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Carbon Fiber Synthesis from Isolated Lignin from Organosolv Fractionation of Bagasse and Eucalyptus

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Abstract: The 50:50 w/w blended of organosolv lignin from the fractionation of bagasse and eucalyptus was successfully converted into carbon fiber. The properties of isolated lignin samples were studied and analyzed by elemental analysis (CHNO), Fourier transform infrared spectroscopic (FT-IR), Nuclear Magnetic Resonance Spectroscopy (H-NMR), thermogravimetric analysis (TGA), gel permeation chromatography (GPC). The images of carbon fibers were observed by scanning electron microscope (SEM). The blended organosolv lignin could be melt spun at 140°C to form lignin fibers. The collected fibers had medium brittleness. The fibers could stabilize at 250°C under air at rate 0.1°C per minute however, some of areas of the fibers were slightly fused. Then, the fibers were carbonized under nitrogen at 900°C. The received blended organosolv lignin based carbon fibers had carbon content at 82.84%. The carbon fibers had smooth surface with the diameter of 13-20 µm. The 50:50 w/w blended of organosolv lignin from bagasse fractionation and organosolv lignin from eucalyptus fractionation had average electrical resistivity of 3×10^{-2} Ωm which had a potential to be used as semiconductor material.

Keywords: Lignin fiber, Fractionation, Organosolv lignin, Melt spinning, Carbon fiber

1. Introduction

Carbon fiber has been used to produce materials in many industries for decades. The carbon fiber industry has grown steadily to fulfill the need of various applications. Nowadays, the properties, applications and manufacturing processes of carbon fiber depend on type of precursors used in the production process. Various types of precursors have been studied to produce high yield carbon fiber with the cost effective production [1]. The most prevalent precursors are pitch derived from petroleum or coal, polyethylene and polyacrylonitrile (PAN). Almost 80% of commercial carbon fibers use PAN as the starting raw material because its superior mechanical properties can be competed to other precursors [2]. However, carbon fiber produced from PAN is expensive and also cause pollution problem. Therefore, there is a need among worldwide industry for a low cost and environmental friendly precursor to solve this problem. Among the precursors for carbon fiber synthesis, lignin is an abundant biopolymer with carbon content above 60% [3-5]. It is known as one of the promising raw materials for synthesizing carbon fiber.

Generally, lignin can be used as raw material for many applications. Potential uses of lignin were classified in different groups as listed: (1) power-fuel-syngas (2) macromolecules or medium term applications and (3) aromatics or longer term applications. The first group can be determined as current or near term applications. Lignin in the first group is used as a carbon source for energy production or is converted in energy carriers such as syngas while the second group will be used in high molecular mass applications like wood adhesives (binders), carbon fiber, and for polymers like polyurethane foams. The third group uses technologies to separate lignin structure into monomers without sacrificing the aromatic rings for production of polymer building blocks, aromatic monomers such as benzene, toluene, and xylene (BTX), phenol, and vanillin [6]. The properties of lignin extracted from biomass depend on its source, syringyl (S), guaiacyl (G) and p-hydroxyphenol (H) monomer proportions [7]. Different monomer proportions in lignin result in different characteristics and perform differently during melt spinning and conversion to carbon fiber [8]. The extraction of lignin from lignocellulose biomass is a significant technique. The extraction processes result in variety of lignin properties such as molecular weight (M_w), purity, etc [9]. The lignin extraction methods can be divided into two main groups which are sulfur and sulfur-free processes. Products from sulfur processes are lignosulfonate and Kraft lignin, which mostly relate to the extraction of lignin from cellulose or produced by pulp and paper industries. The sulfur-free processes include solvent pulping that gives organosolv lignin and soda pulping or alkaline pulping that gives soda lignin.

