

NEW METHODS IN SOLID STATE REACTION ENGINEERING: MOLECULAR MECHANISMS OF CELLULOSE PYROLYSIS

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Abstract

The transition to renewable feedstocks for fuels, chemicals and materials necessitates the development of new reactor technologies for processing solid lignocellulosic materials. Semi-crystalline biopolymers undergo complex chemistry via high temperature catalytic processes producing hundreds of organic compounds which are subsequently upgraded to drop-in replacement chemicals and fuels. Introduction of the PHASR method (Pulsed-Heated Analysis of Solid/Surface Reactions) provides the capability for quantifying hundreds of chemicals evolving on the timescale of milliseconds from high temperature biopolymers. Measurement of fast rates of decomposition and volatile product formation from reacting biopolymers provides the first determination of the apparent energetics and mechanisms of biomass decomposition and a path towards improved biomass-derived liquids.

Keywords

Biomass, Cellulose, Biofuels, Solid Fuel, PHASR

Utilization of non-food, lignocellulosic biomass for large-scale production of biofuels requires a low-cost method for conversion to a liquid mixture with fuel properties conducive to gasoline, diesel and jet engines. High temperature pyrolysis of woody and grassy biomass achieves rapid liquefaction (1-2 seconds) at moderate reaction temperatures (~500 °C) yielding a condensable liquid called 'bio-oil' which can be upgraded to fuels.

Improvement of bio-oil quality including increased stability and energy content rely on optimizing the myriad of reactions from biopolymer to volatile compound^[1]. It is generally known that biomass initially fragments to a liquid before decomposing to volatile organic compounds. However, elucidating these pathways to volatile species has been limited by experimental techniques that can characterize hundreds of organic compounds evolving within a fraction of a second at high temperature.

In this work, we present a new method for measuring the rate of cellulose and biomass decomposition called

'PHASR' (Pulse-Heated Analysis of Solid/Surface Reactions)^[2]. By this experiment, films of cellulose (~10-50 μm) are heated from room temperature to reaction temperature (400-600 °C) at 10⁶ °C/min, maintained for reaction for 10-100 ms, and then rapidly quenched.

Measured kinetics reveal two kinetic regimes of cellulose decomposition, with a distinct transition occurring at 467 °C referred to as a 'reactive melting point', T_{RM} ^[2]. Below T_{RM} , cellulose decomposition is initiated by a low activation energy mechanism, and products are formed primarily from the end of the chain. Above T_{RM} , cellulose decomposes rapidly to a liquid, and products form primarily from intra-chain scission. Measured rates are compared with mechanisms and energetics calculated by DFT. Further work evaluates the role of alkaline earth metal catalysis on cellulose initiation and fragmentation.

[1] *Energy and Environmental Science* **2012**, 5, 7797.

[2] *Chemistry of Materials* **2016**, In Press

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