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Milled Iraqi Phoenix Dactylifera Date Palm Pruning Woods Lignin Qualitative and Quantitative Determination

Mohammed H. Abdul Latif *, Hilal M. Abdullah , and Hanaa G. Attiya .
Department of Chemistry, Ibn Al Haitham College of Education
University of Baghdad , Adhamiya Al- Dilal Square, Baghdad, Iraq.
Email: mohammed21latif@yahoo.com

Abstract
This study aimed to find analytical data base for Iraqi phoenix date palm pruning woods. Lignin has been extracted for five types of Iraqi date palm using Klason lignin method. Weight of extracted lignin ranged from (0.350 g – 0.698 g), and lignin % ranged from (17.5 – 34.9). (waxes, oils, resin, and proteins of wood gums) % ranged from (22.5 – 44.5). FT– IR Characterization showed that the (-OH) phenolic dis appear in all studied lignin samples, and the (4-O-5 inter monomeric lignin linkage) showed strong intensity peaks for Khadrawi, and Jamal AL-Deen samples, and moderate intensities for Maktom, Barhi at, and Fahal. Also (DODO inter monomeric lignin linkage) showed strong intensity peaks for all studied samples. UV – Vis. Characterization showed that the lowest absorption maximum (254 nm) corresponds to Fahal lignin sample, While the highest absorption maximum (275 nm) corresponds to Jamal AL-Deen lignin sample.
Keywords: Milled Iraqi Phoenix, pruning woods, lignin, Quantitative Determination**.**

1. Introduction

The most probable area of origin of the date palm(Phoenix dactylifera L.) was in the country of Iraq. The earliest record from Iraq (Mesopotamia) shows that date culture was probably established as early as 3000BCE. Date palm is one of the oldest fruit crops grown in the arid regions of the Arabian Peninsula, North Africa, and the Middle East. The exact origin of the date is most likely originated from the ancient Mesopotamia area (southern Iraq) [1]. Date palm tree concentrated in Basra Governorate, recent statistic which is considered the largest date palm forest in the world. It is estimated that the number of date palm trees in this Governorate exceeds 13 million with over 400 varieties and cover an area over 50.000 hectares [2]. Despite the large number of Iraqi date palm types, although a little knowledge about these types is yet known. Also the local names of these deferent types may slightly defer from that known in Arab home land .A few studies about these types were published.
Lignin's are synthesized from the oxidative coupling of p-hydroxycinnamyl alcohol monomers and related compounds. These polymers occur mainly in secondarily thickened plant cell walls. They are covalently bound to hemicelluloses and provide strength and rigidity to the cell wall, allowing plants to grow upward. They also provide the vascular system with the hydrophobicity needed for transport of water and solutes [3 - 4]. Lignins have attracted significant research attention because they represent a major obstacle in chemical pulping, forage digestibility, and processing of plant biomass to biofuels. These industries would benefit from processing biomass with either less lignin or a lignin that is easier to degrade [5].
Despite the huge amount of studies concerning lignin structure and polymerization degrees ,although the problem still unsolved to date [6]. Lignin has been extensively reported to be a cross-linked network polymer with many deferent structure [7]. Lignin molecules are derived mainly from three phenyl propane monomers: *p* -coumaryl alcohol, coniferyl alcohol, and synapyl alcohol (Fig. 1). These mono lignols are polymerized by a radical coupling process that links them by carbon-carbon or ether bonds.

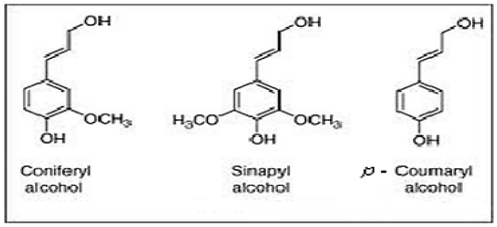


Fig.1. The major building blocks of lignin.