The converting process of lignin to carbon fiber starts with using lignin in melt spinning process. Melt spinning is the most rapid, convenient and commonly used method for forming fibers [10]. The melt spinning of lignin usually performs under inert gas such as nitrogen and argon to reduce oxidation of lignin fiber. The melted lignin is then extruded through spinneret and the spun lignin fiber is then collected by a winder. After that, the fibers must be thermo-stabilized with slow heating rate in air. This can lead to cross-linking in lignin fiber which converts the nature of lignin from thermoplastic to thermoset. This method raises the melting point of lignin and provides stabilized fiber. Thermo-stabilization also prevents deformation of lignin fiber and fiber fusion during the phase of carbonization. Finally, the fibers must be carbonized at high temperature in nitrogen. The inert atmosphere prevents the combustion of lignin fiber. The carbonization process removes all element except carbon from the lignin fiber [4]. Recent works have revealed that the feasibility of converting lignin to carbon fiber depends on the method use to separate lignin from biomass, the selected method must provide high purity lignin and specific thermal properties [10]. Based on our previous study, high purity lignin can be extracted from biomass using organosolv fractionation (in the presence of ethanol/ethyl-acetate/formic acid) [11]. From the organosolv fractionation of lignocellulosic biomass, high purity lignin (up to 85-90%) can be achieved and would be benefit to the melt spinning for carbon fiber synthesis. This paper mainly focuses on determining the optimal conditions of melt spinning of lignin precursor for carbon fiber application. In addition, upgrading of lignin from organosolv fractionation by thermal and chemical treatments will also be studied with an aim to improve the properties of lignin for melt spinning and further carbon fiber synthesis (stabilization/carbonization steps).

2. Experimental

2.1 Organosolv fractionation

The organosolv fractionation process in this paper used condition and method from an organosolv fractionation developed by Mr. Nopparat Suriyachai in 2015 at the Joint Graduate School of Energy and Environment [11]. This fractionation separates lignocellulosic biomass into cellulose, hemicellulose and lignin. In this process, a 600 ml of stainless steel reactor was heated by electric jacket with a thermocouple to measure inside the reactor. Parr 4848 reactor controller was used to control temperature, pressure and speed of the electric stirring during the process. The reaction contained 1 g of bagasse and 10 ml of the solvent mixture at total volume of 100 ml. This experiment used 45g of biomass with 355.5 ml of ternary mixture of ethyl acetate:ethanol: water (32%:25%:43%) was prepared in the presence of 94.5 ml of formic acid promoter (21%). Nitrogen with the pressure at 20 bars was flown into the reactor for purging and adjusting. Then, the reactor controller was set to temperature at 164°C and pressure at 20 bars. Electrical stirring with a stainless paddle was used at 100 rpm for keeping the system homogeneous. After 45 minutes, the reaction was immediately stopped and cooled down by quenching in a water bath. The slurry was filtered through a 20-25 μm filter paper (No.4) to separate liquid (aqueous-organic fraction) from the solid fraction and then washed with ethyl acetate and water until pH of solid fraction is neutral. The solid fraction was dried and kept for further application. The liquid fraction of aqueous-organic mixture was separated into two phase using separator funnel. Aqueous phase (containing hemicellulose and a trace amount of soluble products e.g. soluble lignin, furfural, and 5-hydroxymethylfurfural) and organic phase (containing lignin product).The aqueous phase was drained from the funnel and kept in waste bottle for treatment. The organic phase was heated and stirred on a hot plate at 80°C for 3 hr. to remove solvent from lignin. Then, lignin was dried in the oven at 110°C The yields of isolated lignin was crushed and stored for further process.

2.2 Lignin characterization

Elemental composition CHNO of lignin samples were determined using Elemental analyzer J-Science MICRO CORDER JM10. Dried and powdered samples were placed in a sample crucible. When the crucible was dropped into the reactor, the oxygen environment triggered a strong exothermic reaction. Temperature rose causing the sample to combust. The gas mixture flew into the chromatographic column, where separation takes place. Electrical signals provided percentages of nitrogen, carbon, and hydrogen contained in the sample. Infrared spectra were collected for the analysis of functional group of lignin samples by FT-IR Perkin-Elmer, Spectrum one. Samples were prepared by using KBr pellet method. Infrared spectra were collected in the range 4000-400 cm-1. The resulting spectrum represented the molecular absorption and transmission, creating a molecular fingerprint of the sample. From this methodology, peaks locate of lignin sample were comparing with the standard of any functional group. H-NMR was used for the analysis of chemical structure of lignin samples. Lignin samples are dissolved in a dimethyl sulfoxide (DMSO), and placed in a magnetic field. A radiofrequency generator irradiated the sample with a short pulse of radiation, causing resonance. When the nuclei fell back to their lower energy state, the detector measured the energy released and a spectrum was recorded. GPC-Tetrahydrofuran (THF) system was used for the analysis of M_w of lignin samples. Lignin and polystyrene standard was dissolved in tetrahydrofuran (THF) before injected into the GPC. The M_w of lignin analyzed by GPC were obtained by using the calibration curve of polystyrene standard. SEM-analyzer (JOEL-6000 Japan Inc.) was used for observing characteristic of lignin fiber such as fiber surface and diameter. Lignin fiber was attached to the tape and placed into the instrument. Tiny electron beam scanned across surface of the sample. Electron signals were detected to produce image of the sample.

