MODELING OF RADICAL STRUCTURES IN BIOCHAR USING DFT CALCULATIONS

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Carbon is a key ingredient for producing metals used for cellphones, laptop computers, photovoltaic panels, and related solid state silicon devices employed by mankind. Thus, introduction of an alternative reductant based on bioresources into steel manufacturing without significant investments in a new technology is of high importance and wide impact. The production of iron, steel, and many other metals can employ biocarbon as the needed reductant; but because of cost, coals are usually used instead. The anthropogenic CO_2 emissions can be decreased by substitution of biochar in the production of silicon and metals due to the lower regeneration time of biomass < 10 years compared to 10^6-10^7 years for bituminous coal.

This study aims to develop and to provide knowledge on the biochar structure at the molecular level including the presence of free radicals and oxygen heteroatoms that is essential for the understanding and prediction of biochar valuable properties in metallurgical applications. Both yields and biochar properties are important parameters for the optimization of pyrolysis conditions. Therefore, the pyrolysis conditions for the biochar application as a reducing agent in steel industry were optimized, and the molecular structure of the biochar by the combined use of experimental chemistry (Raman spectroscopy and Fourier transform infrared spectroscopy) and quantum chemistry computations (Density Functional Theory methods) was modified.

The results indicated the formation of stable radicals from biomass pyrolysis at their termination stage which were quantified by the electron spin resonance spectroscopy. Based on the experimental and fitting results, PAH structures were selected as initial compounds for the DFT modeling. The comparison of hydroxylated with methylated PAH structures showed that hydroxylated PAH are excellent candidate to represent the radical structure based on the low bond dissociation energes. The bond dissociation energy of -10 Kcal mol^{-1} is in the range of the best known antioxidants. The results showed that the present DFT model predicts reasonably the biochar molecular structure, and can capture changes in the biochar molecular structure under different pyrolysis conditions.