High porous carbon nanofiber derived from lignosulfonate material

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Abstract. In this study, electrospinning technology, iodine treatment, thermal stabilizing, and carbonization processing were applied to produce lignosulfonate-based carbon nanofibers. The porous structure of the produced lignosulfonate-based carbon nanofibers primarily contained mesopores and a relatively small amount of micropores. Moreover, the increasing amount of sodium lignosulfonate (SLS) as lignin source was also studied. The diameter of fibre was impacted by the additional of SLS that may cause by the alkali content of SLS itself. In electrospun nanofiber phase, the presence of SLS reduce the specific surface area, but contrary increase the specific surface area after the nanofibers were carbonized into carbon nanofiber. Lignosulfonate-based activated carbon fibres can be used as a highly efficient adsorption and filtration material, and further development of its applications would be valuable.

1. Introduction
As a mesoporous and microporous structured material, activated carbon has many promiscuous usage, due to its absorptivity, specific surface area, and hydrophilicity, activated carbon is commonly used as an adsorbent material in food and environment application [1, 2]. Furthermore, it has porous structure that able to interact with the adsorbed subjects chemically or physically to eliminate odorous, coloured or harmful substances. It makes activated carbon is currently used in food, medical, solvent recovery, water treatment, waste gas, fuel cell industries and or even energy storage [3].

Based on the shape and usage, activated carbon can be divided into powdered activated carbon, granular activated carbon, and activated carbon fibre [4]. Activated carbon fibre or usually known as carbon nanofiber (CNF) is commonly prepared by activating the nanofiber that synthesized using common polymer material such as PAN, PVA, cellulose acetate, etc. CNF has many favourable characters such as large surface area, uniform pore size, high adsorptive ability, regenerable, and satisfactory mechanical properties [5, 6]. Industrial applications of general-purpose and high-performance CNF have been widely explored. Researchers have attempted to develop bio-based CNF precursors that are low-cost and environmentally friendly. Among such precursors, lignin is introduced as inexpensive and has a favourable structure as a precursor for the production of CNF [7].

Lignin is one of the natural biopolymers that exists in the cell wall of plants. It is a natural, aromatic, high carbon content, heterogeneous biomacromolecule that has a total worldwide production of approximately 70 million tons/year [8]. However, conventionally, in the pulp and paper industry, chemicals are applied to eliminate lignin during pulping, and technical lignin are produced as byproducts. These are generally trashed or used as a fuel source, but in a very small quantity is used in
commercial applications. For these reasons, lignin is the renewable raw materials that are largely used for the preparation of nanofiber.

The use of technical lignin as precursors to produce CNF has been extensively studied [4, 9]. Particularly, lignosulfonate-based CNF were fabricated through a series of electrospinning and carbonization processes. However, those previous study used acid-based lignosulfonate to synthesize the nanofiber. It makes after carbonization, an activation process needs to be implemented to generate submicron or nanoscale lignin-based Activated Carbon Nanofiber (ACNF) with small diameters and large surface areas. Whereas some previous study provided data that by using alkali lignin, the product of carbon can have high surface area with less separated activation process.

In work, the sodium lignosulfonate were used as lignin source for the electrospinning process to produce nanofiber. The effect of lignosulfonate mass ratio solution was studied to the specific surface area.

2. Experimental

2.1. Materials
The precursor of the Carbon nanofiber was a mixture of Sodium Lignosulfonate (Gac-NaLS grade 3, Green Agrochem) and poly-vinyl alcohol (PVA, Mr = 60,000, Sigma Aldrich). And for stabilisation, technical grade of iodine crystal purchased from UD SIP Indonesia was used. All of the materials were used as received without purification.

2.2. Solution Preparation
The PVA was stirred in distilled water for an hour at a temperature of 85°C. After all of the PVA was diluted, the sodium lignosulfonate (SLS) was then added to the solution to obtain black viscous solution with ratio of PVA and the SLS in the water was 15:0,1.5, and 3% wt/vol. After thawed at room temperature for several hours, the solution was then filled into 50ml scaled modified syringe before ready to be installed in electrospinning device.