The electrical resistance (Ω) of organosolv lignin based carbon fibers can be measured by four-point probe. The four-point probe technique uses four equally spaced probes in contact with a material of unknown resistance. The outer two probes give a direct current. The inner two probes measure the voltage difference. The electrical resistance measurement of carbon fibers in this thesis uses glass plate coated with a thin layer of gold on top as a test pattern. The set of carbon fibers will be placed horizontally across the layer of gold and the four probes will be placed on top of the fibers to measure the electrical resistance of the fibers. The electrical resistance (Ω) is calculated and displayed on the monitor of the instrument.

2.3 Carbon fiber synthesis

Melt spinning of lignin was performed using an assembly extruder. Lignin was melted and extruded through the extruder at 130-150°C with the help of nitrogen flow. A rotating unit rotated at 180 rpm to collect fibers. Lignin fibers were then oxidatively thermo-stabilized by heating the samples to 250°C under air at rate 0.1°C per minute and then hold the samples for 30 minutes at 250°C in a horizontal oven. After that, stabilized fibers were placed in horizontal oven and carbonized under nitrogen. Fibers were heated from room temperature to 600°C at rate 3°C per minute and held for 5 minutes at 600°C and then heated to 900°C at rate 5°C per minute and held for 15 minutes at 900°C.

3. Results and Discussion

3.1 Physical and chemical characteristics of isolated lignins

In this study, lignin samples were dried in 3 periods of time (i.e., 6 hr., 12 hr. and 18 hr.) to study the melting behavior. Organosolv lignin from bagasse could form into fiber however, fused during stabilization while organosolv lignin from eucalyptus could not spin into fiber. Based on Hosseinaei et al, 2017 [8], organosolv lignin from hardwood blended with organosolv lignin from grass was used to produce lignin-based carbon fiber. According to the journal, the 50:50 w/w blended had the best stabilization performance and did not fuse during the thermo-stabilization process. From that, organosolv lignin from bagasse was blended with organosolv lignin from eucalyptus at 50:50 w/w ratio. Organosolv lignin from bagasse fractionation had percent of purity at 89.89% [11]. Organosolv lignin from eucalyptus fractionation had percent of purity at 93.22%.

Table 1. Elemental composition of lignin samples

Lignin samples	C (%)	H (%)	N (%)	O (%)
BG 18 hr.	58.98	5.87	0.73	34.42
BG 12 hr.	55.22	5.78	0.59	38.41
BG 6 hr.	54.41	5.76	0.54	39.29
EU 18 hr.	58.82	5.68	0.37	35.13
EU 12 hr.	59.53	5.85	0.26	34.36
EU 6 hr.	58.05	5.88	0.29	35.78
BG 18 hr. and EU 18 hr.	58.70	5.87	0.44	34.99
BG 18 hr. and EU 12 hr.	58.45	5.95	0.39	35.21
BG 18 hr. and EU 6 hr.	58.73	5.93	0.39	34.95

