Influence of Acid Treatment on Nanoporous Carbon from Lignin

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Abstract

Nanoporous carbon was synthesized via carbonization process by using lignin as a carbon source. Lignin structure has been modified by acid impregnation with 5%wt of nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4), and followed by carbonization at 800 °C for 2 h under flow of N_2. The Influences of acid treatment were investigated through SEM, BET surface, XRD and FTIR. BET surface investigations confirmed that acid treatment caused the formation of carbon from lignin with an increases porous microstructure. Nanoporous carbon performed by impregnation with phosphoric acid shows the highest porosity, compared to sulfuric acid, hydrochloric acid and nitric acid, respectively.

KEYWORDS: GVL; Carbonization; Nanoporous carbon; Lignin; Acid treatment.

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Introduction

Lignin is the most plenteous aromatic polymer on earth. It can be used as a biomass source, but its performance cannot compete with other substrates. However, lignin has a high carbon content (~60 %wt), making it suitable for conversion into porous carbon material [1 − 2].

Nanoporous carbon materials have good features such as high surface area, good chemical and thermal stabilities, which makes them attractive applications [3 − 4]. For example, they have been used as catalyst support [5 − 7] and adsorbent for hydrogen storage as well as CO_2 capture [8]. In particular, it is widely used as adsorbents to remove organic and heavy metal contaminants from water in water treatment and purification [9 − 14]. In addition, it is also used as an electronic device, such as a supercapacitor [15 − 17]. However, nanoporous carbon from lignin is also required to improve the structure to provide better quality. By (2006) Suhas, P.J.M. Carrott and M.M.L. Ribeiro Carrott were used impregnation with chemicals such as KOH or NaOH followed by heating under a nitrogen flow at temperatures in the range 450 − 900 °C. Carbonization and activation proceed simultaneously and the method leads to materials with higher micropore volumes [18].

In this study, we investigated the influence of acid treatment on the structure of nanoporous carbon from lignin by impregnation with four types of acids: nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4). After that brought through the carbonization process. The as-obtained products were investigated using SEM, BET surface, XRD and FTIR.

Materials and Methods

Materials

Lignin Commercial was perchased from SIGMA-ALDRICH Co., Ltd. Nitric acid (65%), Hydrochloric acid (37%), Sulfuric acid (96%) and Phosphoric acid (85%), laboratory-grade were used in this study.

Methods

Fig. 1 shows a schematic representation of the various steps involved in the acid treatment on nanoporous carbon from lignin. Step 1:1 g of

lignin samples were dissolved in 10 ml of deionized water with various acid such as HNO_3, HCl, H_2SO_4 and H_3PO_4 at concentrations 5%wt. Step 2: lignin was dried at 100 °C in order to achieve porous lignin. Step 3: lignin samples were carbonized in a tubular furnace at 800 °C for 2 h under nitrogen atmosphere by employing a 10 °C min^{-1} heating rate. The as-obtained products have been used for further characterization
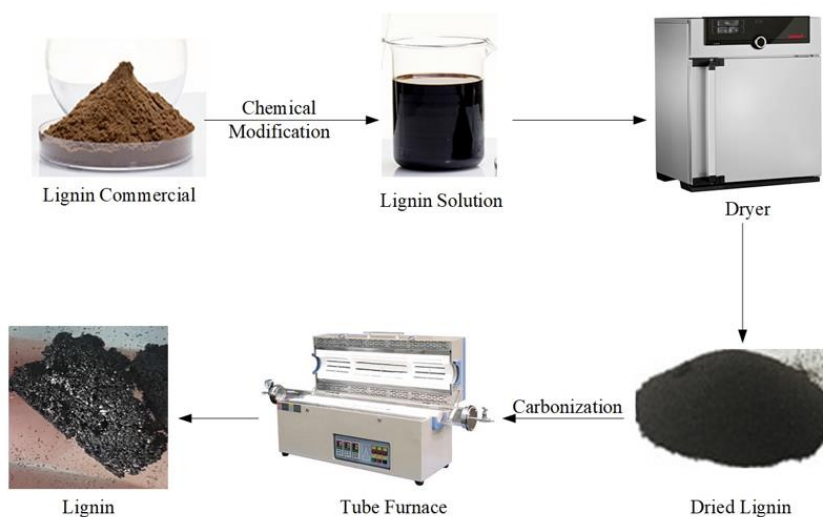