A linkage may occur at any of several different locations on each phenolic unit, causing many different linkage types to be possible. The most common linkage types found in a lignin molecule are *β*-O-4, *α*-O-4, *β*-5, 5-5, 4-O-5, *β*-1, and *β*-*β*
(Fig. 2). Though these are the dominant linkages, at least 20 different linkage types have been identified [8]. The ether type linkages are known to dominate in native lignin, estimated to make up approximately one half to two thirds of the total number of native plant lignin linkages. Mono lignols can be tri functionally linked, forming

branch points within the polymer and giving it a network-like structure. Given the variety of linkages that occur, lignin molecules cannot be depicted as a series of regular, defined repeating units, as traditional polymers are. In contrast, lignin is a highly irregular, complex polymer [9].

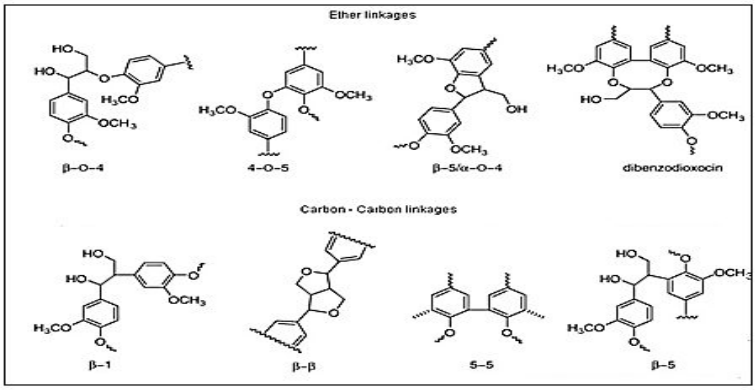


Fig. 2. Common inter monomeric linkages in a lignin molecule

Models have been proposed for lignin from several different sources, though due largely to lignin's complicated nature and the difficulties inherent in lignin analysis, no complete structure of a lignin molecule has ever been identified. The models that have been developed are only representations drawn from analyses of the relative proportions of each lignin unit type and each linkage type (Fig. 3) [8].

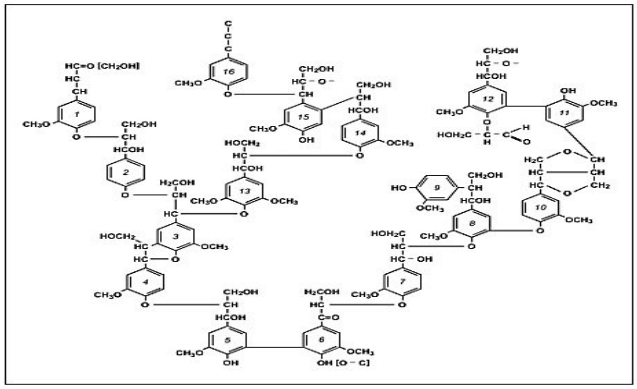


Fig. 3. A structural model of softwood lignin [8]

Recent study has reported a detailed characterization of lignin structure [10]. ^{13}C NMR. study analyzing the residual lignin after Kraft pulps had lower contents of β-O-4-structures and higher contents of condensed structure [11]. There are several methods to isolate lignin from wood ,generally ,where lignin is isolated either by removing non-lignin or lignin components .Usually H_2SO_4 is used to isolate lignin [12].

This research is dealing with the determination of lignin, and (wax, oil, resins, possibly some portions of wood gums) percentages in five different types of Iraqi Phoenix dactylifera Date palm pruning woods and characterization of lignin using UV- Vis., and FT-IR spectrum.

2. Materials and method

2.1.Quantitative determination of lignin, oil, waxes, gum, and protein of Iraqi date palm pruning woods.

Five types of Iraqi date palm pruning woods (Phoenix – Maktom, Phoenix – Barhi Phoenix – Khadrawi Phoenix – Fahal, Phoenix – Jamal AL-Deen,.) were examined by Klason Lignin or sulfuric acid Lignin method. Wood samples were extracted with alcohol – benzene which employed to remove materials, such as waxes, oils, some resins, and possibly some portions of wood gums to avoid the presence of these foreign materials in the lignin residue, [13] this pretreatment method summarized by extracting the wood samples with a minimum boiling – point solution of alcohol- benzene as shown below:

Approximately 2 grams of air-dried pruning wood powder (60 to 100 mesh) are weighed in a tared alundum crucible. The crucible an d its contents are dried to constant weight at 105° C.,-cooled, and weighed. The material is then extracted for 4 hours in a Soxhlet apparatus with a minimum boiling solution of alcohol-benzene. The solvent is removed by suction, the residue washed with alcohol by suction to remove the benzene, and then. Extracted with 400 cc. of hot water in a water bath for 3 hours, filtered, washed with hot water, then with .alcohol, and finally dried. (Washing the residue with alcohol aids in the removal of the pruning wood powder from the crucible after drying.) The dried residue is transferred to a glass Stoppard weighing bottle, and

weighed to calculate the percentage of waxes, oils, protein and gums in each sample, as shown in (Table 1). Then the dried residue stirred, well mixed at room temperature and hydrolysis with 25 cc. of 72 percent sulfuric acid, and maintained at that temperature by keeping it in a bath at 20 ± 1 °C for 2 hours. The resulting, mixture is transferred to an Erlenmeyer flask, diluted with water to make a 3 percent acid solution by adding 575 ml of water, and then boiled for 4 hours under .a reflux condenser . The hydrolyzed residue is filtered on a tared alundum. Crucible, washed free of acid by means of hot water, dried, and weighed. The lignin content (lignin %) was calculated on the basis of the oven-dry sample as shown in (Table 1).

Table 1
Quantitative determination data of different types of IRAQI Phoenix Date -Palm Wood Pruning Lignin.

Sample name	Weight of sample (g.)	Wt. of sample after treatment with Benzene- alcohol mixture (g.)	Wt. of sample after treatment with 72% H_2SO_4 (g.)	Waxes, Oils, Resins, and Gums %	Wood Lignin %
Phoenix- Maktom	2	1.430	0.350	27.5	17.5
Phoenix - Barhi	2	1.500	0.540	25.0	27.0
Phoenix - Khadrawi	2	1.160	0.698	42.0	34.9
Phoenix - Fahal	2	1.110	0.568	44.5	28.4
Phoenix – Jamal AL-Deen	2	1.550	0.525	22.5	26.3

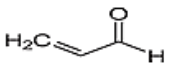
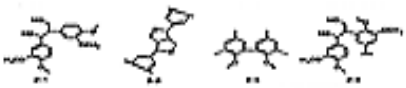
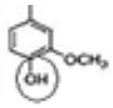
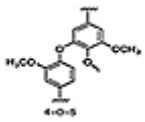
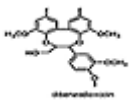
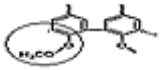
2.2. lignin characterization.
The five isolated dried lignin samples were characterized by FT –IR spectroscopic analysis (Shimadzu FTIR Spectrometer – 30 000:1/ IRAff), and UV-Vis. spectrophotometric analysis (UV – 1800 Shimadzu Spectrophotometer).

3. Results and discussion

3.1. Quantitative determination of lignin.
(Table 1) showed that the weight of extracted lignin from these five different types of IRAQI Phoenix Date - Palm Pruning (2g.) Wood samples ranged from (0.350 g – 0.698 g), and the lignin % ranged from (17.5 – 34.9). Also the highest lignin % was in Khadrawi Pruning Wood, and the lowest lignin % was in Maktom Pruning Wood. The other ingredients (Waxes, Oils, resins and proteins of wood Gums)% ranged from (22.5 – 44.5), where the lowest % was for Jamal AL-Deen Pruning Wood, and the highest % was for Fahal Pruning Wood.
3.2. Characterization of lignin.
3.2.1. FT – IR Characterization.
The lignin samples extracted from Iraqi pruning date palms under study showed convergent peaks of absorption on FT-IR spectrum but with different values can be interpreted as shown in (Table 2) deriving from Figs. (5 – 8).
The stretching vibration absorption of (-OH) group showed convergent peaks values with strong intensities for all studied samples which indicates that all studied samples contain this group in the lignin structure at high concentrations.
Also the stretching vibration absorption of (- C-H) aliphatic group showed convergent peaks values for all studied samples, but the three samples (Maktom at 2939cm^{-1}, Barhi at 2937cm^{-1}, and Jamal AL-Deen at 2939 cm^{-1}) have a strong intensity peaks. The others (Khadrawi at 2941cm^{-1}, Fahal at 2939 cm^{-1}) have a moderate intensity peaks. It can be considered that the three samples contains higher concentrations of monomers in lignin structure than that of the other two samples. The stretching vibration absorption of conjugated carbonyl group showed convergent peaks values for all studied samples with low to moderate intensity peak. Which could means its presence at a low to moderate concentration in these samples. The stretching vibration absorption of aromatic rings and (-C=C-C-and –C=C-C=C-) or (β-1, β-β, 5-5, and β-5 inter monomeric lignin linkage) showed convergent peaks values with strong intensities for all studied samples. Which may explain the existence of these linkages frequently in lignin structure. (C-H) deformation and aromatic ring vibration showed convergent peaks values with strong intensities for all studied samples. Bending vibrations absorptions of (-OH) have no absorption peaks for all studied samples, this means that the (-OH) phenolic group disappear in all lignin samples due to the probability of free radical intermediate formation from the (-OH) phenolic group site which

