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Preparation of super-capacitor from soluble produced from rice straw

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Abstract: Biomass waste was a renewable resource, and its effective utilization was of prime importance, particularly in Thailand, where massive amounts of biomass wastes were generated. Recently, the authors had presented a degradative solvent extraction method that converts biomass waste into high-quality extract at 350°C using petroleum-based solvents. The extracts, called solubles. In this study, the possibility of carbon fiber from soluble to produced supercapacitor had been examined. The solubles were heated in nitrogen atmosphere at 280-320°C to increase the softening point. Then, they were spun into fiber using a mono-hole spinning machine, and then they were stabilized in air at 300°C and were carbonized at 900-1,400°C in nitrogen atmosphere. The carbon fibers had hollow and the specific surface area was around 326 m^2/g. The electrical conductivity of carbonized fiber at 900°C was 32.02 S/cm at electric current of 800 µA. The specific capacitance of the carbonized fiber at 900°C was 46.79 F/g using KCl as electrolyte. These results showed a good potential for producing supercapacitor from soluble produced from rice straw.

Keywords: Carbon fiber, biomass, supercapacitor.

1. Introduction

At present, global warming was a main problem situation due to using energy from fossil fuel worldwide. The utilization of renewable energy sources had thus become increasingly of interest. Biomass was one of the environmentally friendly renewable sources which had recently received growing attention for the replacement of petroleum-based energy sources [1].

Biomass had been being studied in Thailand because Thailand was an agricultural country with many products from agriculture such as rice, cassava, palm and coconut etc. There were waste residues that occur after harvest and processing of agricultural products, including rice straw, rice husk, and bagasse etc. However, there were some limitations in using biomass to generate energy, since it had low energy density, low heating value and high moisture content. Moreover, another problem issue were the biomass collection, transportation and management. Therefore, our research group proposed to upgrade biomass by a degradative solvent extraction [2]. In this process, 1-methylnaphthalene was used as a solvent at 350ºC to upgrade biomass by the selective removing of oxygen functional group as water and carbon dioxide during the treatment. The upgraded product was fractionated into three solid fractions: Soluble, Deposit, and Residue. The soluble could be used to produce carbon fibers since it contained high carbon contents without moisture and ash in its composition [3]. There were elemental compositions in the range of C = 81.0-83.3 wt %, H = 6.1-7.3 wt %, and O = 7.3-11.1 wt %. The properties of Soluble showed almost completely free form ash, completely melts below 100°C, solubles comprised uniform low-molecular-weight compounds, and 60-70% of the solubles were devolatilized below 400°C. The solubles had potential utility for various purposes and constituted the largest yield fraction and have unique properties [4]

On the other hand, Supercapacitors were the type of capacitors in which energy storage was based on charging and discharging processes at the electrode-electrolyte interface. The energy storage in supercapacitors was governed by the same principle as that of a conventional capacitor, however, were preferably appropriate for quick release and storage of energy [5]. There were 3 categories of supercapacitor 1) electric double layer capacitors (EDLC) 2) pseudo-capacitor and 3) hybrid supercapacitors.

In this study, the possibility of using carbon fiber from rice straw in supercapacitor application would be carried out. The effects of carbonization on yield, specific surface area and electrical conductivity would be exanimated. The measurement of CV would be performed to evaluate the performance of rice straw-based carbon fiber for supercapacitor applications.

2. Materials and method

2.1 Material

Soluble extracted from rice straw was produced by using degradative solvent extraction method. This method used 40 g. of rice straw on a dried basis and 1500 ml of A-150 as a solvent were charged into the autoclave reactor. The reactor was heated from room temperature to 350°C at heating rate 5 °C/min and held for 60 min at 350°C. After that, the soluble was also recovered as a solid by removing the solvent by a rotary vacuum evaporator at 150°C and dried in a vacuum oven at 150°C for 24 hr. This material was used as a precursor for carbon fiber production. The properties of rice straw and soluble were showed in Table 1.

