

Research and Development of New Lignin-based Gas Separation Membranes

Hidetoshi Kita, Masahiro Hamano, Makoto Yoshino, Ken-ichi Okamoto and
Masamitsu Funaoka*

Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755-8611, Japan

Fax: 81-836-85-9601, e-mail: kita@po.cc.yamaguchi-u.ac.jp

*School of Bioresources, Mie University, CREST JST, Tsu, Mie 514-8507, Japan

*Fax: 81-592-31-9521, e-mail: funaoka@bio.mie-u.ac.jp

Carbon membranes were prepared by coating thin layers of lignocresol derived from lignin by the phase-separation method and then carbonizing the lignocresol under nitrogen atmosphere at 773-1073K. The thickness of the membrane formed on the outer surface of a porous alumina substrate was about 400 nm judging from SEM observation. The activation energy for gas permeation through the membranes increased with increasing molecular diameter of the penetrant gas, indicating activated diffusion process. The permeation properties were dependent on heating conditions. The increase of carbonizing temperature to 1073K brought about decrease of permeance and selectivity. Gas selectivities of the membrane prepared by carbonizing at 873K were 50, 8, 290 and 87 for CO_2 / N_2 , O_2 / N_2 , H_2 / CH_4 and $\text{CO}_2 / \text{CH}_4$ at 35°C, respectively.

Key words: Lignin, Lignocresol, Renewable Resources, Carbon Membrane, Microporous Membrane, Gas Separation

1. INTRODUCTION

The development of membrane processes for the separation of gas mixtures has made remarkable progress during the last two decades and strong interest exists in the synthesis of membranes that exhibit both higher gas permeabilities and selectivities than presently available polymers[1].

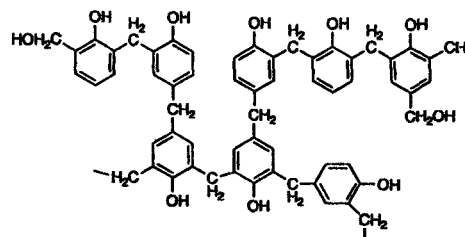
On the other hand, in order to sustain the production of materials for human life under a sound ecological system, it is important to produce functional materials from renewable resources, and not from fossil resources. Among renewable resources the forest provides excellent raw materials, carbohydrates (cellulose and hemicellulose) and polyphenol (lignin) in both quantity and quality. Although the carbohydrates have been incorporated into human life for a long time, lignin has scarcely been utilized.

Recently one of us has developed a new process for separating lignocellulosics into lignin and carbohydrates[2]. The separated lignin derivatives have several structural characteristics, for example highly phenolic and highly stable.

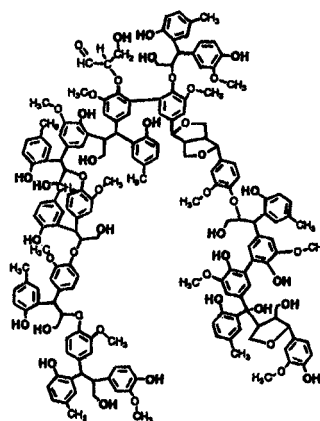
Here, we report the preparation of carbon membranes by pyrolyzing lignocresol and the gas permeation properties. Lignocresol was selected on the basis of high carbon yield and thermosetting properties without deforming during heating and pyrolysis.

2. EXPERIMENTAL

Lignocresol was synthesized from native lignin (Hinoki) by the phase-separative treatment with cresol and sulfuric acid [2]. Figure 1 shows schematic structures of lignocresol together with commercially available phenolic resin.



Phenolic resin



Lignocresol

Fig. 1 Schematic structures of lignocresol and phenolic resin

A porous cylindrical substrate of α -alumina was supplied by NOK Co. The substrate had a mean pore diameter of 140 nm with a porosity of about 40% and its dimensions were 2.25 mm outer diameter, 1.8 mm inner diameter and 20 mm length. The membranes of lignocresol were formed by a dip process in which the porous substrate capped with Teflon tape was dipped into the 10-30 mass% lignocresol solution in MeOH or MEK for 30 min at room temperature. The coated substrate was then pulled out at a rate of 1 cm/min. Figure 2 shows schematic diagram of a composite membrane formation.

