PRIMARY IDENTIFICATION OF EUCALYPTUS (*Eucalyptus camaldulensis*) WOOD LIGNIN MONOMERS BY FT-IR SPECTROSCOPY

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ABSTRACT

Lignin samples were isolated from Eucalypt wood (*Eucalyptus camaldulensis*) by kraft process, and then all samples were examined and tested with Fourier Transform Infrared Instrument Technique for identifying the types of lignin monomers units from their spectra.The Lignin monomers spectra chart showed these peak bands(616.80, 795.11, 876.96, 1057.14, 1127.19, 1458.74, 1509.21, 1542.05 , 1636.26, 1735.68, 2863.72,2922.35, 2967.95, 3447.01,and 3650.56 cm^{-1}).No evidence for methoxyl group bands were observed, though all monomers of the tested lignin in this investigation which obtained from Eucalypt wood by KRAFT process consist mainly of P-hydroxy phenyl propane units.

INTRODUCTION

Fourier Transform Infrared spectroscopy (FT-IR) is an analytical technique used to identify the functional groups of the organic (and in some cases inorganic) materials. This technique measures the absorption of various infrared light wave lengths by the materials interest. These bands identify specific molecular components and structures (Silverstein and Webster, 1998).The first astronomical application of Fourier Transform spectroscopy experinced in the late 1950's and early 1960's when J. cones and coworkers obtained high resolution and high quality spectra. To day commercial Fourier Transform Infrared spectrometer are widely available aided by fast computers which perform Fourier Transforms in flash , vise infrared (Socrates,1994).

Recently the Fourier Transform Infrared (FT-IR) is used as a fast, reliable and easy analytical tool for wood and wood derivatives because of its improved spectral quality and is meaning full difference spectra which can be obtained even in region of high background absorption and the ability to detected small changes in bands overlapped by strong bands undergoing (Rutherford *etal.*, 2004).

Lignin is after cellulose, the principal constituent of wood structure of higher plant.

Infrared spectroscopy in the near IR region wave length 2.5-1.5μm ,wave number 4000-600 cm^{-1} is useful as physical method for characterizing lignin and its derivatives, and their spectrum is characteristic property of compound with exactly known structures ,there are several uncertainties with the interpretation of lignin IR ,the variation in lignin structures and compositions due to the origin sample ,the isolation procedure are the causes of different spectra measuring of lignin(Alobydi *etal.*,2004).

Fengel and Wegener(1989) give the elemental composition and methoxy content of the analytical and technical lignin isolated from *Eucalyptus regnons* ,

the results show 56-60% of carbon content and the methoxy contents reach to 18-22%,   these

results differed than the carbon content of the softwood lignin which reaches about 60-65% where as therefore, IR spectra of lignin shows several major absorption bands which can be assigned empirically to structural groups.

Chemists cleared that the empirical formula of lignin based on a phenyl propane (C9)unit is $C_9H_{8.83}O_{2.37}(OCH_3)_{0.96}$ in coniferous lignin ,and $C_9H_{8.9}O_3(OCH_3)_{1.45}$ in deciduous lignin and it appears that there are about 3 sringyl propane unit for every 2 guaiacyl propane units in deciduous lignin (Sarkanen *etal.*,1967).

So for the all reasons above our investigation was put to study the different absorption bands of the Kraft lignin extracted from *Eucalyptus camaldulensis* by using the Fourier Transform Infrared technique and to find out and identify the structural units and the functional groups of it.

MATERIALS AND METHODS

Wood & wood cooking: A log at about1.5m of *Eucalyptus camaldulensis* was bought from a local Mosul markets, then it was barked and chipped with a multiknifes chipper in one of a local industry according to (ASTM-584, 1968).All chips were screened by vibration tray at about 1.6-2.2 cm in size.5000 gm of the chips had been randomizing obtained and subjected in a digester in the technical institute of Mosul (Othmer, 1967).

A white liquor was made by mixing 250 gm of sodium sulphate -5-hydrate RS, 550 gm of potassium hydroxide powder, 250 gm of sodium carbonate, and 30 liters of tape water, the liquor added to the wood chips in the digester and the cover of the digester closed tightly, then the mixture was cooked in the digester for 5hrs, 160C°, and at (7 bars) pressure. After the completing of the digestion periods the black liquor was separated from the digested wood chips.

The black liquor was Acidified by sulfuric acid (72% Conc.) which was added to it at several batches to reduce the pH level in the black liquor from (pH12) to (pH 8)at this point the acidification was stopped at and at that level the precipitated Kraft Lignin had been seen at the bottom of the container. The precipitated Lignin was separated by decantation and washed for several times by water then put in oven for 24hrs for drying it at 50C°.