2.2 Carbon fiber preparation

Carbon fibers were produced from extracted soluble in 4 steps. The first step called pretreatment of soluble, soluble was heated under nitrogen atmosphere at conditions 320ºC for 40 minutes with a heating of rate 10°C/min. Then, the pretreatment soluble was spun to fibers at 280-320°C by melt spinning method using a mono-hole continuous spinning machine at the winding speed 150 m/min under nitrogen atmosphere. The as-

spun fiber derived obtained from the pretreatment soluble, which are black and brittle. Then, the as-spun fibers were continuously stabilized at 300ºC for 60 min. with a heating rate of 0.5°C/min. under air flow. Approximately 0.4 g. of thermal stabilized fibers were used to make tablet by using a hydraulic shop press machine at 400°C with a heating rate 10°C/min. and held under the applied pressure less than 16 bars for 10 minutes. The mold diameter used in tablet preparation was 13 mm. Finally, the fiber tablet (see Figure 1) was heated up from room temperature to 900, 1,200 and 1,400ºC, with a heating rate of 10°C/min under nitrogen and held in a tube furnace. After that, studied a composition of carbonized fiber and choose the best of temperature of carbonized for activated carbon fiber.

Table 1. Proximate analysis and ultimate analysis and yield of rice straw.

Ultimate analysis (wt%, d.a.f.)	Samples	
	Rice straw	Soluble
C	47.0	80.3
H	6.5	6.8
N	0.6	1.7
O (diff)	45.9	11.2
Proximate analysis (wt%, d.b)		
VM.	72.2	66.4
FC.	12.0	33.6
Ash	15.8	0.0
Yield (wt%, d.a.f.)	-	31.0

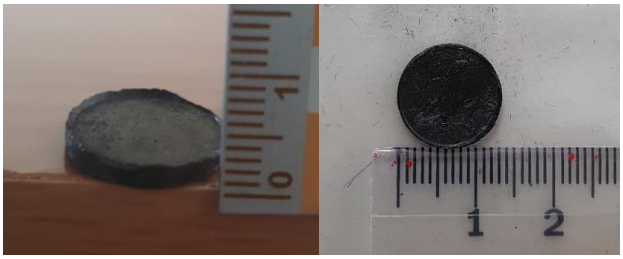

Figure 1. carbon fiber table

2.3 Analyses of carbon fiber

Soluble, as-spun fiber, stabilized fiber and carbon fiber were characterized by various analyses. The softening/melting point of samples was analyzed by using a thermo-mechanical analyzer (Shimadzu, TMA 60). The TMA estimated a relative displacement of sample in aluminum pan under 10 g. of sample under nitrogen atmosphere and heated up from room temperature to 600°C with heating rate 10°C/min. The proximate analysis of sample for fining the physical composition of samples include moisture, ash and volatile matter examined by using thermo-gravimetric analyzer (Shimadzu, TMA 50). The ultimate analysis of sample for finding the chemical composition of sample include carbon (C), hydrogen (H), oxygen (O) and nitrogen (N) examined by using CHN corder (J-science, JM 10 CHN). The morphology of fiber for finding the cross section and diameter of fiber in condition as spun fiber, stabilized fiber and carbonized fiber at 900, 1,200, 1,400°C respectively, examined by using scanning electron microscope (Hitachi, SU5000). The surface area of fiber examined by using automated adsorption apparatus (BEL, belsorp mini II) to estimate BET surface area and nitrogen adsorption isotherm of carbon fiber in condition carbonized fiber at 900, 1,200, 1,400°C respectively, the raman spectroscopy was a method for finding the chemistry to study a structural of carbon fiber in condition carbonized fiber at 900, 1,200, 1,400°C respectively, by spectroscopic technique. The electrical conductivity of carbon fiber tablet in condition carbonized fiber at 900, 1,200, 1,400°C respectively, examined by using 4-point probe method (Jandel RM3). The cyclic voltammetry was a method for finding the capacitance of carbon condition carbonized fiber at 900, 1,200, 1,400°C respectively, by using Autolab PGSTAT 302 N.

2.4 Electrochemical measurements

The cyclic voltammetry (CV) curve measured by 3 electrode system in a galvanostatic mode [6] include 1. Working electrode for put and cover ACF on the platinum mesh 2. Counter electrode made from platinum mesh 3. Reference electrode made from Ag/AgCl and using 1 M KCl and 1 M KOH as an electrolyte. The CV curve measured by using potential range -2 to 2 V, and using scan rate 10, 20, 50, 100 mV/s.