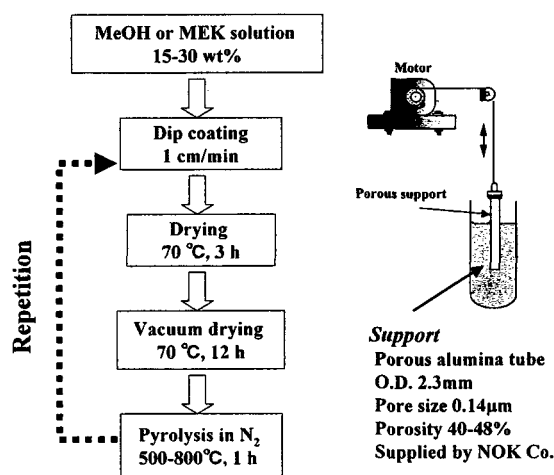


Fig. 2 Schematic diagram of membrane formation

After air-drying at 70 °C for 3 hours and then vacuum-drying at 70 °C for 12 hours, the membrane was carbonized at 500-800°C for 1 h under nitrogen atmosphere with a heating rate of 5 °C/min and then allowed to cool down to ambient temperature. The coating-carbonization cycle was repeated.

Gas permeation rates through the membrane were measured at 35-105 °C and 1 atm using a vacuum time-lag method as shown in Figure 3. Single component gas was fed to the outer side of the membrane in a permeation cell, which was placed in a thermostated air-bath.

Thermogravimetry-mass spectrometry (TG-MS) was carried out on a Rigaku TG8120-Shimadzu GCMS-QP5050.

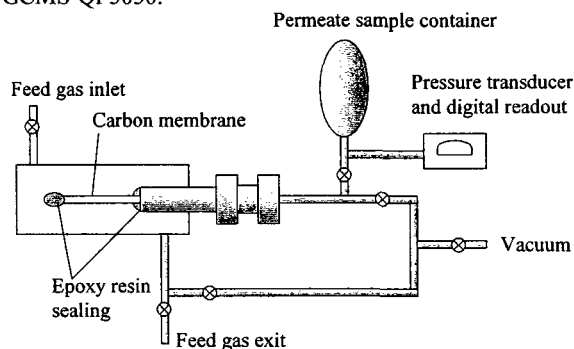


Fig. 3 Schematic diagram of single gas permeation

Scanning electron microscopy (SEM) was measured using Hitachi S2300.

3. RESULTS AND DISCUSSION

Figure 4 shows thermograms of lignocresol and commercially available phenolic resin (Bellpearl S-895 supplied from Kanebo Ltd.) heated at a heating rate of 5°C/min. Under nitrogen atmosphere, the weight of lignocresol rapidly decreased by approximately 45% in the range of 350-450°C and then gradually decreased by 55% at 800°C, while the weight loss of phenolic resin was approximately 40% at 800°C.

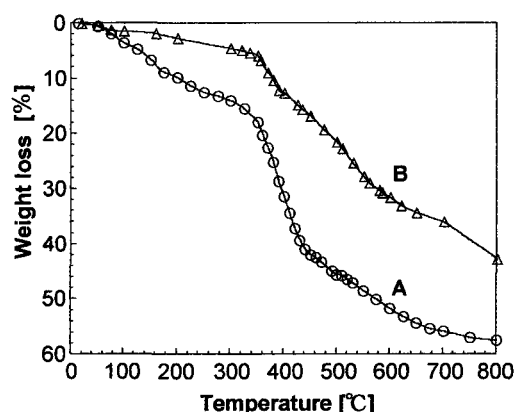


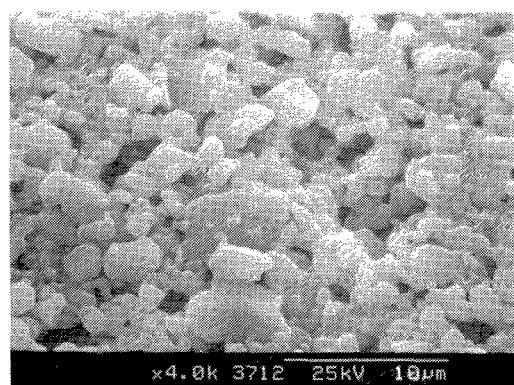
Fig. 4 Thermograms of lignocresol (A) and phenolic Resin (B) at heating rate of 5°C/min in N₂

