


Communication

Novel Tubular Carbon Membranes Prepared from Natural Rattans

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Received: 7 December 2018; Accepted: 29 January 2019; Published: 1 February 2019



Abstract: The novel tubular carbon membranes produced from natural materials are, for the first time, reported. The novelty of this idea is to use natural rattans as precursors for making carbon membranes to address the challenges of cellulose polymers. The rattan precursors were carbonized to present evenly distributed channels inside the tubular carbon membranes. Each channel has an inner diameter of 2×10^{-4} m with a dense-selective inner layer and a porous outer layer. Future work on selection of suitable rattans, proper pre-treatment, carbon structure tailoring can be conducted to open a new research field of carbon membranes/materials.

Keywords: rattan; tubular carbon membrane; carbonization; gas separation

1. Introduction

Membrane technology possesses many advantages such as small footprint, low capital and operating cost, and being environmentally friendly to be an alternative technology for gas separation compared to the conventional separation technologies (e.g., cryogenic distillation, chemical and physical absorption). He et al. reviewed the polymeric and inorganic (carbon, ceramic, metallic, zeolites, etc.) membranes for various gas separation processes [1], and membrane gas separation is expected to play an important role in the selected environment and energy processes, such as CO₂ capture, natural gas sweetening, biogas upgrading, and hydrogen purification. The polymeric membranes are dominating the current industrial gas separation, but the trade-off of permeability/selectivity as well as the chemical and mechanical stabilities limits their applications in the adverse conditions (e.g., high pressure and/or high temperature processes). Developing alternative carbon membranes shows a nice potential.

Carbon membranes are ultra-microporous inorganic membranes made from the carbonization of polymeric precursors such as polyimide, polyacrylonitrile (PAN), poly(phthalazinone ether sulfone ketone), poly(phenylene oxide) and cellulose derivatives [2]. In the last decade, great attention was placed on the development of supported carbon membranes [3,4] and self-support carbon membranes [5]. Ceramic-supported carbon membranes was reported for high temperature applications (e.g., H₂/CO₂ separation from syngas and carbon membrane reactors) [6]. However, preparation of a thin, defect-free carbon-selective layer on the top of support, increase of the compatibility between support and carbon layer and reduction of the production cost are still challenging [7]. Self-supported flat-sheet and hollow fiber carbon membranes prepared from polyimide precursors for CO₂/CH₄ and olefin/paraffin separation have been reported in the literature [8,9], but the main challenge of the high production cost due to the non-commercial polyimide polymers hinders the upscaling. The Membrane Research (Memfo) team at the Norwegian University of Science and Technology (NTNU) developed the cellulosic-based hollow fiber carbon membranes with relatively good separation performance for CO₂/N₂, CO₂/CH₄ separation [10–14]. However, there are still challenges related to: (1) hollow fiber precursors drying; (2) module construction due to the fragile and brittle carbon fibers; and (3) low gas

permeance with a symmetric structure. Thus, seeking novel precursors for preparation of asymmetric carbon membranes with high performance, low cost, good mechanical strength and easy module construction (e.g., tubular) is essentially required to bring carbon membranes into future applications in gas separation processes.

The natural rattan materials have unique tubular structure as shown in Figure 1. For the rattan plants, water is initially absorbed from the underground and transported through the large channels from bottom to the top of trunk, and can also pass through the wall to the branches (further to leaves), which indicates a porous structure along the channel wall of rattan materials. The previous work reported on the production of artificial bones from rattan woods by carbonization at high temperature (e.g., 800–2000 °C) [15]. Moreover, the rattan materials are mainly composed of cellulose, with small amounts of hemicellulose and lignin, and the chemical structure of rattan is quite similar to the regenerated cellulose hollow fibers. Therefore, in principle, self-supported tubular carbon membranes can be prepared by carbonization of rattan materials.