The charge/discharge (GCD) test conducted on batteries test system [7] in a potential range -2 to 2 V, and current density of 0.1 A/g by using 1 M KCl and 1 M KOH as an electrolyte. Then, the specific capacitance (C, F/g) could be calculated from charge/discharge curve according to Eq (1).

$$C = \frac{I\,\Delta t}{m\,\Delta V} \quad (1)$$

Where C was the specific capacitance of supercapacitor in unit F/g, I/m was discharge current density in unit A/g, ΔV was a discharge voltage, Δ t was a discharge time.

3. Result and discussion

3.1 SEM image, adsorption isotherm and raman spectroscopy of carbon fiber

Figure 2, showed the SEM image of fiber in condition as-spun fiber (a,b) and carbonized fiber at 900, 1,200 and 1,400ºC (c-h) respectively. The diameter of fiber was measured using ImageJ program and the average value of 40 samples was used as average diameter. It was shown that the fiber prepared from pretreated soluble at 320ºC had hollow. The average diameter of fiber in condition as-spun fiber and carbonized fiber at 900, 1,200 and 1,400°C were 37.92, 18.17, 23.93 and 28.37 µm. respectively, and the average diameter of hollow for fiber in condition as-spun fiber and carbonized fiber at 900, 1,200 and 1,400°C were 35.93, 9.52, 14.76 and 24.89 µm. respectively. Figure 3 showed the nitrogen adsorption isotherm of carbonized fiber at 900, 1,200 and 1,400°C. The nitrogen adsorption isotherms of fiber were type I of the IUPAC standard adsorption isotherm, which was a typical microporous carbon. The BET surface of carbonized fiber at 900, 1,200 and 1,400°C were 326, 124 and 55 m^2/g. Table 2 showed surface area, total pore volume and average pore diameter of carbonized fiber at 900, 1,200 and 1,400°C. Figure 4 showed the raman spectroscopy of carbonized fiber at 900, 1,200 and 1,400°C. The raman shift of D band was 1,340.48 cm^{-1} and raman shift of G band was 1,592.24 cm^{-1}. Table 3 showed the ratio of ID/IG of raman shift. The carbonized fiber at 1,400°C had the lowest ID/IG ratio and the carbonized fiber at 900°C had the highest ID/IG ratio. These results of ID/IG ratio explained the carbonized fiber at 1,400°C was the structure of carbon as diamond as higher than carbonized fiber at 900°C.

Table 2. Surface area, total pore volume and average pore diameter of carbonized fiber at 900, 1,200 and 1,400°C.

Samples	**Surface area (m^2/g)**	**Total pore volume (cm^3g^{-1})**	**Average pore diameter nm.)**
Carbon fiber at 900°C	326	0.19	2.33
Carbon fiber at 1,200°C	124	0.08	2.47
Carbon fiber at 1,400°C	55	0.06	4.48

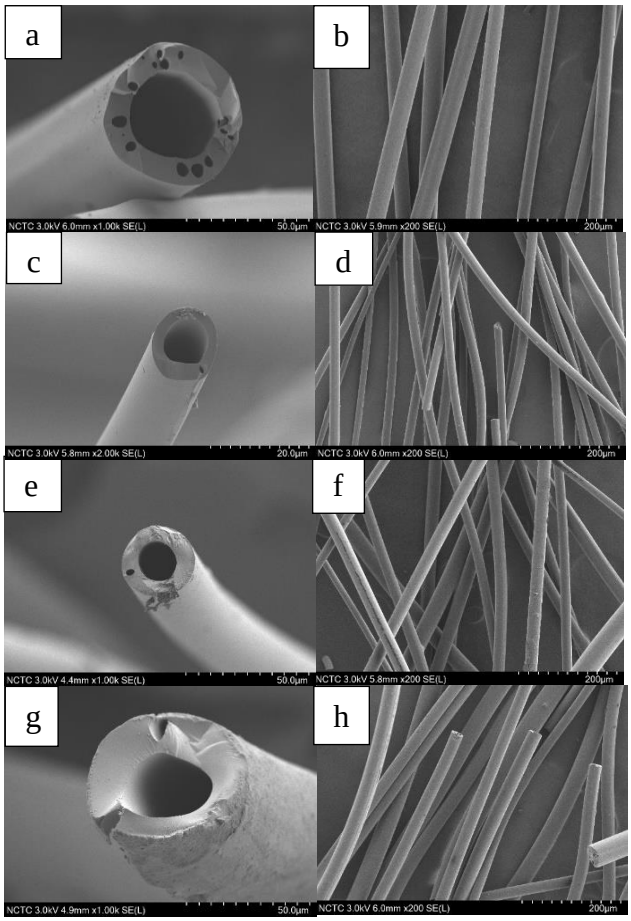

Figure 2. SEM image of fiber in condition as-spun fiber (a,b) and carbonized fiber at 900 (c,d), 1,200 (e,f) and 1,400°C (g,h).