Table 2. Bands of infrared spectra of lignin samples

Band position (cm^{-1})	Chemical group
3417	O-H stretch
2938-2844	C-H stretch in methyl and methylene groups
1719	C = O stretching of unconjugated ketones, carbonyl and in ester groups (regularly of carbohydrate origin); conjugated carboxylic acids absorb around 1700 cm^{-1}
1605	Aromatic skeletal vibrations plus C = O stretch
1515	Aromatic skeletal vibrations
1462	C-H deformations in methyl and methylene groups
1428	Aromatic skeletal vibrations combined with C-H in plane deformation.
1371	Aliphatic C-H stretch in CH_3
1328	S ring and condensed G ring
1266	G ring and C = O stretch
1218	C-C, C-O and C = O stretch; (G condensed > G etherified)
1170	C = O in conjugated ester groups
1118	Aromatic C-H in-plane deformation, assigned as characteristic of both G ring and S ring
1039	Aromatic C-H in-plane deformation, attributed to contribution from uncondensed G ring
835	C-H out-of-plane in position 2 and 6 of S ring and in all positions of H units

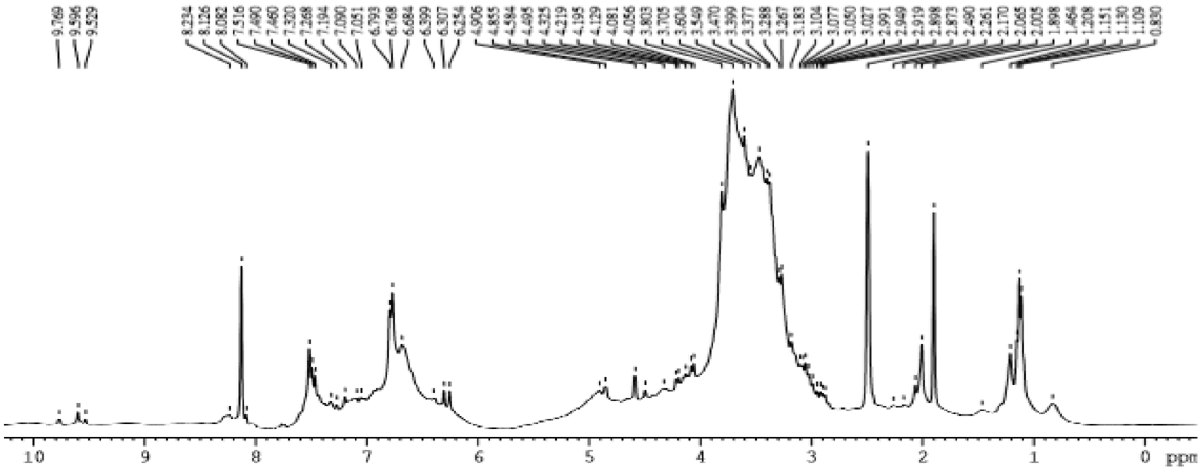

Figure 1. H-NMR spectra of organosolv lignin from bagasse fractionation.

Table 1 shows the elemental composition of all lignin samples. The carbon content of organosolv lignin from bagasse increased as the drying period increased while the carbon content of organosolv lignin from eucalyptus increased from 6 to 12 hours of drying period but decreased when dried at 18 hours. All blended samples had almost the same carbon content. The possibility of making carbon fiber from lignin should have carbon content over 60% [12] and have percent ash of less than 0.1% [1]. All lignin samples had no ash content, however, they had carbon content slightly lower than 60%.

Figure 1 shows that the effect of time during the drying process and the 50:50 w/w blended of organosolv lignin from bagasse and eucalyptus had low impact on the functional groups in lignin samples. Table 2 provides the band of infrared spectra of lignin samples [13-14].

The H-NMR of lignin samples was performed. The signals between 6.0 to 8.0 ppm represent the aromatic protons in G and S units which can be mostly found in grass and hardwood lignin. The signals at 6.7-6.8 ppm exhibit the aromatic proton in G units. The peak at 6.6 ppm relate to S units. Based on the H-NMR spectra (Figures 2-3.), organosolv lignin from bagasse had higher G units than S units. The bagasse lignin can be spun into fibers but they fused during the stabilize process while organosolv lignin from eucalyptus contained lower G units than S units. The eucalyptus lignin possessed more condensed structure however, couldn't be spun into fibers. The effect of blending organosolv lignin from eucalyptus with organosolv lignin from bagasse can improve the properties of lignin which showed better result of fibers in stabilization. Table 3 lists the structural assignments of signals in H-NMR of BG 18 hr. and EU 6 hr. [15-16].