Infrared spectroscopy: Several samples of Eucalypts Kraft Lignin with potassium bromide pellets were made. Each sample was prepared by milling (5 milligram) of the extracted lignin and pressed with potassium bromide to form apellet from each other (Gracin, 2001).

The fourier transform infrared spectrophotometer of the name Tensor 27 Broker co., Germany. The ratio of 1:100 was used as infrared source with the adenterated triglycine sulfate detector. This instrument was scanned from 4000 to

400 reciprocal centimeters (cm⁻¹); averaging to scans at 1.0 cm⁻¹ interval with a resolution of 4.0 cm⁻¹ .All spectra were normalized after acquisition to a maximum absorbance.

RESULTS & DESCUSSION

The FT-IR spectra of the Eucalyptus Kraft Lignin samples showed typical absorption bands. Figure (1) shows all spectra band result an FT-IR chart, where as table (1) summarizes all wave numbers of the peak absorption monitored in Figure (1) with there corresponding descriptions and intensities.

As it is shown in Figure (1) and table (1), the first peak absorption is at the fingerprint region of about $616.80 \mathrm{cm}^{-1}$ which is mean a bending vibration in an out plane of γ C - H involving in the aromatic ring of the Lignin monomers with weak intensity, this result is accepted with Haw and Schultz (1985) ,and Wallis *etal.* (1996) indicates the region between $670-580 \mathrm{cm}^{-1}$ which involve ion vibrations of SO₄, sulfide, mercaptan with medium intensity.

Table (1): Vibration descriptions, frequencies, and the intensities of lignin monomers .

Description	Frequency,cm⁻¹	Intensity
Bending vibration in (γCH) in out of plane of the aromatic ring of the lignin monomers.	616.80	Weak
Stretching vibration for methyl groups (CH₃).	795.11	Strong
Bending vibration for hydrogen atoms in an out plane of the phenyl ring.	876.96	Strong
Stretching vibration for υ(C=O) of the alcohol.	1057.14	Broad &Shoulder
Stretching vibration of the ether groups.	1127.19	Weak
Stretching vibration of υ(C=C) in the aromatic ring.	1458.74 1509.21 1542.05	Medium
Stretching (nonconj) vibration band for υ(C=C) in aliphatic chain.	1636.26	Medium
Stretching vibration of the aliphatic aldehyde and ester groups.	1735.68	Very weak
Stretching vibration for methylene groups.	2863.72 2922.35	Medium
Asymmetric Stretching of methyl groups.	2967.95	Medium
Stretching vibration for hydrogen	3447.01	Very strong and broad

| bonds in lignin monomers.		
Stretching vibration for free separated alcohol and phenol.	3650.56	Strong and sharp

The second peak band is at 795.11cm^{-1} level in the same figure give a description of the methyl stretching vibration with strong intensity, the result agree with (Pandey, 1999),while and Raymond (2004) said that the region between $800 - 770 \text{ cm}^{-1}$ mentioned to the substituted meta- di of the aromatic ring in Lignin.

The peak band at 876.96 cm^{-1} monitors the bending vibration of the hydrogen atoms at an out of the plane of the phenyl ring in Lignin units, however, Kotilainen etal.(2000) describes the absorption with a weak intensity in region between $890 - 820 \text{ cm}^{-1}$ of the aliphatic peroxides (C-O-O-C) which fragments from lignin at the digestion period of wood chips by Kraft processes, other literatures like (Amen *etal.*,2001) stressed that the γ C-H bending vibration at an out plane of the conjugated molecules.

Figure (1) also shows a band at 1057.14cm^{-1} which referred to the stretching vibration of alcohol caused by the combination or overlapping of C-O as a result of several deformation in lignin by the action of the chemical used in the wood digestions, Kondo(1997) said that the $1100 - 1000 \text{ cm}^{-1}$ region concerning a sugar or poly saccharide moieties due to the width and the intensity of the resulting band, while the weak intensity of the region between $1070-1000 \text{cm}^{-1}$ mentioned on the bending of the aromatic mono substituted in plane.

Another band at 1127.19cm^{-1} position indicates stretching vibration of ether groups caused by base actions on the wood chips during the cooking period.

