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Thermal Behaviour Of Coconut Coir Husk (Cch) And Extracted Lignin

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ABSTRACT

As the one of abundant renewable resource, lignocellulosic biomass has been acknowledged for potential use to produce chemicals and biomaterials. Lignin is an amorphous, polyphenolic material arising from enzymatic dehydrogenative polymerization of three phenylpropanoid monomers coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol. In this research, extraction of lignin from Coconut Coir Husk (CCH) was studied by thermal analysis in order to characterize their thermal behavior and to identify their constituents by the aid of their thermogravimetric curves and to determine their heat capacity by means of DSC and TGA. The FTIR was also used to determine constituents present in CCH and lignin CCH. The thermal exotherm of the lignin CCH were higher than CCH due to the removal of carbohydrates and other impurities from coir husk. In the other words, the lignin content could defer the thermal curing reactions. In addition, the TGA results shown that the removal of aliphatic sugars and increase aromatic structures can improve the thermal stability of lignin compare to CCH.

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INTRODUCTION

There are several different ways in which the abundance of renewable natural resource can be solved. CCH, an abundant agricultural lignocellulosic is a short fiber, a little flexible and hard when compared to the other fibers. The hardness of fiber is associated mainly to the presence of lignin, which is also responsible for the yellowish colour and for the brown colour to the mature coconut. The inner part of coconut fiber that covers the shell containing of the nut and the part is generated as a waste in the processing of coconut fruit. The composition of the fiber is about 5% of water soluble, 3% of pectin and related compounds, 0.3 % of hemicellulose, 46 % of lignin and 2 % of ash [1]. Thus, the coconut fiber can be classified as a lignocellulosic. Lignocellulose is a low cost biomass that is abundantly available. The main constituents of a biomass are cellulose, hemicelluloses and lignin.

Lignin is the second most abundant polymer in nature after cellulose, appears as promising candidate. It is a phenolic polymer built up by oxidative coupling of three major C6-C3 (phenylpropanoid) units, namely syringyl alcohol (S), guaiacyl alcohol (G), and p-coumaryl alcohol (H) which form a randomized structure in a three-dimensional network inside the cell wall. An aryl-aryl ether type is the major interunit linkage.

Furthermore, lignin seems to be particularly associated with the hemicelluloses polysaccharides even though 20 different types of bonds present in lignin itself. In addition, a small portion of lignin units remains as phenolic being linked only by C-C bonds, such as β -5, β -1, β -5, β - β and α - β linkage. In brief, it can strongly affect the reactivity of the polymer even though this phenolic moiety represents a low fraction of the total lignin [2]. For the application, lignin is used as a cement water reducer, cement grinding aids, bitumen emulsion, drilling mud regulator, plugging agent, viscosity breaking agent, surfactant and dye dispersant.

Lignin has bonding itself and then through the phenol, aldehyde or other modification method, the bonding will be improved. Therefore, it can be used as rubber intensifier, polyolefin and rubber packing. Lignin is also used in composite materials. Lignin has natural similarity for cellulose; it can deal with natural hemp fiber

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surface. At the same time, the bond strength between resin and fiber is increasing. Furthermore, lignin molecular structure enclosed with a variety of active groups, so it can be used in the agroforestry [3]. After degradation slowly by microorganisms in the soil, it can be converted into humus; it has certain inhibition for unerase activity, promoting the growth of plants, improving soil conditions [4].

Many attempts and efforts have been made to utilize lignocellulosic and wood waste by using chemical or biochemical processing methods. Several techniques have been intensively studied and developed such as olification, liquefaction and plasticization [5]. Biomass liquefaction is one of these novel techniques. Many studies has been done by researches on the techniques of wood liquefaction in the presence of an organic which is it is one of the thermochemical conversion processes of biomass. A comprehensive study on liquefied CCH has not yet been clearly established so those need the further study on it. Therefore, the studies on the wood liquefaction had been reviews in order to study the CCH liquefaction. The wood can be liquefied in the presence of phenol or polyhydric alcohols with an acid catalyst at a temperature of 120 °C to 180 °C or without a catalyst at approximately 250 °C. The effects of various factors have been investigated such as liquefaction time, temperature, catalyst content and the amount of reagent solvent on the liquefaction efficacy. Other than that, the liquefied wood also had been studied on the physical characteristics and also their chemical characteristics. The liquefied products can be used to prepare phenolic resin, polyurethane foams and adhesives [6].