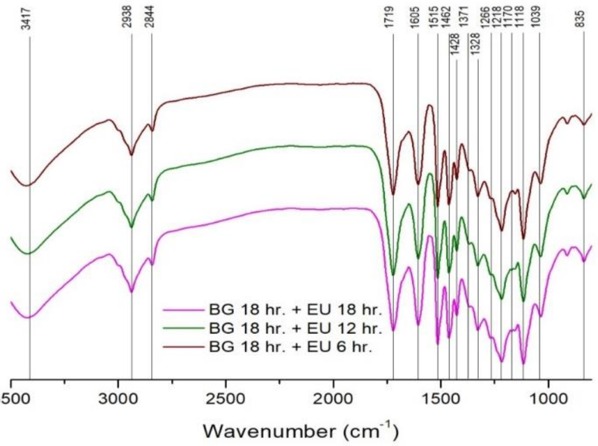

Figure 2. FT-IR spectra of blended organosolv lignin.

Table 3. Assignment of signals in H-NMR of BG 18 hr. and EU 6 hr.

ppm	Assignment
0.8-1.5	Aliphatic moieties in lignin fraction
2-2.2	Methyl protons adjacent to double bonds
2.5	Protons in DMSO
3.4-3.8	Protons in methoxyl group
4-4.7	Hγ and Hβ in β-O-4 structures
6.6	Aromatic protons in S unit
6.7-6.8	Aromatic protons in G unit
9.6	Formyl protons in cinnamaldehyde units
9.8	Formyl protons in benzaldehyde units

Table 4. Molecular weight of lignin samples

Lignin samples	M_w	M_n	M_z	Polydispersity
BG 18 hr.	1,739	919	2,867	1.893
BG 12 hr.	1,313	728	2,046	1.804
BG 6 hr.	1,273	728	1,945	1.749
EU 18 hr.	2,670	1,170	5,386	2.282
EU 12 hr.	2,458	1,117	4,743	2.201
EU 6 hr.	2,287	1,077	4,355	2.122
BG 18 hr. and EU 18 hr.	2,160	991	4,425	2.181
BG 18 hr. and EU 12 hr.	1,926	933	3,675	2.065
BG 18 hr. and EU 6 hr.	2,077	1,012	3,837	2.053

Figure 3. Organosolv lignin fibers

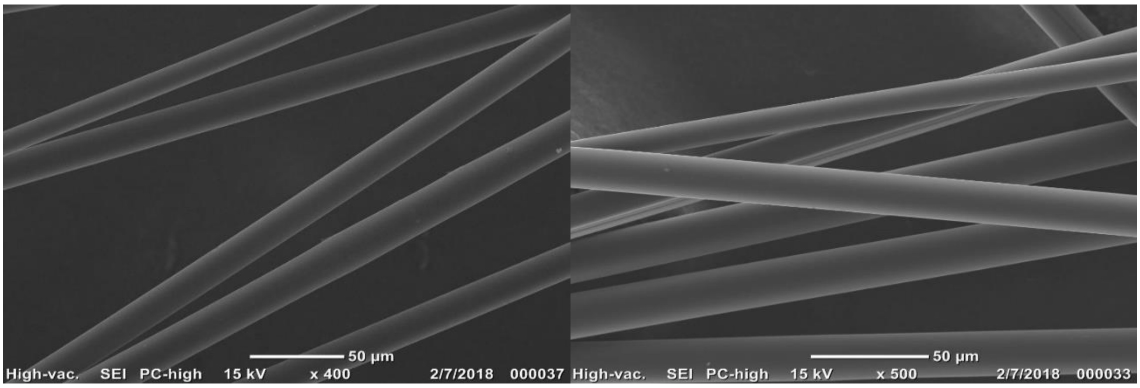

Figure 4. SEM image of blended organosolv lignin based carbon fiber.

As shown in Table 4, all lignin samples had M_w around 1,200-2,600 atomic mass unit. The result showed that the M_w of both organosolv lignin from bagasse and eucalyptus samples increased as the period of time during the drying process increased. Base on the review, lignin with low M_w is easier to spin but hard to stabilize [17].