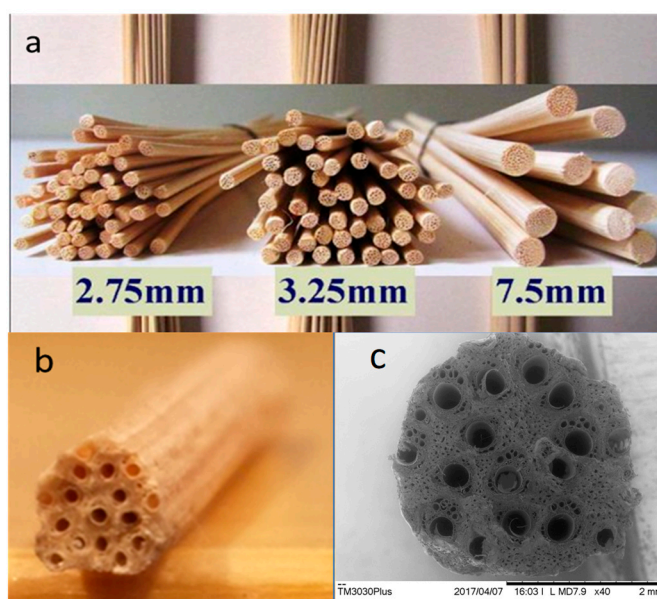


Figure 1. Cross-section of rattan materials: (a) rattans with different outer diameters (2.75 mm to 7.5 mm); (b) tested rattan (outer diameter, $d_o = 3.25 \times 10^{-3}$ m); (c) SEM image.

2. Material and Methods

The natural rattans with an outer diameter of 3.25×10^{-3} m were provided by the Institute of Process Engineering, Chinese Academy of Sciences. Acetic acid was purchased from Sigma-Aldrich (Oslo, Norway). The raw rattan was pre-hydrolyzed using an acetic acid aqueous solution (50 vol.%) at 90 °C overnight to partly remove hemicellulose, and increase the cellulose content in the precursors. The pre-treated rattan was carbonized in the furnace up to 550 °C using the protocol reported in the previous work [14]. Thermogravimetric analysis (TGA) from TA Instruments (New Castle, DE, USA), model Q500 and scanning electron microscopy (SEM) from Hitachi High Technology (TM3030 tabletop microscope, Lidingö, Sweden) were used to characterize the structure, morphology and property of rattans and carbon membranes.

3. Results and Discussion

The Thermogravimetric Analysis (TGA) study on one type of rattan material showed the similar weight loss compared to the deacetylated cellulose acetate (DCA) precursors reported in our previous work [14] (shown in Figure 2, raw rattan, acetic acid processed rattan (AA (acetic acid pretreated) rattan), and DCA materials). A relatively low decomposition temperature range (220–320 °C) was

found due to the present of hemicellulose and lignin in rattan materials compared to the regenerated cellulose (DCA) precursor (290–350 °C) which contained almost pure cellulose. Pre-hydrolysis of wood using acetic acid at high temperature was reported to partly remove hemicellulose, and increase the cellulose content [16], which has also been documented from the TGA results (AA rattan in Figure 2). Compared to the raw rattan materials, the decomposition temperature of the pre-treated rattan shifted towards the DCA precursor. The carbonization experiments of pre-treated rattan precursors (i.e., rattans soaked in a 50 vol.% acetic acid for 2 h) were conducted at the final temperature of 550 °C, and the SEM images of the cross-sections of carbon membranes are shown in Figure 3. It was found that rattan precursors can be carbonized under the controlled carbonization condition and presented the evenly distributed channels inside the tubular carbon membranes (Figure 3a), and each channel (inner diameter, $d_i = 2 \times 10^{-4}$ m) showed an asymmetric structure with a dense-selective inner layer and a porous (from parenchyma cells) outer layer (Figure 3b). The outer diameter of the prepared carbon membrane was reduced to 2.2×10^{-3} m (shrinkage of around 30%). The prepared carbon membranes showed a very porous structure, which indicates the processability in the preparation of carbon membranes from natural rattan precursors. However, the carbon membrane may have defects in the carbon matrix due to the high amount of residual lignin and hemicellulose existing in the rattan precursors. By applying a proper pre-treatment (to remove most hemicellulose and lignin), a suitable post-treatment can potentially mitigate the risk of the formation of microvoids. It is worth noting that the influences of cellulose content, pre-treatment of rattan precursors and carbonization procedure (especially final temperature, heating rate, etc.) are expected to be crucial to prepare high selective carbon membranes. The understanding on how the pore structure can be tuned by the employment of the pre-treatment for the precursor and optimization of carbonization procedure is also very important. It should be noted that the focus of this work is to report the preparation of carbon materials from a new biorenewable precursor of rattans, and no systematic gas permeation testing and characterization are included. Thus, the extended research work on selection of suitable rattans, proper pre-treatment, carbon structure tailoring should be further investigated to open a new research field in the development of natural rattan-based carbon membranes for gas separation.

