PORE ENGINEERING AND SURFACE FUNCTIONALIZATION OF BIOCHARS FROM SUGAR BEET PULP

Süleyman Şener Akın, Micro and Nanotechnology Department, Middle East Technical University
sener.cheeng@gmail.com
Ali Bertan Kır, Micro and Nanotechnology Department, Middle East Technical University
Feyza Kazanç, Mechanical Engineering Department, Middle East Technical University

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In this study, we explored combinations of thermochemical and wet chemistry processes, including slow pyrolysis, hydrothermal carbonization, physical/chemical activation, wet impregnation, and acid leaching, utilizing agricultural biomass, specifically sugar beet pulp (SBP), as the representative carbon source. The biomass samples were doped with nitrogen agent (melamine) and alkali agents (NaOH and KOH). Pyrolysis of these samples was performed under N2 atmosphere at 700 °C with a heating rate of 10 °C/min in a horizontal tube furnace. As a pre-treatment, the biomass or biochar samples were mixed with two different 0.5 M KOH or NaOH solutions, prepared with and without melamine, and heated to 70 °C for 3 hours (1:0.5(melamine):0.8 for NaOH and 1:0.5(melamine):1.1 for KOH). The samples were then heated to the target temperature of 700 °C at a heating rate of 10 °C/min under a CO2 atmosphere and kept at the target temperature for 30 minutes. Finally, the carbon samples were washed with a 1M HCl solution and rinsed with water until a neutral pH was achieved. On the other hand, the hydrothermal carbonization was conducted at 200 °C with a heating rate of 5 °C/min for 18 hours with an L/S ratio of 12 to obtain oxygen-rich biochars. Melamine powders were added before the hydrothermal carbonization. Considering the anticipated low surface area of hydrochars, further physical and chemical activation under a CO2 atmosphere was performed.

Based on the BET results, the SBP-K-CO2 sample displayed the highest specific surface area at 1487 m2/g, while the lowest specific surface area of 12 m2/g was observed in the SBP-M-CO2 sample. The presence of KOH contributed to higher specific surface areas in both the SBP-K-CO2 and SBP-MK-CO2 samples compared to the SBP-N-CO2 and SBP-MN-CO2 samples treated with NaOH. The combination of a lower dosage of KOH and CO2 atmosphere resulted in uniform microporosity, confirmed through H1 type hysteresis. On the other hand, NaOH contributed to the formation of mesopores, as indicated by a slight jump in the relative pressure range from 0.4 to 0.7 and a further increase from 0.8 to 1.0, signifying a Type IV isotherm with H4 type hysteresis, thus confirming the presence of hierarchically porous structures. Furthermore, the co-doping of melamine and NaOH resulted in enlarged pores and an expected mesopore-dominant structure, evident through the validation of a high-pressure jump in the range of 0.9 to 1.0 relative pressures, indicating an H2 type hysteresis. When compared to the direct pyrolysis of doped biomass samples, SBPC samples exhibited lower specific surface areas after further physical activation under a CO2 atmosphere. Additionally, alkali agents or melamine did not contribute to mesopore formation or significant pore development. It was observed that increasing pyrolysis temperatures (>500 °C) increased hydrophobicity and aromaticity, thus rendering wet pre-treatment ineffective in efficiently doping alkali and nitrogen agents for SBPC obtained at 700 °C due to the hydrophobic nature of SBPC. Hydrochars yielded a hierarchical porous structure for HSSC-CO2 and HSSC-MK-CO2, as evidenced by a slight jump in the relative pressure range from 0.4 to 0.7 and a further increase from 0.8 to 1.0, indicating a Type IV isotherm with H4 type hysteresis, confirming the presence of mesopores within the hierarchically porous structure.

In conclusion, our one-pot pyrolysis approach under an active atmosphere and alkali agents allows for tuning the porosity of biochar from microporous to mesoporous and creating a hierarchical porosity structure.

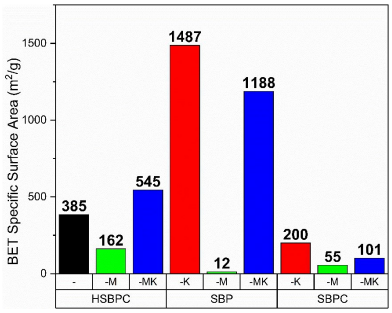

Figure 1: BET Results of SBP, SBPC and HSBPC samples

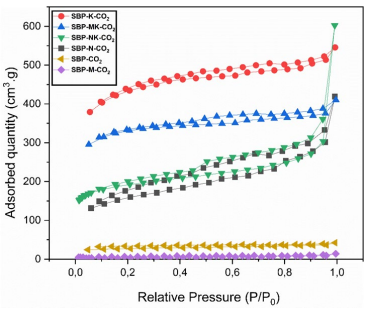

Figure 2: Isotherms of CO_2 pyrolysis of raw and doped SBP samples