consume these groups configures the ether linkages. The aromatic ether aryl (4-O-5 inter monomeric lignin linkage) showed convergent peaks values with strong intensity peaks for (Khadrawi at 1278 cm-1, and 1222 cm-1, and Jamal AL-Deen at 1274 cm^{-1}, and 1219 cm-1) samples, and moderate intensities for (Maktom at 1274 cm^{-1}, and at 1217 cm^{-1}, Barhi at 1273cm^{-1}, and at 1219 cm^{-1}, and Fahal at 1278 cm^{-1}, and at 1217 cm^{-1}), and this means that (4-O-5 inter monomeric lignin linkage) probability is higher in Khadrawi, and Jamal AL-Deen lignin's structures. The stretching vibration absorption of cyclic ether large ring stretching (DODO inter monomeric lignin linkage) showed convergent peaks values with strong intensities for all studied samples. This indicates its strong existence probability in all types. The stretching vibration absorption of alkyl substituted ether (O – CH_3 or O – CH_2) showed two convergent peaks values with weak intensities for all studied samples, except Jamal AL-Deen at (1165 cm^{-1}) showed one absorption peak with moderate intensity. This means that the alkyl substituted ether (O – CH_3 or O – CH_2) dis appear in all studied samples lignin structures due to the probability of free radical intermediate formation from the ether (O – CH_3 or O – CH_2) site which consume these groups configures the other types of ether linkages. The stretching vibration absorption of vinyl ether (in phase C- O - C stretch.) showed convergent peaks values, with weak intensities for all studied sample, Which could means its presence at a lower concentrations in all probable lignin structures.

Table 2
FT-IR peaks of lignin and its inter monomeric linkages.

Vibrational groups and remarks	Inter monomeric lignin linkage structure	Phoenix - Maktom lignin	Phoenix - Barhi lignin	Phoenix - Khadrawi lignin	Phoenix- Fahal lignin	Phoenix – Jamal Al-Deen lignin
		Peak frequency wave number cm^{-1}	Peak frequency wave number cm^{-1}	Peak frequency wave number cm^{-1}	Peak frequency wave number cm^{-1}	Peak frequency wave number cm^{-1}
-OH stretching vibration		3408 (s)	3414 (s)	3421 (s)	3421 (s)	3385 - 3414 (s)
C-H stretching vibration		2939 (s)	2937 (s)	2941 (m)	2939 (m)	2939 (s)
Conjugated carbonyl stretching		1697 (w)	1701 (m) and 1685 (w)	1697 (w)	1697 (w)	1695 (m)
aromatic rings and (-C=C-C-and –C=C-C=C-) or (β-1, β-β, 5-5, and β-5 inter monomeric lignin linkage)		1608(s) and 1498(s)	1608 (s) and 1508 (s)	1608 (s) and 1508 (s)	1608 (s) and 1508 (s)	1608 (s) and 1506 (s)
C-H deformation and aromatic ring vibration		1458 (s)	1458 (s)	1458 (s)	1458 (s)	1456 (s)
Bending vibrations of (-OH) phenolic bonds		---	---	---	---	---
Aromatic ether aryl (4-O-5 inter monomeric lignin linkage)		1274 (m) and 1217 (m)	1273 (m) and 1219 (m)	1278 (s) and 1222 (s)	1278 (m) and 1217 (m)	1274 (s) and 1219 (s)
Cyclic ether large ring stretching (DODO inter monomeric lignin linkage)		1111 (s)	1114 (s)	1114 (s)	1112 (s)	1112 (s)
Alkyl substituted ether (O - CH_3 or O – CH_2 stretch)		1165 (w)	1166 (w)	1166 (w)	1165 (w)	1165 (m) and 1041 (w)
Vinyl ether (in phase C- O - C stretch)		850 (w)	850 (w)	852 (w)	852 (w)	852 (w)

Abbreviations used in the table; w, weak, m, moderate, s, strong.