Table 3. The ratio of ID/IG from raman shift.

Samples	Intensity	ID/IG
Carbonization at 900°C	70.38	0.82
	85.64	
Carbonization at 1,200°C	243.59	1.13
	214.94	
Carbonization at 1,400°C	268.84	1.36
	197.04	

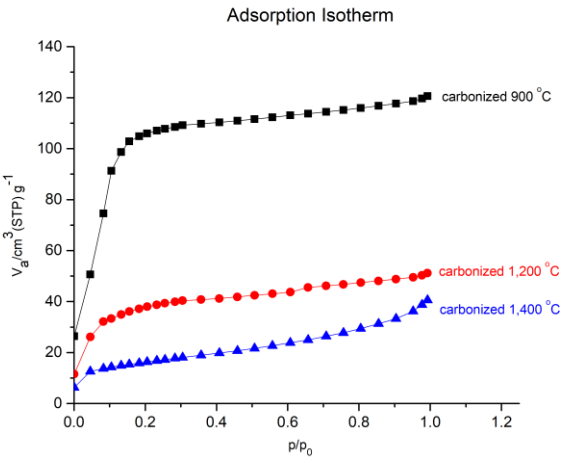

Figure 3. The nitrogen adsorption isotherm of carbonized fiber at 900, 1,200 and 1,400°C.

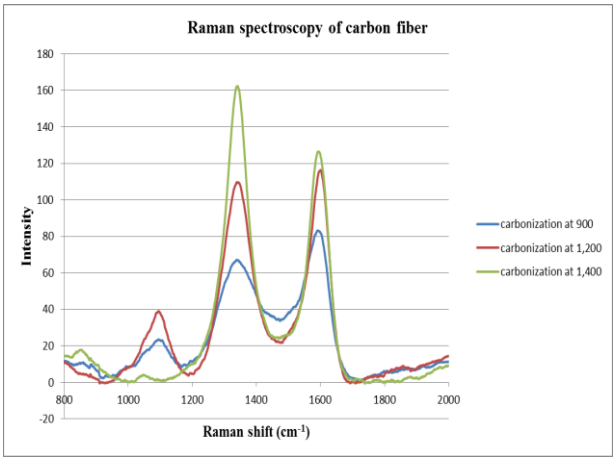

Figure 4. The raman shift of carbonized fiber at 900, 1,200 and 1,400°C.

3.3 Electrical conductivity of carbon fiber

Table 4 showed the electrical conductivity of carbon fiber tablets prepared from carbonized fiber at 900, 1,200, 1,400°C respectively. The results showed that the electrical conductivity of the carbon fiber tablet decreased with increasing carbonization temperature. The carbon fiber tablet prepared from carbonized fiber at 900°C had the highest electrical conductivity, which was 32.02 S/cm at electric current of 800 µA. Alencherry et al. reported that the electrical conductivities of activated carbon were 0.84-1.19 S/cm [8]. So, it was shown that our carbon fibers had larger electrical conductivity than those from the literature.

Table 4. The electrical conductivity of carbon fiber tablet.

Carbonization Temperature (°C)	Thickness (cm.)	Electric current (µA.)	Conductivity (S/cm)
900	0.21	600	13.92
		800	32.02
1,200	0.27	600	7.55
		800	11.78
1,400	0.30	600	7.25
		800	8.61

3.4 Electrochemical

The specific capacitance value of ACF measured from charge/discharge curve (see Fig. 5) followed from equation 1. The charge/discharge (GCD) test conducted on batteries test system in a potential range -2 V to 2 V, and current density of 0.1 A/g by using 1 M KCl and 1M KOH as an electrolyte. Table 5 showed the capacitance value of carbon fiber prepared at 900°C by using 1 M KCl and 1 M KOH as an electrolyte. It was found that the specific capacitance measured by GCD method using 1 M KCl as an electrolyte was higher than that using 1 M KOH. The specific capacitance was 46.79 F/g for 1 M KCl and 40.91 F/g for 1 M KOH.

