THERMAL EVOLUTION OF BIOCHAR AND ITS PHYSICOCHEMICAL PROPERTIES DURING HYDROTHERMAL GASIFICATION

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Biochar is a recalcitrant carbonaceous material obtained from pyrolysis and gasification of biomass and other biogenic wastes. Some of the promising biochar applications to be discussed in this presentation includes char gasification and combustion for energy production, soil remediation, carbon sequestration, catalysis, and development of activated carbon and specialty materials with biomedical and industrial uses. Several factors such as pyrolysis/gasification temperature, heating rates and residence time are the limiting factors that determine the biochar properties such as fixed carbon, volatile matter, mineral matter, surface area, porosity and pore size distribution, alkalinity, electrical conductivity, cation-exchange capacity, etc. This paper will comprehensively review the evolution of biochar from several lignocellulosic biomasses influenced by gasification temperature and residence time. Lower pyrolysis/gasification temperatures produce biochar with higher yields and greater extent of volatile matter, electrical conductivity and cation-exchange capacity. On the other hand, higher pyrolysis/gasification temperatures generate biochar with a greater extent of aromatic carbon, alkalinity and surface area with microporosity.

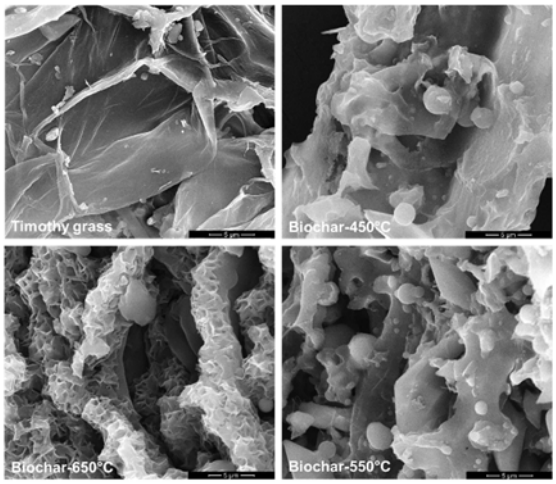

Figure 1 – SEM imaging of timothy grass biochars generated at different supercritical water gasification temperatures (450-550°C) at 23-25 MPa

This study is focused on the gasification of timothy grass as a model energy crop for hydrogen-rich syngas production through supercritical water gasification. Timothy grass was gasified in the pressure range of 23-25 MPa in supercritical water to investigate the impacts of temperature (450-650°C) and reaction time (15-45 min) on the physicochemical development of biochar. Highest H_2 (5.15 mol/kg) and total gas yields (17.2 mol/kg) with greater carbon gasification efficiency (33%) and lower heating value (2.21 MJ/m^3) of the gas products were obtained at 650°C with 1:8 timothy grass-to-water ratio for 45 min of gasification. Timothy grass biochars were characterized through proximate (moisture, ash, volatiles and fixed carbon), ultimate analysis (CHNS), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy (SEM), BET surface area, particle size distribution, pH and electrical conductivity to understand their thermal evolution to rising temperature and reaction time.

As the temperature increased from 450 to 650°C, extreme thermal denaturation of biochar (Figure 1) through dehydration, bond breakages and formation of transformational products resulted causing their aromatization. The increase in temperature resulted in the lowering of moisture and volatile matter contents in the biochars while increasing ash and fixed carbon levels. The rise in gasification temperature caused an increase in carbon and nitrogen contents in the biochars compared to raw timothy grass. With the increase in carbon content in biochars, their calorific value gradually improved from 24.9 MJ/kg (at 450°C) to 28.9 MJ/kg (650°C), which were significantly greater than raw timothy grass (18.6 MJ/kg). Biochars generated at 650°C showed a reduction in O, H and aliphatic C–H bonds in the FTIR spectra, thereby increasing the aromatic C–C bonds. Compared to raw timothy grass, the H/C and O/C atomic ratios reduced dramatically in biochars generated at high temperatures and longer residence times due to dehydration, dehydrogenation, demethanation, decarboxylation and decarbonylation of organic components. With the increase in gasification temperature and residence time, the biochars exhibited higher extent of ash, pH, surface area and pore volume. In contrast, biochars derived at lower gasification temperature showed lower magnitude of electrical conductivity and cation-exchange capacity.