Fig. 1 Schematic of the various steps involved in the acid treatment on nanoporous carbon from lignin

Characterization Techniques

The samples were characterized for morphology, phase and chemical structure, and surface area by Scanning Electron Microscope (SEM), X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR) analysis, and BET surface analysis, respectively.
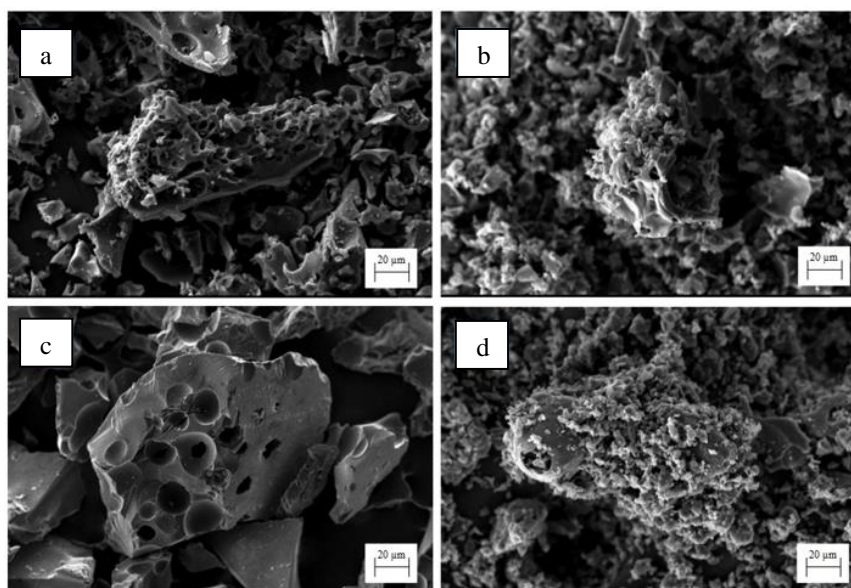
Results and Discussion

Fig. 2 SEM micrographs of the as-obtained lignin with different acid treatment. (a) HNO_3 (b) HCl (c) H_2SO_4 (d) H_3PO_4

The morphology was investigated by Scanning Electron Microscope (SEM). Fig. 2 shows the SEM images of the as-obtained lignin with different acid treatment. It was found that acid treatment caused the formation of carbon from lignin with an increases porous microstructure. By lignin impregnation with phosphoric acid (Fig. 2(d)) is showed the highest porous structure, followed by sulfuric acid (Fig. 2(c)), hydrochloricacid (Fig. 2(b)) and nitric acid (Fig. 2(a)), respectively.

Lignin impregnation with H_3PO_4 sample has the highest porous structure might be due to phosphoric acid, can dissociate H^+ more than other acids resulted in the high rate interaction during a chemical activation since this phenomenon increases the porosity of carbon. This can be confirmed by the results of the BET surface shown in Table 1, which shows that lignin impregnation with phosphoric acid has a surface area of 1,148.19 m^2 g^{-1}, followed by lignin impregnation with nitric acid, sulfuric acid and hydrochloric acid have surface area of 744.13, 609.23 and 604.65 m^2 g^{-1}, respectively.