The purpose of this paper was to investigate the CCH and lignin CCH's thermal properties by using Differential Scanning Calometry (DSC) and Thermogravimetric Analysis (TGA). In order to analyze their functional groups, FT-IR analysis also used. In this work, the lignin CCH will be extracted from CCH by using alcohol-benzene method in order to remove unemployed component of CCH. The CCH was grinded into powder form before extraction process by using blender and pulverizer were carried out.

Methodology:

Materials:

The coconut coir husk (CCH) was used which obtained from Arau, Perlis. The CCH was grinded into powder form by using industrial blender and pulverizer before sieving by using 213 nm siever. Then, CCH was dried for 24 hours in an oven at 90 °C. Ethanol, benzene and sulfuric acid (72 %) were obtained from Zarm Scientific & Supplies Sdn. Bhd., Butterworth, Pulau Pinang. Sulfuric acid was used as catalyst for the extraction process.

Experimental Procedures:

Extraction of Lignin from CCH:

Method of extraction of lignin from CCH was carried out according to the procedure reported by Li Jinjing [3]. Briefly, 3.5 g CCH powder and 200 mL ethanol-benzene as solvent was transferred into a 500 mL five-neck glass reaction flask equipped with a reflux condenser, thermometer and an electrical stirrer and were reflux for 6 hours with stable boiling of liquid. After extracted with ethanol-benzene, the CCH powder were transferred to a Buchner funnel and washed with ethanol. Then the powder was returned to the extraction flask and extracted with 95 % ethanol for 4 hour. After that, the sample was transferred to a Buchner funnel again and then it was washed with distilled water. Then, the CCH was transferred to a 1000 mL Erlenmeyer flask and boiling distilled water was added. The flask was heated in a water bath at boiling temperature for 1 hour. After the heating, the powder were filtered with a Buchner funnel and then washed with boiling distilled water. Then, the sample was allowed to air-dry at room temperature.

1 g sample was placed in beaker and added with 15 mL cold sulfuric acid. The beaker was kept in a bath for 2 hours with watch glass cover. Afterwards, the solid solution was transferred from the beaker to the flask and water was added. The solution was then boiled for 4 hours in a flask reactor fitted with a reflux condenser. Finally, the lignin was transferred to the filter and then washed with hot water. The lignin was dried at room temperature.

Characterization of CCH and lignin CCH:

Structural and thermal characterization of CCH and lignin CCH was carried out through Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). FT-IR measurements of CCH and CCH lignin sample were taken using Perkin-elmer, US and each scan was recorded in the 4000 to 450 cm^{-1} region. DSC measurements of CCH and lignin CCH were performed using Perkin Elmer DSC7. Approximately 10 ± 0.25 mg samples were placed in a hermetic pan and sealed. DSC scans were performed at a heating rate of 5 °C/ min from 25 to 200 °C under nitrogen environment. TGA measurements were taken using Perkin-elmer with pyris diamond 6 setup operating in nitrogen environment. Samples for each measurement were maintained at 10.0 ± 5 mg and scans were performed from 20 to 600 °C at 10 °C/ min to observe thermal degradation and stability of each lignin based on its sources.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FT-IR):

The structural characterization of CCH and lignin CCH was studied using this technique. The FT-IR spectra of a representative CCH and lignin CCH were illustrated in Fig. 1. The corresponding assignments and bands for CCH and lignin CCH are summarized in Table 1 based on literature.