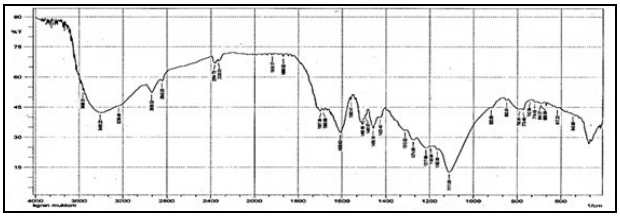


Fig. 4. FT – IR Spectrum of Phoenix – MAKTOM pruning lignin.

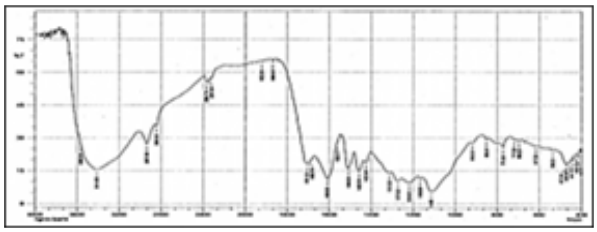


Fig. 5. FT – IR Spectrum of Phoenix – BARHI pruning lignin.

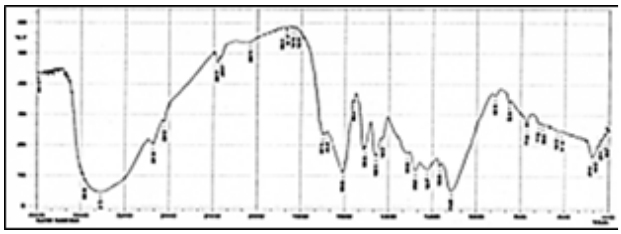


Fig. 6. FT – IR Spectrum of Phoenix – KHADRAWI pruning lignin.

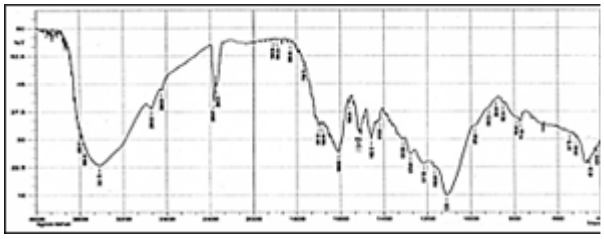


Fig. 7. FT – IR Spectrum of Phoenix – FAHAL pruning lignin.

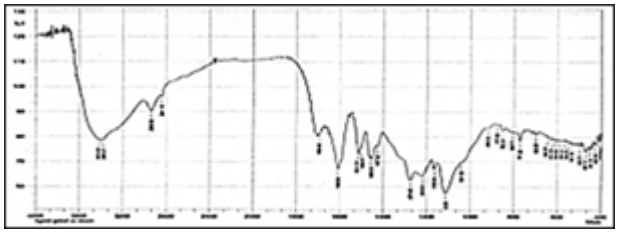


Fig. 8. FT – IR Spectrum of Phoenix – JAMAL AL-DEEN pruning lignin.

3.2.2. UV – Vis. Characterization.

A five samples of Klason Lignin of the studied Iraqi Phoenix date palm pruning woods were dissolved in ethanol (80%) to prepare five solutions of (100 mg / L) concentration in 10 ml volumetric flasks. UV-Vis. scanning spectrum has been recorded, (Table 3) show the spectral data of λ – maxes and absorbencies derived from Figs. (9 – 13).