2.3. Electrospinning
Electrospinning was performed in the horizontal direction (Figure 1) with electrospinning equipment was based on our previous research [6, 10]. The black solution was carried out in a Terumo plastic 50 ml syringe with needle an inner diameter 0.8 mm (21 gauge). The steady flow rate was maintained by the Cole Parmer Instrument Co. syringe pump at 1 ml per hour. A high voltage power supply was connected the needle and the collector. The applied voltage at 15 kV was applied to the polymer solution and using 10 kV was applied onto a rotary collector device. Previously, the rotary collector device was wrapped by a 15 cm x 30 cm of aluminium foil around rotating cylinder. The distance from needle to collector was 10 cm. The rotary collector was rotated with a speed of 100 rpm in a room temperature for 7 h, respectively, and the measured relative humidity percentage was between 55 and 65%.
2.4. *Iodine Treatment, Thermal Stabilization and Carbonization*

After peeled off from the aluminium foil on rotary collector, the electrospun obtained was then placed with iodine in the sealed bottle and heated at 80 °C for 24 h before the carbonization process. After that, the iodine-treated electrospun lignosulfonate nanofiber mat was thermally stabilized by gradually heated in the air at temperatures of 100, 150, and 200°C for an hour at each temperature. It was then followed by carbonization under nitrogen flow with a flow rate of 25 mL/ minute at 400 °C for an hour, and then 700°C for an hour following the highest temperature of activated carbon from lignin in previous study [11]. The generated activated carbon nanofibers were washed with the mineralized water until the washing water was neutralized.

2.5. *Characterization*

To examine the morphology of the nanofiber and carbon nanofiber, scanning electron microscope (SEM, HITACHI FLEXSEM-100) equipped with Dispersive Energy X-Ray Spectroscopy (EDS) was used. The specific surface area was obtained from the Brunauer-Emmett-Teller (BET) method by measurement of nitrogen adsorption-desorption isotherms (Quantachrome instrument, NOVA1200e).

3. *Result and Discussion*

Before applied as precursor in synthesizing nanofiber, we need firstly know the possibility of SLS itself to be treated as activated carbon. Therefore, the SLS was treated following our previous research [11]. And the result is described as below (Figure 2)
As can be seen above (Figure 2(a)), the carbon morphology obtained from SLS show rough surface that comprises numerous hole with average diameter 400 nm that represent active side, describing that the carbon has been activated. This is further provided by nitrogen adsorption-desorption data (Figure 2(b)) that showing BET graph type II that indicates that the pore is focused on the first layer. The specific surface area obtained was 1168.241 m²/g with pore volume of 1.211 cc/g and averaged pore diameter of 4.15 nm. As supporting data, Table 1 showing that high amount of alkali that may increase the active side of carbon derived from SLS.

Table 1. Content of activated carbon from SLS obtained from EDS

| Element | Wt% |
|---------|-----|
| C-O     | 21.47 |
| S       | 5.95  |
| Alkali  | 35.10 |
| Cl      | 21.08 |
| Impurities | 16.4 |

The homogenous of carbon content in solution is one of important factor in electrospinning polymer/inorganic composite. In other study that involve particulate material as compositied additive to polymer, sonication is an effective way for mixing polymer/inorganic composite [6]. Since SLS is water-soluble material, sonication is no need to make the mixture become heterogenous. The electrospun mats obtain brown smooth fibre while only PVA fibre mats had white colour. The brown colour of 1.5 wt.% and 3 wt.% of SLS was darker by the increasing of SLS content.

Figure 3 shows the results of SEM observations on 15 % w/v PVA samples added with various concentration of SLS. The addition of 1.5 wt.% has been able to change the morphology of PVA fibres to be thinner from average 650 nm to 280 nm. The distribution of diameter fiber is becomes wider as well. Increasing of SLS to 3 wt.% produces fibre that is still relatively heterogeneous in diameter but numbers of diameter distribution is more concentrate to 300 nm.

