

COMPLETE PYROLYSIS OF CELLULOSE FOR INTEGRATED CATALYTIC BIOMASS PROCESSING

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Summary

Particles of microcrystalline cellulose approximately 300 μm in diameter thermally decompose on high temperature (700 $^{\circ}\text{C}$) inorganic surfaces coated with Rh-based reforming catalyst to an intermediate liquid. The intermediate liquid maintains contact with the surface permitting high heat transfer which results in an internal thermal gradient within the particle. Conversion from solid to liquid occurs along the internal thermal gradient finally resulting in a fully liquid droplet which completely boils to vapors.

Keywords

Alternate Energy, Green CRE, Chemical Feedstocks from Biomass

Introduction

Advanced biomass processing technologies based on pyrolysis require the introduction of catalysts to direct conversion chemistry for optimal selection of fuels and chemicals.^{1,2} Direct utilization of catalysts in the pyrolytic process can only occur in a continuous biomass reactor provided the biopolymers thermally decompose to species that can interact with active catalytic sites. Similarly, the byproduct formation of char and solid residues must be avoided to maintain catalyst integrity and permit continuous processing.

This paper examines the catalytic processing of microcrystalline cellulose particles in direct contact with high-temperature Rh-based reforming catalysts supported on alumina surfaces in the presence of oxygen. Conversion of the particle generally occurs by endothermic decomposition of cellulose to volatile, condensable organic compounds and non-condensable gases (CO , CO_2). However, the dominant mode of heat transfer to the particle is unknown, as well as the state of the particle during the conversion process, the rate limiting phenomenon (heat transfer or conversion chemistry), and the physical interaction between the particle and the surface.

Experimental Description

Particles of cellulose (Avicel, FMC Biopolymer) were sieved to an average size of 300 μm determined by light scattering. Sieved samples were dried in flowing nitrogen overnight. As shown in a scanning electron micrograph in Figure 1, the cellulose feedstock consisted of semi-

crystalline microstructures resulting in a void fraction of 30-50%.

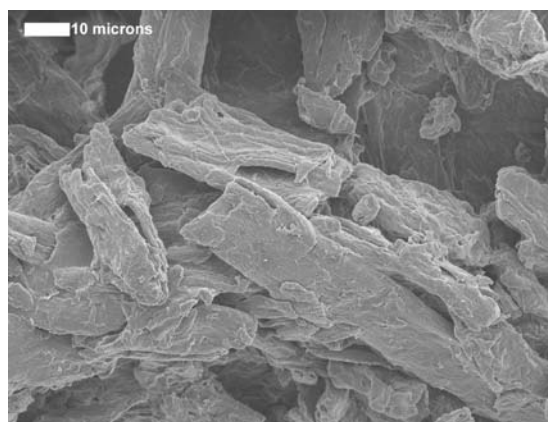


Figure 1. Micrograph of microcrystalline cellulose reveals a high void fraction material with semi-crystalline microstructures.

An alumina surface was prepared by compressing $\gamma\text{-Al}_2\text{O}_3$ powder into a disk 2 mm thick and 22 mm wide, and sintering at 800 $^{\circ}\text{C}$ for 30 hrs and 1180 $^{\circ}\text{C}$ for 8 hrs. Rh and Ce (2.5 wt% each) were co-applied to the support by wet impregnation, drying, and calcination at 600 $^{\circ}\text{C}$ for 6 hours.

The catalytic surface was heated from below by a butane torch permitting surface temperature adjustment by varying the torch-to-surface length. Air flowed over the top of the catalytic surface at four liters-per-minute. Particles of cellulose were directly applied to the surface

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by a particle delivery tube. Particle conversion was recorded with high-speed photography using a Photron Fastcam Ultima APX permitting determination of the particle state, dimension (height, width), total conversion time, and volume (by calculation).

Results and Discussion

Particles of cellulose observed with high-speed photography (1 ms temporal resolution) were independently tracked allowing measurement of their conversion time. As shown in Figure 2, particles of cellulose on an 825 °C Rh-Ce/Al₂O₃ surface exhibit a linear relationship between total conversion time and the square of the initial particle radius. This relationship indicates that particle conversion is overall heat-transfer limited.^{3,4}

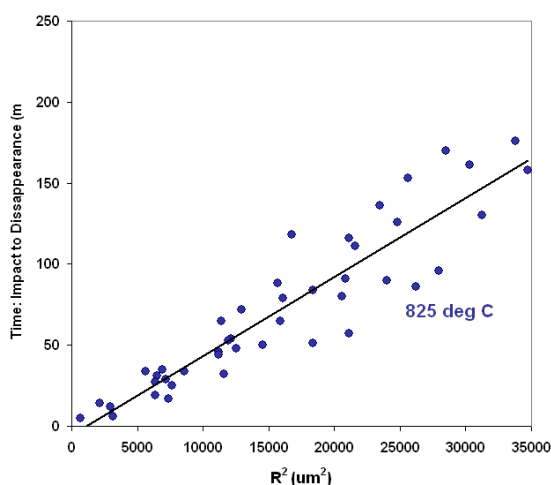


Figure 2. Total conversion time of particles of microcrystalline cellulose as a function of the initial diameter of the particle squared on 825 °C Rh-Ce/Al₂O₃ surfaces.

Direct observation of the cellulose particle also reveals that conversion occurs through three phases clearly distinguishable by particle dimension measurements with time. The particle initially comes to rest for 20-30 ms on the surface and is heated by radiation and gas convection. The second phase is initiated by the formation of a liquid intermediate along the bottom of the particle. This liquid layer appears to travel up the particle for 80-120 ms as the internal solid material reactively melts and collapses on the particle void fraction. During this phase, conduction between the inorganic surface and the cellulose intermediate liquid is the dominant mode of heat transfer.

Complete conversion by decomposition chemistry to a fully liquid droplet exists for the last 10-25 milliseconds. During this phase, the complete droplet volume was calculated from measurements of the particle height and width assuming a hemi-spherical droplet as shown in Figure 3. By assuming the change in enthalpy for complete devolatilization is 538 kJ kg⁻¹, the heat transfer rate to the particle was estimated as 3.4 ± 0.2 MW m⁻².⁵

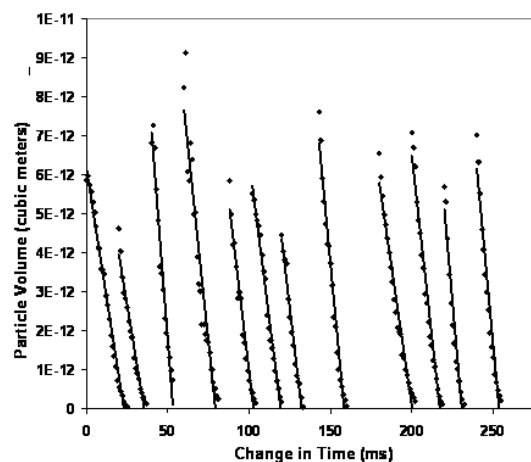


Figure 3. Volume of multiple liquid droplets of comprised of cellulose-derived intermediate liquid as a function of time on a 700 °C Rh-Ce/Al₂O₃ surface..

High heat transfer rate to the particle is possible due to the intermediate liquid produced between the original solid portion of the particle and the inorganic catalytic surface. Despite the high temperature of inorganic surface (>700 °C), the intermediate cellulose-derived liquid maintains contact (wets) with the surface exhibiting a measurable contact angle. Forming within the liquid intermediate are gaseous bubbles which rise to the top of the liquid droplet and pass into the gas phase. Complete conversion to volatile components was observed without the formation of solid, char-like residues.

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