Activated Carbon by Chemical Activation of Lignin with Potassium Hydroxide

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INTRODUCTION

The NARA co-products team is seeking to generate value-added co-products from the lignin produced during the conversion of softwood forest residuals to jet fuel. During this research, activated carbon (AC) was produced by chemical activation with potassium hydroxide (KOH). The objective of these experiments was to gain an understanding of the effect of temperature and KOH- to- lignin ratio on the surface area, pore volume, and pore size distribution of the AC materials.

METHODS

- Lignin was obtained after Mg^{2+} bisulfite pretreatment of Douglas Fir forest residuals followed by enzymatic hydrolysis (saccharification). The lignin was air-dried overnight and then further dried at 60°C to constant weight.
- The lignin granules were ground into powder and mixed with 50% KOH (aq.) to obtain a mixture of KOH and lignin with KOH:lignin ratio of 2, 3, or 4 (w/w). The mixture was then dried overnight at 105°C in air.
- The dried mixture was then heated in N_2 atmosphere in a tube furnace at 10°C/min from room temperature to 150°C, held one hour at 150°C to remove moisture, then heated further at 10°C/min to 700, 750, or 800°C and held for one hour.
- After cooling the furnace under N_2, the mixture was washed thoroughly to separate KOH from the AC. AC was first with water, then with 10% HCl (aq.), then again with water. The washed AC was then dried at 105oC.
- Gas physisorption analysis was used to investigate the effect of KOH:lignin ratio and temperature on the micro- and mesoporous structure (< 50 nm in size) of the different AC materials. Scanning electron microscopy was also used to visualize the macroporous structure (> 50 nm).

RESULTS

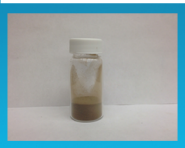

Figure 1: Lignin powder before mixing with KOH and carbonization.

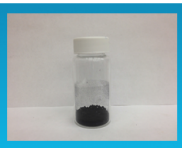

Figure 2: AC powder after carbonization, washing, and drying.

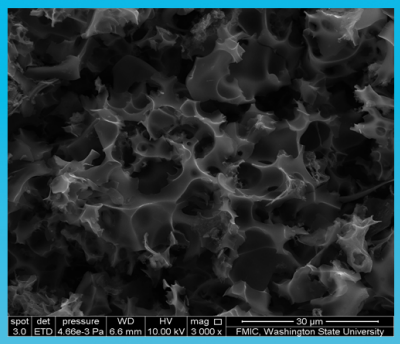

Figure 3: Scanning electron micrograph of KOH: Lignin AC prepared at 750°C and KOH: Lignin ratio of 3:1. Scale bar = 30 µm

ADSORPTION ISOTHERMS

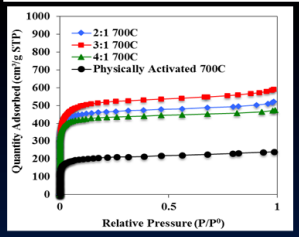

Figure 4: Nitrogen adsorption isotherms for samples prepared at different KOH :lignin ratios (2, 3, and 4). An isotherm for a sample prepared by physical activation with CO_2 is also shown.

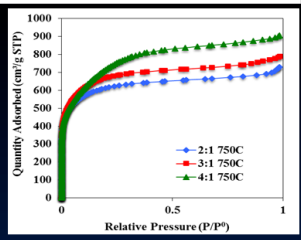

Figure 5: Nitrogen adsorption isotherms: Data for samples prepared by chemical activation with KOH at different KOH: lignin ratios (2, 3, and 4) are shown

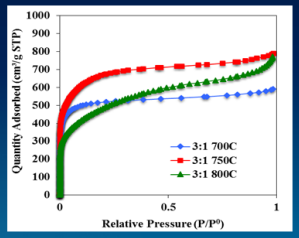

Figure 6: Nitrogen adsorption isotherms: Data for samples prepared by chemical activation with KOH at a constant KOH:lignin ratio of 3 are shown.

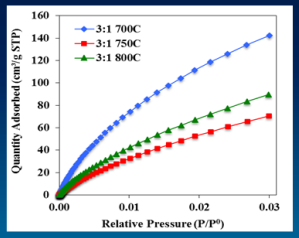

Figure 7: Carbon dioxide adsorption isotherms: Data for samples prepared by chemical activation with KOH at a constant KOH:lignin ratio of 3 are shown.

POROSITY DATA

Type of Activation	Max. Temp. (°C)	KOH: Lignin ratio (w/w)	Total Pore Volume (cm^3/g)	Mesopore Volume (cm^3/g)	Micropore Volume (cm^3/g)	Mesopore/ Micropore Ratio (v/v)	Apparent BET surface area (m^2/g)
Physical (CO_2)	700	n/a	0.37	0.05	0.29	0.17	791
Chemical (KOH)	700	2	0.78	0.07	0.63	0.11	1719
Chemical (KOH)	700	3	0.92	0.08	0.73	0.11	1989
Chemical (KOH)	700	4	0.74	0.04	0.62	0.06	1705
Chemical (KOH)	750	2	1.13	0.19	0.83	0.23	2236
Chemical (KOH)	750	3	1.22	0.20	0.91	0.22	2405
Chemical (KOH)	750	4	1.41	0.43	0.84	0.51	2487
Chemical (KOH)	800	3	1.20	0.51	0.55	0.93	1691

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PORE SIZE DISTRIBUTION

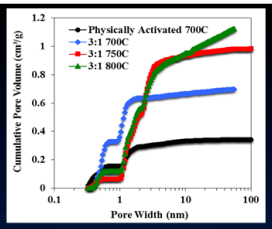

Figure 8: Pore size distributions of selected AC materials calculated with nonlocal density functional theory (NLDFT) The cumulative pore volume as a function of pore width is shown for AC prepared by both physical and chemical activation.

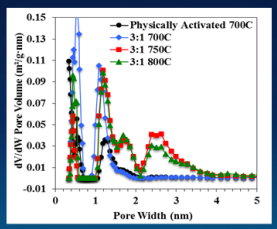

Figure 9: Pore size distribution of chemically and physically activated carbon materials produced in this work. The differential pore size distribution is shown in the pore size range of 0.3 – 5 nm.

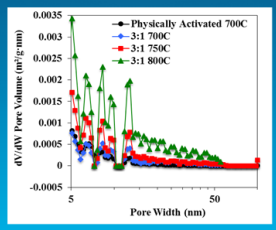

Figure 10: Pore size distribution of chemically and physically activated carbon materials produced in this work. The differential pore size distribution is shown in the pore size range of 5 - 100 nm.

CONCLUSION

- Microporous AC materials with high surface area and pore volume can be prepared by chemical activation of NARA lignin with KOH.
- The pore volume, surface area, and pore size distribution are all dependent on the KOH:lignin ratio and maximum carbonization temperature.
- Materials prepared at lower temperature are microporous (pores smaller than 2 nm) while higher temperature leads to broadening of the pore size distribution to include mesoporosity (2 – 50 nm).

ACKNOWLEDGEMENT

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