Table 1 Surface area of the lignin with different acid treatment

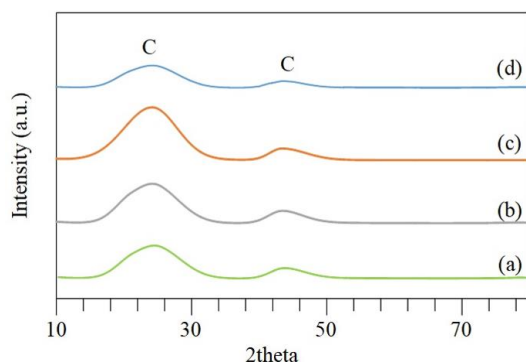| Acid	Surface area (m^2 g^{-1})
Nitric acid (HNO_3)	744.13
Hydrochloric acid (HCl)	604.65
Sulfuric acid (H_2SO_4)	609.23
Phosphoric acid (H_3PO_4)	1,148.19

Fig. 3 XRD patterns of the as-obtained lignin with different acid treatment. (a) HNO_3 (b) HCl (c) H_2SO_4 (d) H_3PO_4

The XRD patterns of the as-obtained lignin with different acid treatments were shown in

Fig. 3 It was found that the structure of lignin impregnation with acid was amorphous carbon structure. The two peaks were found at 2 theta positions of 23.97 and 43.59, indicating that the lignin structure had carbon as the main component.
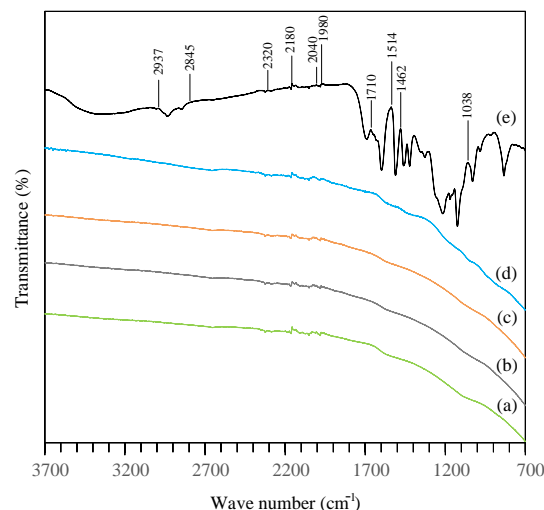

Fig. 4 FTIR spectra of the as-obtained lignin with different acid treatment. (a) HNO_3 (b) HCl (c) H_2SO_4 (d) H_3PO_4 and lignin (Raw material)

The functional group in lignin can be identified from the FTIR spectra is shown in Fig. 4. The FTIR spectra of prepared samples indicated characteristic peaks of lignin that show the bands centered around 2937 and 2845 cm^{-1}, predominantly arising from CH stretching in aromatic methoxyl groups. At the band between 1980 and 2040 cm^{-1}, it is represented a ring conjunction C=C stretch of coniferyl/sinapyl alcohol and C=O stretch of coniferaldehyde/sinapaldehyde, respectively. While, the band at 2180 cm^{-1} represents –C (triple bond) C– stretching vibration of alkynes and the band at about 2320 cm^{-1} is due to C-H stretch in OCH_3 symmetric, indicating that in the lignin structure composed of type alkyl, aliphatic and aromatic compounds. In the carbonyl/carboxyl region, weak to medium bands are found at 1705 – 1720 cm^{-1}, originating from unconjugated carbonyl/carboxyl stretching. Aromatic skeleton vibrations at 1514 cm^{-1} and the C–H deformation combined with aromatic ring vibration at 1462 cm^{-1} are common for lignin. The aromatic C–H deformation at 1038 cm^{-1} appears as a complex vibration associated with the C–O, C–C stretching and C–OH bending in polysaccharides.

After the carbonization process, the lignin structure in the volatile material decomposes from the main structure when the temperature increase.

Conclusion

Nanoporous carbon from lignin impregnated with four types of acids: phosphoric acid, sulfuric acid, hydrochloric acid and nitric acid was investigated. As acid treatment, it was found that porous microstructure of carbon was increased due to the effects of chemical activation. The carbon with the highest porous structure was obtained by impregnation lignin with phosphoric acid, followed by nitric acid, sulfuric acid and hydrochloric acid, respectively.

Acknowledgements

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