Three bands at 1458.74 cm^{-1}, 1509.21 cm^{-1}, 1542.05 cm^{-1} levels show also a stretching vibration of υC=C bond in the aromatic ring ,these results are in line of White(1994) who found that the IR spectra at $1470 - 1400 \text{ cm}^{-1}$ range was for C-H deformation and the aromatic ring vibration, but Baldock and Smernik(2002) said that the range between $1613 - 1471 \text{ cm}^{-1}$ wave numbers gave an indication on the skeletal aromatic ring vibration, therefore, all last results enable us to prove the existence of lignin in the unknown preparations, whereas the band between $1600 - 1500 \text{ cm}^{-1}$ wave numbers gave us the differentiation between softwood and hard wood Lignin's bands intensities(Faix,1991) .
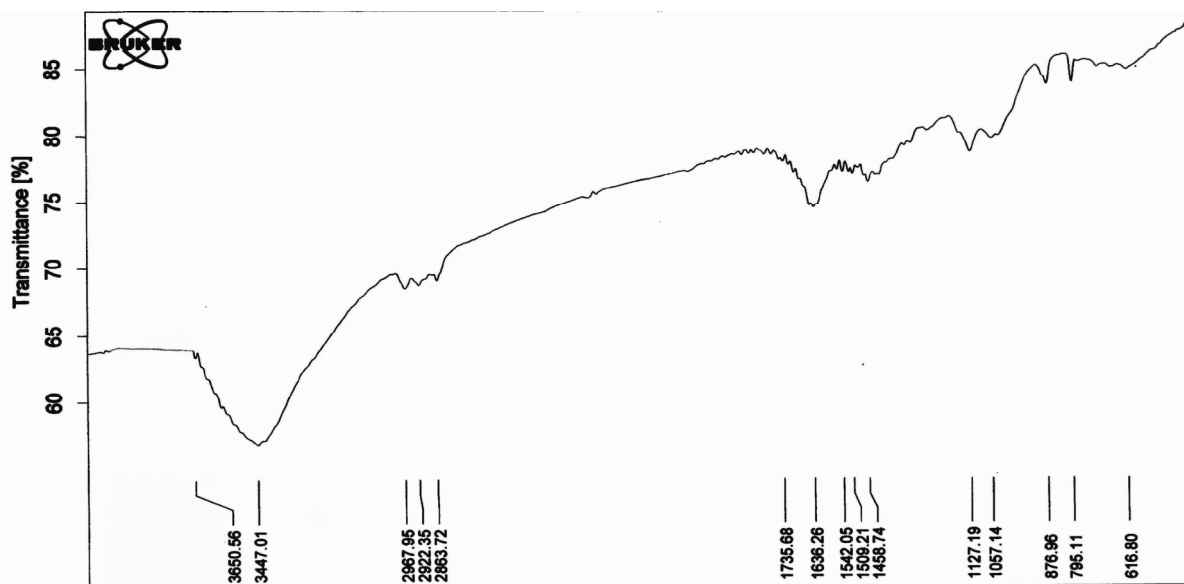
A $1636\ cm^{-1}$ position shows a broad peak spectrum with medium intensity stretching vibration of νC=C of the aliphatic chain with medium intensity because the spectrum of these double bonds in chain appears at the range between 1620-1680 cm^{-1} with var. intensities, Stark *etal.* (2004) also saw a broad band of the carbonyl group at ~1600 region due to the separated carbonyl and carboxyl compound of the elevated temperatures within the digestion periods.

There are also a stretching vibration of the aliphatic aldehyde and ester group at $1735\ cm^{-1}$ wave number level as we can see in figure (1) and table (1). Because of the Acetyl of uronic ester of the poly saccharids residues appeared at the range between $1740 - 1735\ cm^{-1}$ wave numbers and it might be interfered with carbonyl group bands.

Two bands at 2863.72-2922.35 wave number levels show a stretching vibration for the metheylene groups; these results indicate the absence of the methoxyl group's bands which often appears at about the range 2830-2815 cm^{-1} wave numbers (Alobydi *etal*. 2004).

The $2967.95\,cm^{-1}$ wave number peak band show a stretching vibration for the methyl group, because the methyl (CH$_3$) group seem always to appear between two distinct bands near 2962cm^{-1} and 2872cm^{-1}, which were described as an asymmetric and symmetric stretching, respectively if several methyl groups are existed in the tested compounds with sevral intensities as it reported by Dam *etal*. (2004).

A significant band appeared at about $3447.01\,cm^{-1}$w.n. with strong and abroad intensity of stretching vibration refer to intra molecular hydrogen bonds in the lignin monomers, hydroxyl groups, and alcohol's of the lignin units which fragment during the wood digestion period, whereas the absorption bands range of the intra molecular hydrogen bonds are between 3590-3420 cm^{-1}and caused a cis isomer in the Para hydroxy phenyl structures of the lignin (Kubo and Kadla, 2005).

The last peak band is at $3650.56\,cm^{-1}$w.n. level as figure (1) shows a sharp stretching vibration for the free separated alcohol bonded and phenols from the wood lignin.