Two regions of peaks were obtained in every Klason Lignin samples which had the absorption maximum at wavelength of (204 – 225) nm, and (254 – 275) nm. The appearance of these characteristic peaks in the lignin spectrum originated from non-condensed phenolic groups (aromatic ring) in lignin [14] for the absorbance maximum values at short wavelengths, and Cyclic ether large ring (DODO inter monomeric lignin linkage) for the absorbance maximum values at long wavelengths. Which is in a good agreement with the suggestion of FT – IR spectrum data in (Table 2). The lowest absorption maximum (254 nm) corresponds to Fahal lignin sample, indicates that the Cyclic ether large ring (DODO inter monomeric lignin linkage) has a lowest existence probability. While the highest absorption maximum (275 nm) corresponds to Jamal AL-Deen lignin sample, indicates that the Cyclic ether large ring (DODO inter monomeric lignin linkage) has a higher existence probability.

Table 3
The UV absorbance of Klason Lignin of the studied Iraqi Phoenix date palm pruning woods.

Klason Lignin	Short wavelengths (nm).	Absorbance (A)	Long wavelengths (nm)	Absorbance (A)
Phoenix-Maktom	204	2.535	272	0.666
Phoenix - Barhi	213	3.519	271	1.202
Phoenix Khadrawi	229	3.623	272	1.822
Phoenix - Fahal	224	3.809	254	0.750
Phoenix – Jamal AL-Deen	225	2.182	275	1.142

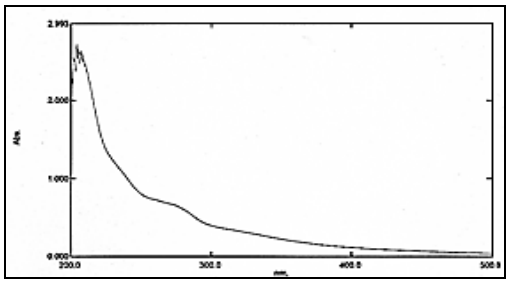


Fig. 9. UV-Vis. Spectrum of Phoenix – MAKTOM pruning lignin

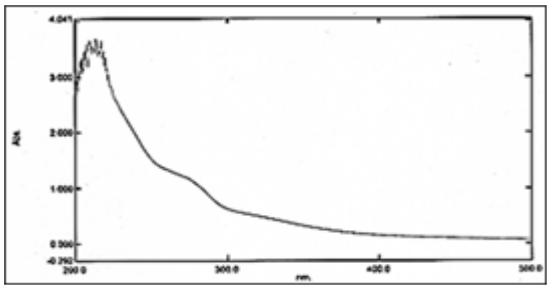


Fig. 10. UV-Vis. Spectrum of Phoenix – BARHI pruning lignin.

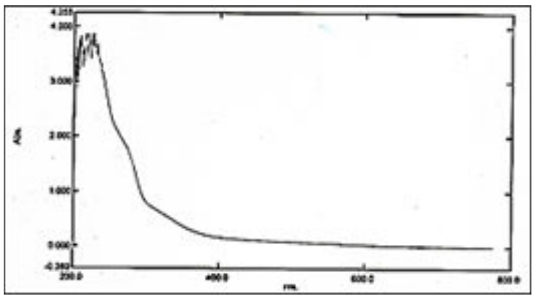


Fig. 11. UV-Vis. Spectrum of Phoenix – KHADRAWI pruning lignin

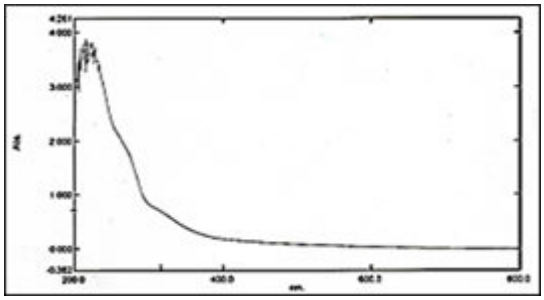


Fig. 12. UV-Vis. Spectrum of Phoenix – FAHAL pruning lignin

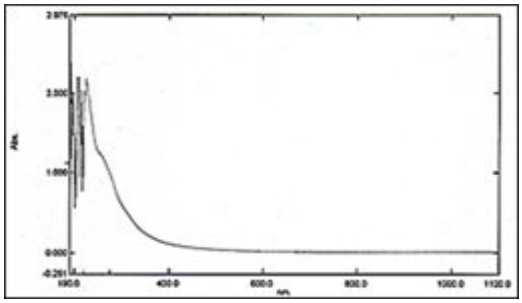


Fig. 13. UV-Vis. Spectrum of Phoenix – JAMAL AL-DEEN pruning lignin.