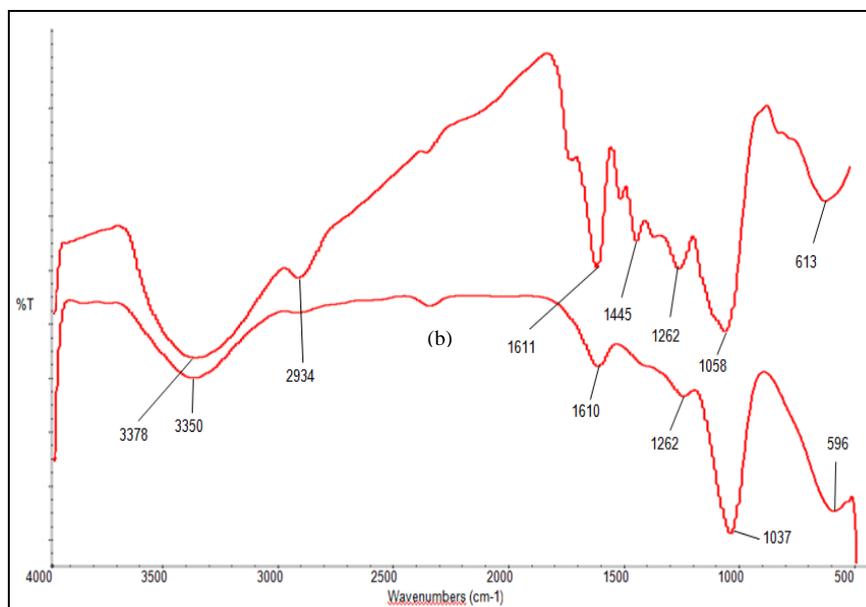


Fig. 1: FT-IR spectra of (a) CCH and (b) lignin CCH

It has revealed that the IR spectra of CCH and lignin CCH are quite similar, implying the similarity of structure between them but different the intensity of peaks. Nevertheless, the IR spectrum of CCH showed the high intensity of peaks than the lignin CCH. This is due to the presence of lignin, celluloses and hemicelluloses in the CCH [3]. For the lignin CCH, all the organic materials that presence in the CCH have been removed using the liquefaction process.

Table 1: FT-IR assignment of the CCH and lignin CCH.

Wavenumber (cm ⁻¹)	Assignment		References
	CCH	Lignin CCH	
3378,3350	The intensity of peaks for phenolic and methylol – OHstretch was wide and quite high	The intensity of peaks for phenolic and methylol –OHstretch was low	[7]
2934	C-H stretching of methyl or methylene groups	-	[8]
1611,1610	Aromatic C=C stretch and gave the high intensity of peaks	Aromatic C=C stretch and gave the low intensity of peaks	[9]
1262	The peak is phenolic OH bending and C-O stretch which gave quite high the intensity of peaks	The peak is phenolic OH bending and C-O stretch which gave low intensity of peaks	[10]
1037,1058	C-OH stretching vibration on the peak which gave low intensity of peak	C-OH stretching vibration on the peak which gave high intensity of peak	[1]
613,596	Adjacent 5H, phenol	Adjacent 5H, phenol	[11]

Differential Scanning Calorimetry (DSC):

Thermal stability studies on lignin extracted from CCH and CCH were carried out through DSC where heat of reaction was measured. The DSC curves of CCH and lignin CCH are shown in Fig. 2 and the results obtained are summarized in Table 2. From Fig. 2, the CCH and lignin CCH exhibited similar curing behavior and their DSC curves showed a main exothermic peak at 30.98 and 31.06 °C, depending on the lignin content in both materials. This peak was related with the condensation of phenolic and methylol groups to form methylene bridges [12]. The exothermic peak of CCH was lower than lignin CCH due to the presence of carbohydrate and other impurities [13].

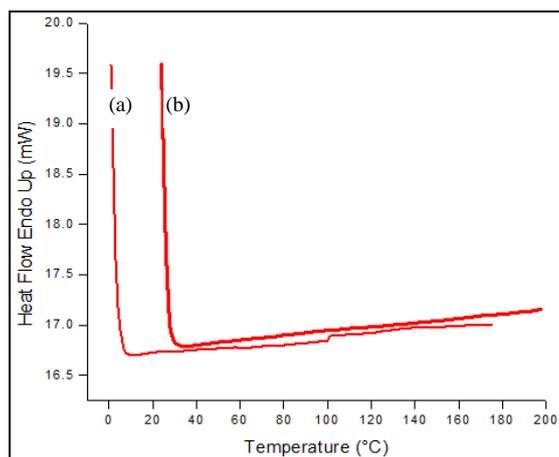


Fig. 2: DSC curves of (a) CCH and (b) lignin CCH.

In addition, Wang *et al.* [13] also reported when the lignin was the majority component in the material, the lignin reactivity would affect the thermal cure reactions, thus deferring the thermal curing process.

Table 2 DSC results for the CCH and lignin CCH

Sample	Onset temperature (°C)	Peak temperature (°C)	Endset temperature (°C)
CCH	23.88	30.98	130.50
Lignin CCH	23.88	31.06	196.96

The endset temperature measurements obtained from DSC was observed which lignin CCH is higher than CCH at 196.96 and 130.50°C, respectively. This is happen because more energy is needed to break down the bonds in lignin compositions yielding a more stable and flame retardant material [14].