From the results and bands obtained above. It can be concluded that the lignin of *Eucalyptus camaldulnsis* in this study consisted nearly of equal units of ploy hydroxy phenyl propane as it shown in figure (2)with the absence of the

methoxyl groups because of that the guaiacyl and sringyl units formed the heart of the Lignin polymer whereas the P-hydroxy phenyl propane units form the surface of the polymer in addition to the demethylation of the lignin monomers caused by sulfite ions as it is shown in the model of the reaction in figure (3) due to the higher nucleophility of the sulfite and hydrogen sulfite, which caused a cleavage of some methyl- aryl ether bond depending on the current pH levels , therefore these results are accepted with Nuopponen *etal*. (2004).
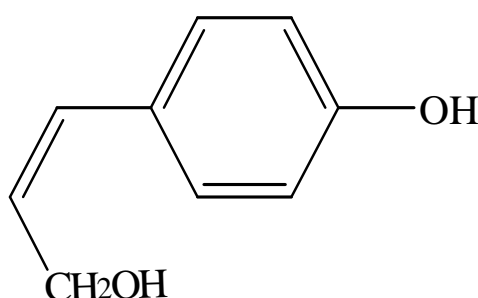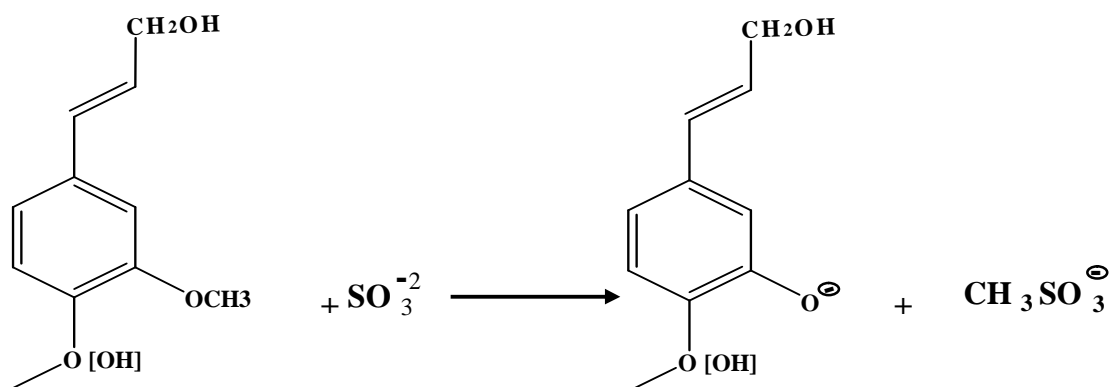

Figure (2): P-hydroxy phenyl propane unit ,   the mean monomer of the tested lignin in the study .

التشخيص الأولي لوحدات لكنين خشب اليوكالبتوس (*Eucalyptus camaldulensis*)البنائية باستخدام مطيافية ألأ FT-IR
Figure (3): The demethylation reaction for lignin units by sulfiteion

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الخلاصة
تمكنت الدراسة من التشخيص المبدئي لللكنين المستخلص من أخشاب اليوكالبتوس *Eucalyptus camaldulensis* وتم استخلاص اللكنين باستخدام طريقة كرافت ثم أخذت عينات من اللكنين المستخلص

وتم تحليلها باستخدام المطيافية تحت الحمراء FT-IR لغرض تشخيص الوحدات البنائية المتكون منها اللكنين . حيث أظهرت هذه المطيافية حزم الامتصاص التالية(٦١٦.٨٠، ٧٩٥.١١ ، ٨٧٦.٩٦ ، ١٠٥٧.١٤، ١١٢٧.١٩ ، ١٤٥٨.٧٤ ، ١٥٠٩.٢١ ، ١٥٤٢.٠٥ ، ١٦٣٦.٢٦ ، ١٧٣٥.٦٨ ، ٢٨٦٣.٧٢ ، ٢٩٢٢.٣٥ ، ٢٩٦٧ ، ٣٤٤٧. ، ٣٦٥٠.٥٦ سم⁻¹). ولم تظهر أية حزمة امتصاص تمثل مجاميع الميثوكسي الموجودة في الوحدات البنائية للكنين ضمن العينات قيد الدراسة ، لذلك فان وحدات اللكنين المستخلص من خشب اليوكالبتوس بطريقة كرافت في هذه الدراسة تعد خالية من مجاميع الميثوكسي ، وإن وحدات البارا- هيدروكسي فنيل بروبان تمثل الوحدات الرئيسية الوحيدة التي يتشكل منها اللكنين في هذه الدراسة .

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