3. Conclusions

Different nature of studied Phoenix date palm pruning woods have been discovered . Highest lignin % was in Khadrawi Wood, and lowest lignin % was in Maktom Wood. FT – IR spectrums showed that (-OH) phenolic group disappear in all samples due to the probability of free radical intermediate formation from (-OH) phenolic group site. UV – Vis. spectrums showed that lowest λmax.(254 nm) corresponds to Fahal lignin, indicates that cyclic ether large ring (DODO) has lowest existence probability. While highest λmax. (275 nm) corresponds to Jamal AL-Deen lignin, indicates that cyclic ether large ring (DODO) has highest existence probability.

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References
[1] Chih Cheng T. Chao1, Robert R. Krueger2, The Date Palm (Phoenix dactylifera L.), Overview of Biology, Uses, and Cultivation, Hortscience vol. 42(5) p.1077-1082 August 2007.
[2] AI-Dekaili, A. A. and J. A. AI-Dejaili, Fruits Production. Ministry of Higher Education Press, Mousil 1989.
[3] Boerjan W, Ralph J, Baucher M: Lignin biosynthesis. Annu Rev Plant Biol, 54: pp. 519-546, 2003.
[4] Ralph J, Lundquist K, Brunow G, Lu F, Kim H, Schatz PF, Marita JM, Hatfield RD, Ralph SA, Christensen JH et al.: Lignins: natural polymers from oxidative coupling of 4- hydroxyphenylpropanoids. Phytochem Rev, 3: pp.29-60 , 2004 .
[5] Ruben Vanholme, Kris Morreel, John Ralph and Wout Boerjan, Lignin engineering, Current Opinion in Plant Biology, 11: pp. 1–8, 2008.
[6] Claudia Crestini, Federica Melone, Marco Sette, and Raffaele Saladino, Milled Wood Lignin: A Linear Oligomer, Biomacromolecules, 12, pp. 3928−3935, 2011.
[7] Ralph J., Lundquist K.,Brunow, G., Lu F., Kim H.,Schatz P.F., Marita J.M., Hatfield R.D., Ralph S.A., Christenensen J.H., Boerjab W, Phytochem. Rev. Lignin , Natural polymer from oxidative coupling of 4 – hydroxyphenyl propanoids, 3, pp.29 – 60 ,2004.
[8] Whetten, R. W., MacKay, J. J., and Sederoff, R. R.. Recent advances in understanding lignin biosynthesis. Annual Review of Plant Physiology and Plant Molecular Biology 49(1), pp. 585-609, 1998.
[9] Dence, C. W. and Lin, S. Y. Introduction. In “Methods in Lignin Chemistry” (S. Y. Lin and C. W. Dence, eds.), pp 3-19. Springer-Verlag, Berlin, 1992.
[10] Alder, E. Lignin chemistry – past, present, and future. Wood Science and Technology 11, pp. 169-218, 1977.
[11] Higuchi T., Lignin biochemistry: Biosynthesis and biodegradation, Wood Sci. Technol., 24, pp. 23 – 63, 1990.
[12] Qiang Wang, Kefu Chen,Jun Li, Guihua Yang, Shanshan Liu, and Jun Xu, The solubility of Lignin from Bagasse in A 1,4 – Butane Diol / Water system, Bio Resources, 6(3) pp. 3034 -3043, 2011 .
[13] Peter M. Froass, Arthur J. Ragauskas, Jian-er Jiang, Nuclear Magnetic Resonance Studies. 4. Analysis of Residual Lignin after Kraft Pulping, Ind. Eng. Chem. Res., 37, pp. 3388-3394, 1998.
[14] López M, Huerta-Pujol O, Martínez-Farré FX, Soliva M. Approaching compost stability from Klason lignin modified method: Chemical Stability Degree for OM and N quality assessment, 2010.
[15] Ibrahim, M. N. Mohamad, Azian, H. & Yusop M. R. Mohd 2006. http://www.penerbit.utm.my/onlinejournal/44/F/JTJun44F7.pdf Accessed on 28 May 2011.

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