

NON-COVALENT CATALYTIC AND INHIBITORY INTERACTIONS BETWEEN CELLULOSE AND LIGNIN DURING WHOLE BIOMASS FAST PYROLYSIS

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Production of renewable energy and chemicals from lignocellulosic biomass is projected to grow significantly in the coming decades with increased global concerns on the energy shortage and potentially environmental consequences caused by fossil fuel consumption. Fast pyrolysis is a promising thermochemical method to convert biomass feedstocks into biofuels or biomass-derived chemicals in a simple manner, but its product distribution is inherently non-selective due to its complex compositions and entangled pyrolysis reaction pathways.

In this study, reaction pathways and chemical kinetics of cellulose fast pyrolysis in the presence of lignin are investigated using microreactor experiments and quantum-chemistry *ab initio* density functional theory (DFT) calculations. Our DFT calculations revealed a new intramolecular hydroxyl-activated mechanism via concerted glycosidic bond cleavage for mid-chain activation of cellulose pyrolysis and subsequent depolymerization to produce levoglucosan (LG). The calculated activation energies for cellulose activation and depolymerization are 50.8 and 40.9 kcal/mol, respectively, using a two-chain cellulose model, agreeable with experimental values. Investigation on the hydroxyl-activated mechanism during cellulose fast pyrolysis in the presence of lignin further reveals that lignin functional groups containing hydrogen bond acceptors (red regions in Fig. 1), such as ethers, hinder β -1,4 glycosidic bond cleavage of cellulose, while lignin functional groups solely bearing hydrogen bond donors (green regions in Fig.1), such as alcohols, promote LG formation. As a result, the presence of lignin near the reaction center of cellulose activation could cause complex non-covalent catalytic or inhibitory effects, dependent on the types of the lignin moieties nearby. For example, our DFT calculations using model lignin compounds suggest that the Unit G lignin monomer and the G-55-G lignin linkage would accelerate cellulose activation (catalytic), while the Units S and H lignin monomers and the G-bO4-G and G-bO5-G lignin linkages would cause inhibitory effects (Fig.1a). In addition, lignin-derived pyrolysis products could also accelerate (catalytic) or decelerate (inhibitory) cellulose activation. Our work suggests that guaiacol, catechol, and phenol could all cause non-covalent catalytic effects and anisole could cause non-covalent inhibitory effects on the mid-chain activation of cellulose fast pyrolysis (Fig. 1b). Our work also examined formation pathways leading to glycolaldehyde (GA), and 5-hydroxymethylfurfural (5-HMF) as representative pathways to small oxygenated molecules and furans, respectively. Results from the microreactor experiments were found to be consistent with the DFT calculations. This work lays the first foundation of understanding the molecular-level interactions and chemical kinetics between the biomass constituents during the fast pyrolysis of the whole biomass.

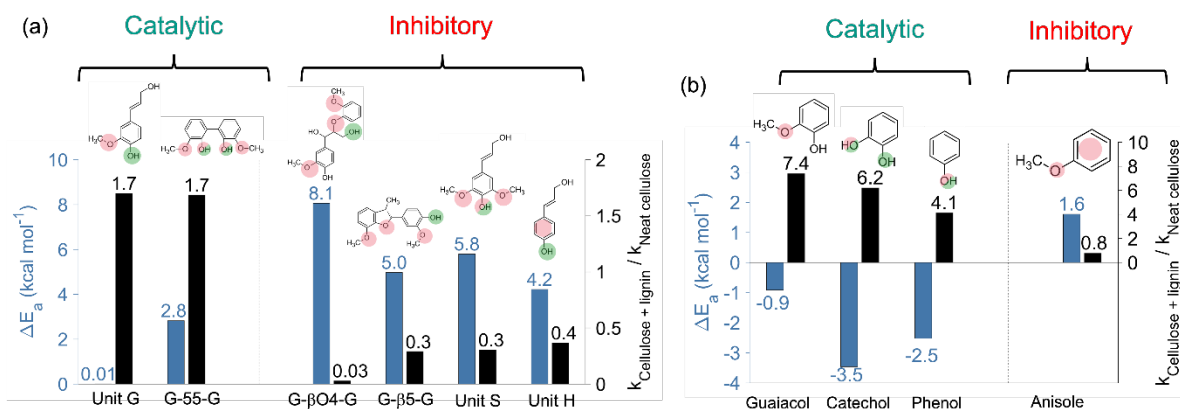


Fig. 1. The DFT calculated change of activation energy (ΔE_a) in mid-chain activation of cellulose fast pyrolysis when cellulose is exposed to (a) model lignin monomers and linkages and (b) model lignin-derived pyrolysis products. Red regions of the molecules are found to cause non-covalent inhibitory effects, and green regions of the molecules are found to cause non-covalent catalytic effects. The overall effect a molecule causes can be either catalytic (when k ratio is larger than 1) or inhibitory (when the k ratio is smaller than 1).