Thermogravimetric analysis (TGA):

Thermal stability and decomposition of CCH and lignin CCH have been determined using TGA under nitrogen environment. TGA curves expose the weight loss percentage of materials with respects to the temperature of thermal degradation. In addition, thermal degradation data shows the weight loss of the materials and the first derivative (DTG) indicates the corresponding rate of weight loss. In Fig. 3 and 4 illustrated that the weight loss of CCH and lignin CCH in inert or nitrogen atmosphere. The Fig. 3 shows the weight loss for CCH which is 5.67% initiated at 63°C associated with the presence of absorbed water in raw CCH, 14.84% at 231°C and 35.99% at 311°C. The initial degradation of CCH occurs at about 200°C which can be identified using the pyrolysis process. Then, the second peak of weight loss on CCH was around 200 - 320°C which indicated the hemicelluloses degradation and followed by branching structure of cellulose after its complete degradation [15]. The third exothermic peak of CCH, lignin degrades between 280 and 500°C and leads to the formation of more stable material such as char. At 600°C about 44.97% of non-volatile residue still remained in solid form and were not completely burned [8].

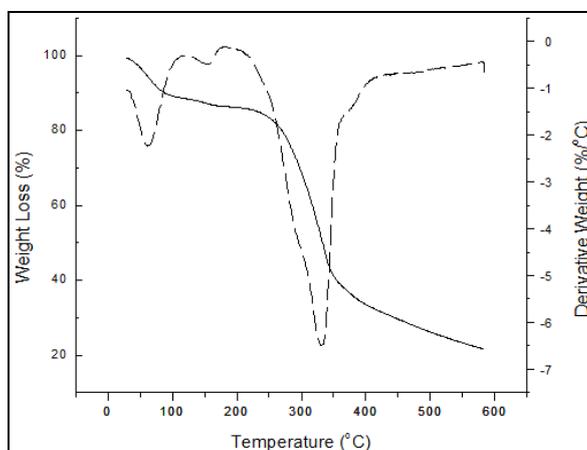


Fig. 3: Thermal Analysis of CCH.

In Fig. 4 showed the initial weight loss of lignin CCH at 74°C associated with water evaporation and second weight loss temperature between 222°C and 268°C indicate the degradation of hemicelluloses. The temperature with maximum rate of weight loss of lignin appeared at 390°C. Thermal degradation in this temperature range involved fragmentation of inters unit linkage, releasing monoric phenol into the vapour phase [16].

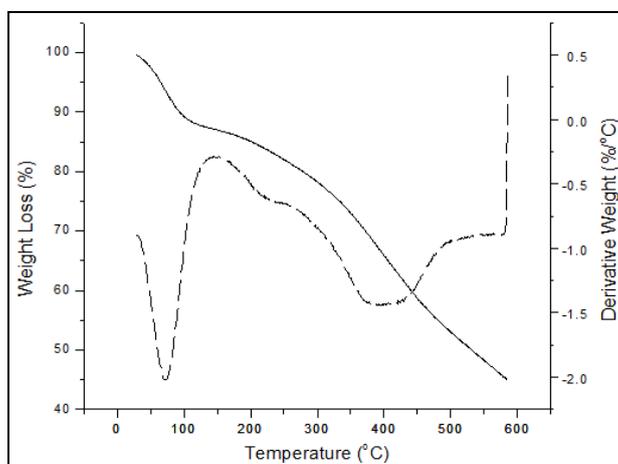


Fig. 4: Thermal Analysis of lignin CCH.

Conclusion:

The present investigation to the CCH and lignin CCH was characterized through FT-IR, DSC and TGA testing methods. By using FT-IR technique, the CCH and the lignin CCH could be characterized well. The thermal properties of the both materials were observed using DSC and TGA. The heat of reaction of the CCH and lignin CCH samples was observed by using DSC. From the main exothermic peak and endset temperature measurements, it is representative that the exothermic peak temperature of lignin CCH is higher than CCH. It might be reasonable due to the presence of carbohydrates in the lignin would encourage the curing process. Thus, it is show that the lignin reactivity would affect the thermal cure reactions, thus deferring the thermal curing reactions. TGA was used to observe the degradation of the CCH and lignin CCH. The thermal stability for the CCH exhibiting 5.67%, 14.84% and 35.99% of mass losses in the first, second and third mass loss stages, respectively. However, the lignin CCH has mass loses about 8% humidity in the first decomposition stage and about 20% in the second stage. Thus, from the TGA results, it shown that the lignin CCH is stable at high temperature compare to CCH. This is due to removal of aliphatic sugars and increase aromatic structures that improved the thermal stability of lignin.

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