![Figure 3. SEM images of electrospun PVA/SLS fibres with various SLS contents of: (a) 0 wt. %, (b) 1.5 wt.%, and (c) 3 wt.%](image)

Figure 4 is the typical nitrogen physisorption isotherm plot for the nanofiber developed in this study. It is all most similar to type IV(a) [12], although the knee part is not as bent as a typical IV(a) isotherm. This indicates that the material mainly consists of mesopores and a relatively small amount of micropores. Based on the hysteresis loop shape, the lignin-based fibre can be categorized as the H2-b type.
However as shown from the volume adsorbed (Figure 4(b) and (c)), followed by the specific surface area provided by nitrogen adsorption-desorption isotherm (Table 2), the increasing of SLS content decrease the pore of fibre itself. Furthermore, compared to PVA nanofiber, the pore diameter and pore volume of electrospun nanofiber that contain SLS describe significant reduction. It may caused by the characteristic of alkali content in SLS that become a natural surfactant so it reduce the surface tension that later become the pore potential. That is why the micropore side of the nanofiber is slightly reduced as figured in the graph above.

### Table 2. Nitrogen adsorption-desorption of nanofiber at various SLS concentration

| Sample             | Specific surface area (m²/g) | Pore diameter (nm) | Pore volume (cm³/g) |
|--------------------|-------------------------------|--------------------|---------------------|
| Nanofiber 0.0 wt.% SLS | 72.414                        | 12.3492            | 0.2236              |
| Nanofiber 1.5 wt.% SLS | 70.218                        | 2.6889             | 0.0519              |
| Nanofiber 3.0 wt.% SLS | 60.698                        | 7.8262             | 0.1188              |

After passing iodine treatment, thermal stabilizing, and carbonisation process at 700°C, it can be shown in Figure 5. The adsorption–desorption isotherm curve of the carbon nanofiber (CNF) sample indicates the Type IV-a isotherm for CNF with SLS content of 1.5 wt.% and Type I isotherm for CNF with SLS content of 3 wt.% according to the IUPAC classification that the curve is concave to the relative pressure axis. The appearance of a nearly horizontal plateau indicates a small external surface area compared to the total surface area.

### Figure 5. Nitrogen adsorption–desorption isotherms of Carbon nanofiber with (a) 0 wt.% , (b) 1.5 wt.%, and (c) 3 wt.% of sodium lignosulfonate content.
Table 3. Nitrogen adsorption-desorption of carbon nanofiber at various SLS concentration

| Sample            | Specific surface area (m²/g) | Pore diameter (nm) | Pore volume (cm³/g) |
|-------------------|-----------------------------|-------------------|---------------------|
| CNF 0.0 wt.% SLS  | 292.986                     | 3.5358            | 0.3384              |
| CNF 1.5 wt.% SLS  | 496.547                     | 4.8445            | 0.6014              |
| CNF 3.0 wt.% SLS  | 703.615                     | 2.4373            | 0.4287              |

Interestingly, contrary to the previous phenomenon, after transformed into carbon nanofiber, the specific surface area of CNF got dramatically increase by the additional and increasing content of SLS. And as described in Table 3, the pore size of CNF supported by 3 wt.% of SLS perform slightly micropore rather than others. It may cause by the conversion of SLS into activated carbon support the increasing of micropore side of nanofiber.

4. Conclusions
In summary, a study about carbon nanofiber was prepared via electrospinning using Sodium Lignosulfonate as the source of lignin and PVA as the source of polymer. The SLS as affordable lignin-based material was proved as promising material to be used as lignin source, since the high of alkali content can provide a high porous of carbon nanofiber. The increasing content of SLS will reduce the surface area of nanofiber and the average fibre diameter. But contrary increase the porous after it was converted into carbon nanofiber. Furthermore, this research is potentially continue to some of application such as a pigment adsorbent or even more the carbon source of energy storage or battery application.

5. References
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Acknowledgement
The authors are grateful for the financial support provided by the “Deputi Bidang Penguatan Riset dan Pengembangan Kementerian Riset dan Teknologi/Badan Riset dan Inovasi Nasional” through the research grant under Contract No. No: 3/E1/KP.PTNBH/2020