Even small amounts of inorganic salts change the distribution of guaiacols from lignin decomposition and act as catalysts for the scission of the main functional groups [7].

REFERENCES

[1] X. J. Guo, S. R. Wang, K. G. Wang and Z. Y. Luo. 2011. Experimental researches on milled wood lignin pyrolysis based on analysis of bio-oil. Chem. Res. Chinese Universities, vol. 27, pp. 426-430.
[2] V. Bridgwater and G. V. C. Peacocke. 2000. Fast pyrolysis processes for biomass. Renewable and Sustainable Energy Reviews, vol. 4, pp. 1-73.
[3] J. Kjällstrand, O. Ramnäs and G. Petersson. 2000. Methoxyphenols from burning of Scandinavian forest plant materials. Chemosphere, vol. 41, pp. 735-741.
[4] E. Ranzi, A. Cuoci, T. Faravelli, A. Frassoldati, G. Migliavacca, S. Pierucci, S. Sommariva. 2008. Chemical kinetics of biomass pyrolysis. Energy Fuels, vol. 22, pp. 4292-4300.
[5] J. A. Caballero, R. Font, A. Marcilla. 1996. Kinetic study of the secondary thermal decomposition of Kraft lignin. J. Anal. Appl. Pyrolysis, vol. 38, pp. 131-152.
[6] J. Li, B. Li, X. Zhang. 2002. Comparative studies of thermal degradation between larch lignin and manchurian ash lignin. Polym. Degrad. Stab., vol. 78, pp. 279-285.
[7] M. Brebu and C. Vasile. 2010. Thermal degradation of lignin- A review. Cellulose Chem. Technol., vol. 44 , pp. 353-363.
[8] Q. Liu, S. Wang, Y. Zheng, Z. Luo and K. Cen. 2008. Mechanism study of wood lignin pyrolysis by using TG–FTIR analysis. Journal of Analytical and Applied Pyrolysis, vol. 82, pp. 170-177.
[9] M. Kleen and G. Gellerstedt. 1991. Characterization of chemical and mechanical pulps by pyrolysis – gas chromatography / mass spectrometry, J Anal Appl Pyrolysis. Vol. 19, pp. 139-152.
[10] B. R. T. Simoneit, W. F. Rogge, M. A. Mazurek, L. J. Standley, L. M. Hi1demann and G. R. Cass. 1993. Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion, Environ. Sci. Techno, vol. 27, pp. 2533-2541.

International Science Index, Materials and Metallurgical Engineering Vol:5, No:8, 2011 waset.org/Publication/7020

[11] L. M. McKenzie, W. M. Hao, G. N. Richards and D. E. Ward. 1995. Measurement and modeling of air toxins from smoldering combustion of biomass, Environ Sci Technol, vol. 29, pp. 2047-2054.
[12] D. K. Shen, S. Gu, K. H. Luo, S. R. Wang, M. X. Fang. 2010. The pyrolytic degradation of wood-derived lignin from pulping process. Bioresource Technology, vol. 101, pp. 6136-6146.
[13] I.Brodin, E. Sjöholm and G. Gellerstedt. 2010. The behavior of kraft lignin during thermal treatment. Journal of Analytical and Applied Pyrolysis, vol. 87, pp. 70-77.
[14] J. Jungho, A. T. Geoffrey, L. Yu-Chuan, R. C. Torren, S. Jiacheng, Z. Taiying, Y. Bin, E. W. Charles, C. W. Curtis and W. H. George. 2010. Depolymerization of lignocellulosic biomass to fuel precursors: maximizing carbon efficiency by combining hydrolysis with pyrolysis. Energy Environ. Sci., vol. 3, pp. 358–365.
[15] J. N. Murwanashyaka, H. Pakdel and C. Roy. 2001. Separation of syringol from birch wood-derived vacuum pyrolysis oil. Separation and Purification Technology, vol. 24, pp. 155-165.
[16] J. Kjällstrand, O. Ramnäs and G. Petersson. 1998. Gas chromatographic and mass spectrometric analysis of 36 lignin-related methoxyphenols from uncontrolled combustion of wood. J. Chromatogr. A. 824: 205-210.
[17] B. R. Pimenta, M. Vital, R. Bayona and R. Alzaga. 1998. Characterization of polycyclic aromatic hydrocarbons in liquid products from pyrolysis of Eucalyptus grandis by supercritical fluid extraction and GC/MS determination. Fuel, vol.77, pp. 1133-1139.

International Science Index, Materials and Metallurgical Engineering Vol:5, No:8, 2011 waset.org/Publication/7020