3.2 Carbon fiber synthesis from isolated lignin samples

From all isolated lignin samples, only 4 lignin samples could be spun into fiber which were BG 18 hr., BG 12 hr., BG 18 hr. blend with EU 12 hr. and BG 18 hr. blended with EU 6 hr (Figure 4.). All samples that could be spun started melting at 110°C but they were too viscous to flow. Samples could be melt spun into fibers at the temperature between 130-150°C. Then, they reached the high melt flow at 160°C. At this temperature, they could not be spun because they were too watery and flew out of the extruder as droplets instead of fiber. Crosslinked occurred at 180°C. From the observation, the appreciable melting temperature where organosolv lignin from bagasse could be spun with the highest yield was at 130°C and 140°C for blended organosolv lignin. BG 18 hr. and BG 12 hr. had medium brittleness but the BG 18 hr. had higher fiber yield than BG 12 hr. The fibers from BG 18 hr. blends EU 12 hr. can be collected at very low amount. The fibers were thin and had high brittleness while the fibers from BG 18 hr. blends with EU 6 hr. showed almost the same properties as fibers from BG 18 hr. but the yield was slightly less than BG 18 hr.

Based on the M_w of lignin samples, organosolv lignin from bagasse and blended organosolv lignin with M_w in the range of 1,300-2,000 atomic mass unit could be spun into fiber while organosolv lignin from eucalyptus had M_w over 2,000 atomic mass unit could not be spun into fiber. BG 18 hr. was selected to stabilize as it had the best properties compared to BG 12 hr. The fibers were stabilized under air at the rate of 0.5°C per minute and 0.1°C per minute to 250°C and hold for 30 minutes. The yield of thermos-stabilized fibers at both rates were 70%. From the observation, the fibers were severely fused during stabilized at rate of 0.5°C per minute while the fibers stabilized at rate 0.1°C per minute were moderately fused. The 50:50 w/w blends of BG 18 hr. and EU 6 hr. fibers were selected to stabilize under air at rate 0.1°C per minute to 250°C and hold for 30 minutes. The yield of selected fibers after the process were 73.69%. From the observation, most of the fibers were not fused however, there were some areas that the fibers were slightly fused causing them stuck together. From the stabilization process, blended organosolv lignin that had M_w over 2,000 atomic mass unit improved the fusing during the process.

The stabilized fibers of 50:50 w/w blends of BG 18 hr. and EU 6 hr. were carbonized under nitrogen at rate 3°C per minute to 600°C and held for 5 minutes. Then, heated to 900°C at rate 5°C per minutes and held for 15 minutes. The yield of carbonized fibers were 51.73%. The fibers had carbon content of 82.84%. Figure 5 shows the image of carbon fibers. Blended organosolv lignin based carbon fiber had smooth surface with the diameter of 13-20 µm. The carbon fibers had average electrical resistivity of $3x10^{-2}$ Ωm which is comparable to the electrical resistivity of semiconductor material such as silicon and germanium.

4. Conclusions

Organosolv lignin from bagasse with higher G units than S units could be spun into fibers while organosolv lignin from eucalyptus with lower G units than S units could not. On the other hand, organosolv lignin with lower G units than S units could form at high temperature as it had more condensed structure but organosolv lignin with higher G units than S units was fused at the same condition. Based on melt spinning and thermo-stabilization process, organosolv lignin with M_w in the range of 1,300-2,000 atomic mass unit could be spun into fiber while organosolv lignin with M_w over 2,000 atomic mass unit improved the fusing during thermo-stabilization. After carbonization, carbon fibers of 50:50 w/w ratio blended of BG 18 hr. and EU 6 hr. had carbon content at 82.84%. Blended organosolv lignin based carbon fiber had smooth surface with the diameter of 13-20 µm. The lignin based carbon fibers in this thesis could not do the tensile test because the fibers were brittle. As the carbon fibers did not offer mechanical properties which required for many structural applications, electrical resistance of the carbon fibers were tested and had average electrical resistivity of $3x10^{-2}$ Ωm which had a potential to be used as semiconductor material.

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