The gaseous products evolved from lignocresol in the range of 350-450°C included methylphenol, dimethylphenol and several compounds with higher molecular weight together with traces of carbon dioxide and methanol. Adsorption and desorption isotherms of nitrogen for the heat-treated lignocresol belongs to the type I sorption isotherms, indicating the presence of micropores.

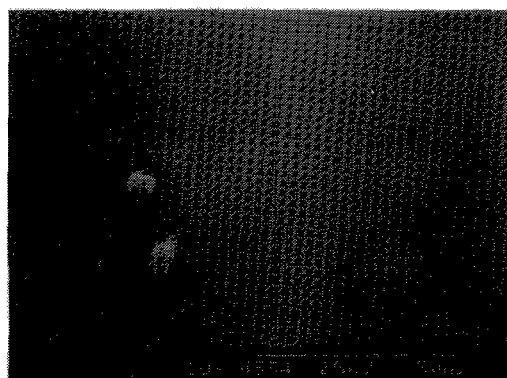
SEM observation of the carbon membrane indicated that there were no cracks but pinholes at the surface of single-coated layer, however, multiple coated samples indicated a non-porous carbon layer. An example of the cross-section of the coating membrane prepared on the substrate is shown in Figure 5. The thickness of the carbon layer was about 400 nm.

Figure 6 shows an effect of carbonizing temperature for the gas permeation rates through lignocresol membranes at 35°C. Permeation rates of He, H₂, CO₂ and O₂ through lignocresol membranes carbonized at 500-700°C were enhanced by 1 order magnitude compared with the precursor and permeation rates through the membranes carbonized at 500 and 600°C decreased in the order of increasing kinetic molecular diameter of the penetrant gas.

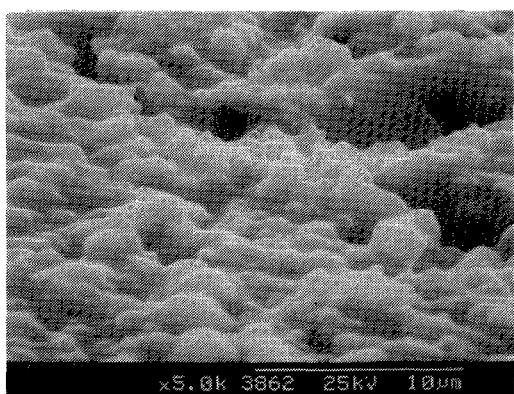
Figure 7 shows the temperature dependence of gas permeation rates through lignocresol membrane carbonized at 600°C for 1 h. Gas permeation rates increased with increasing temperature and the activation energy for the gas permeation through these membranes increased with increasing molecular diameter of the gases. These results indicate these membranes behave



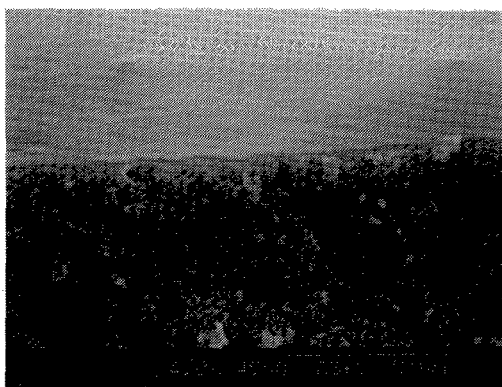
(a) Surface of porous alumina support



(c) Surface coated by MEK solution of lignocresol (30mass%) of 4 times



(b) Surface coated by MEK solution of lignocresol (15mass%) of 4 times



(d) Cross section of (c)

Fig. 5 SEM photo of surface and cross section of lignocresol membrane carbonized at 500°C for 1 h