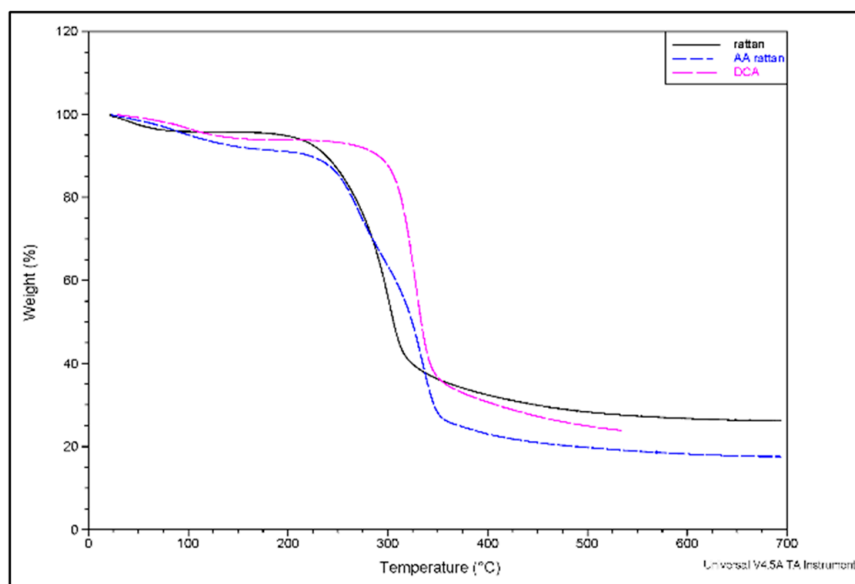


Figure 2. The TGA results of rattan (dark line), AA rattan (blue dashed line), and DCA (pink dashed line).

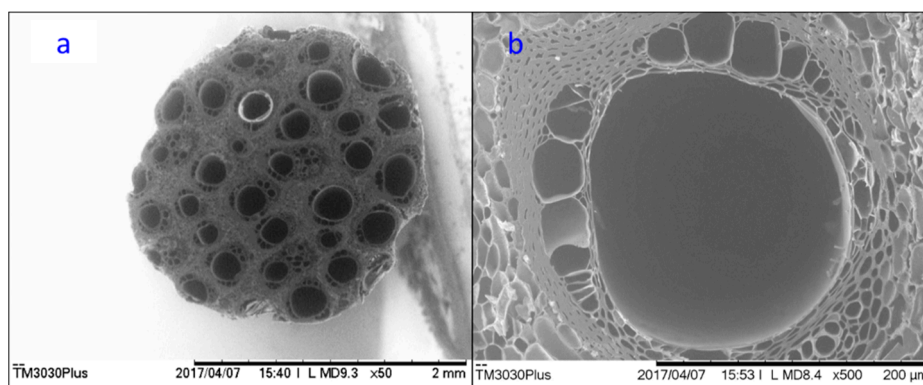


Figure 3. SEM images of the tubular carbon membranes from the rattan precursor: (a) the whole tubular ($d_o = 2.2 \times 10^{-3}$ m); (b) single channel ($d_i = 2 \times 10^{-4}$ m).

4. Conclusions

The natural rattan-based carbon membranes were successfully prepared by carbonization of tubular rattan at a final temperature of 550 °C. The prepared carbon membranes showed a very porous structure. Some defects may exist in the carbon matrix due to the presence of lignin and hemicellulose which need to be avoided by applying suitable pre-treatment methods. The novel tubular carbon membranes made from natural rattans will open a new research field for the development of carbon materials for gas separation, but the intensive research activities should be conducted to explore its potential.

Author Contributions: X.H. performed the experiments, data analysis, and writing of the paper.

Funding: This research received no external funding.

Acknowledgments: This work was conducted in the Department of Chemical Engineering at the Norwegian University of Science and Technology. The author acknowledges Arne Lindbråthen and Yunhan Chu for the discussion of the results.

Conflicts of Interest: The author declare no conflict of interest.

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