Fig. 5 showed the charge/discharge curve of carbon fiber prepared at 900°C by using 1 M KCl (Fig. 5a) and 1 M KOH (Fig. 5b). It was found that the IR drop, the gap between the end of charge and the start of next charge, was greater for KOH than that of KCl. IR drop exhibits the resistance between electrode and electrolyte. The greater IR drop means the electrolyte is not appropriate. So, KCl was considered as an appropriate electrolyte for carbon fiber in this study.

Table 5. The capacitance of carbon fiber prepared at 900°C.

Sample	Capacitance value (F/g) by using current density 0.1 A/g	
	1 M KCl	1 M KOH
Carbon fiber at 900°C	46.79	40.91

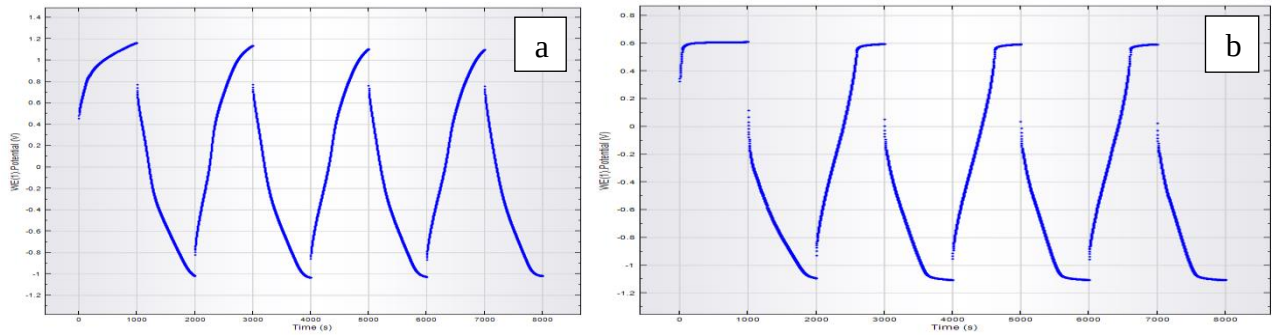

Figure 5. The charge/discharge curve of carbonized fiber at 900°C by using 1 M KCl (a) and 1 M KOH (b) as an electrolyte.

Hye-Min Lee et al. [9] studied electrochemical behavior of activated carbon fiber produced from pitch-based. They found that the specific capacitance of the activated carbon fiber was 21.6 F/g. Fujishige et al. [10] prepared EDLC electrode from activated carbon produced from Bamboo cellulose and found that the specific capacitance was 44 F/g. Comparing the specific capacitance from literatures, it was found that the carbon fiber prepared from this study shown greater specific capacitance. So, these results showed a good potential for producing supercapacitor from soluble produced from rice straw.

4. Conclusion

A possibility of utilizing carbon fiber produced from rice straw in supercapacitor application was examined. The Soluble was spun into fiber at 280°C by melt spinning method using a mono-hole continuous spinning machine. Then, the as-spun fibers were continuously stabilized at 300ºC for 60 min. The stabilized fibers were pressed into tablet at 400°C under compression pressure of 16 bar using a hydraulic shop press machine. Finally, the fiber tablets were carbonized at 900, 1,200 and 1,400ºC to produce carbon fiber tablets. SEM image of carbonized fiber showed smooth surface of carbonized fiber and the diameters of the fiber were fiber around 9-20 µm. The BET surface area of the carbonized fiber at 900, 1,200 and 1,400°C was 326, 124 and 55 m^2/g, respectively. The electrical conductivities of carbonized fiber decreased with increasing carbonization temperature. The carbon fiber tablet prepared from carbonized fiber at 900°C had the highest electrical conductivity, which was 32.02 S/cm at electric current of 800 µA. This result showed that the carbonized fiber at 900°C was the best condition for preparing EDLC supercapacitor. The specific capacitance of the carbonized fiber at 900°C was 46.79 F/g using KCl as electrolyte. These results showed a good potential for producing supercapacitor from soluble produced from rice straw.

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