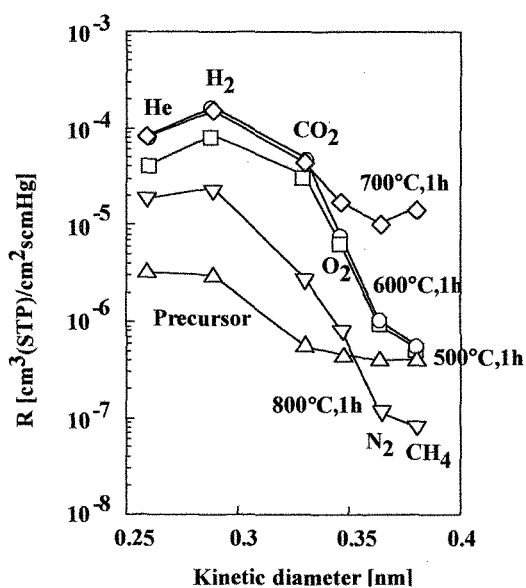


Fig. 6 Effect of carbonizing temperature for the gas permeation rates through lignocresol membranes at 35°C

more like "molecular sieves". The increase of carbonizing temperature to 800°C, however, brought about the decrease of permeance and selectivity because of the decrease of the micropore volume.

Table I summarized gas separation factors of carbonized lignocresol membranes. The activation energy for the gas permeation through these membranes increased with increasing molecular diameter of the gases, except for CO₂ as shown in Table II.

Table I Gas Separation Factors of Carbonized Lignocresol membranes at 35°C

Pyrolysis	H ₂ /CH ₄	CO ₂ /CH ₄	CO ₂ /N ₂	O ₂ /N ₂
Prepolymer	7.4	1.4	1.4	1.2
500°C, 1h	160	60	36	7.1
600°C, 1h	290	87	50	8.0
800°C, 1h	290	35	30	7.6

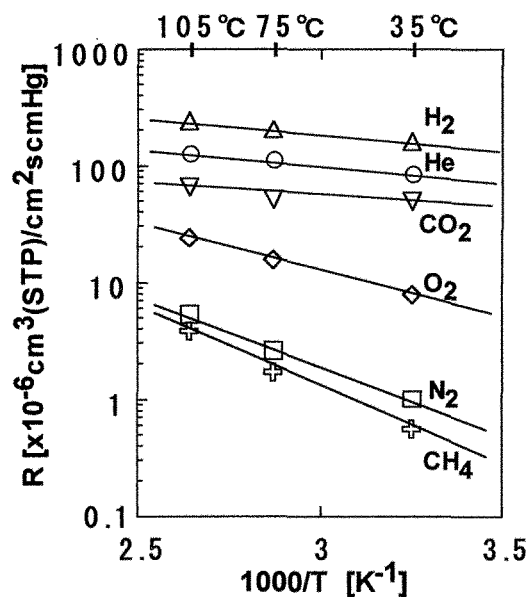


Fig. 7 Temperature dependence of gas permeation rates through lignocresol membrane carbonized at 600°C for 1 h

Table II Activation Energy of Gas Permeation(kJ/mol)

Pyrolysis	H ₂	He	CO ₂	O ₂	N ₂	CH ₄
Prepolymer	10	11	-	-	-	-
500°C, 1h	4.5	5.0	4.7	11	18	23
600°C, 1h	5.2	5.6	3.6	15	23	26
800°C, 1h	14	12	6.4	13	14	-

Activation energy of CO₂ permeation is smaller than those of He and H₂, which seems to be caused by adsorption and surface flow of CO₂. Thus, the carbon membrane does offer good selectivity for separation of CO₂/CH₄ and CO₂/N₂. Lignocresol membrane carbonized at 600°C showed the highest membrane performance. It may, therefore, be concluded that carbon membranes derived from lignin-based materials provide one of promising candidates for the separation of CO₂.

The present work was supported by CREST of JST(Japan Science and Technology).

4. REFERENCES

- [1] S. A. Stern and W. J. Koros, *Chimie Nouvelle*, **18**, 3201(2000).
- [2] M. Funaoka and S. Fukatsu, *Holzforschung*, **50**, 245(1996).

(Received December 20, 2001; Accepted March 18, 2002)