Natural Catalysts for Molten Cellulose Pyrolysis to Targeted Bio-Oils
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1.0 Introduction. The U.S. Department of Energy has selected high temperature conversion of lignocellulosic biomass as one of its primary pathways for development into the next decade[1]. Within DOE – Energy Efficiency and Renewable Efficiency, a recent March 2015 roadmap has targeted 2017 and 2022 as significant targets for developing $3/gallon-of-gas-equivalent[2]. These goals have led to aggressive development of applied research at national laboratories focusing on high temperature liquefaction (>350 °C) and higher temperature processes including fast pyrolysis, in-situ catalytic pyrolysis, and ex-situ catalytic pyrolysis[3]. For example, application-focused research includes a multi-ton per day pyrolysis system focusing on maximizing liquid hydrocarbon yield. Therefore, there exists a significant opportunity for a parallel fundamental research program within basic energy sciences that can provide molecular insight into the catalytic reactions and kinetics of metal-promoted biomass chemistry.

Inorganic impurities in lignocellulosic biomass occur naturally and are required for biological function of important energy feedstocks. These metals including calcium and magnesium reside in ionic form within the cell walls of wood and grassy biomass materials in the range of 5-20 mg/g-biomass. Despite low concentration, the presence of catalytically active metals dramatically alters the chemistry of gasification, pyrolysis, liquefaction and torrefaction applications. As the reactions proceed to completion, the metal ions form solid oxides which accumulate and are removed as solid ash. As shown in Fig. 1, common biomass feedstocks for energy applications have large quantities of calcium and magnesium which form micron-scale solid particles at high temperature.

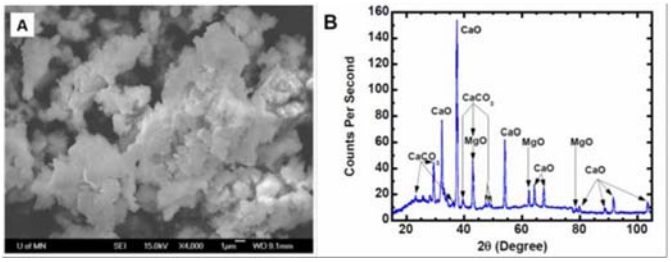

Fig. 1. Natural Catalysts. A. Ash particles obtained from the pyrolysis of Aspen wood fibers. **B.** X-ray diffraction of wood ash identifies calcium and magnesium oxides.

Our **goal** was to identify the catalytic mechanisms that control cellulose decomposition for three specific pathways. Despite decades of research effort into studying high temperature (>400 °C) biopolymer chemistry, the molecular mechanisms leading to major products such as levoglucosan, furans, pyrans and light oxygenates such as acetic acid remain unknown. The development of novel computational methods together with the advances in computing power that have occurred over the past decade have enabled the simulation of large complex carbohydrates and have allowed for a detailed analysis of the elementary reactions and corresponding energetics for some of the major pathways (e.g. levoglucosan formation) that have been proposed. Initial efforts have established an important foundation for detailed simulations that provide a more realistic accounting of reaction media, comprehensive analysis of the possible pathways, elementary steps and their corresponding energetics and the development of microkinetic simulations.

Despite progress, there are still a number of important challenges in modeling these systems which arise from the complexity of solid/melt mixtures that form the expansive network of reactions that can occur and uncertainty in calculated energetics due to the accuracy of the computational methods employed, the pathways considered, and the existence of unknown but kinetically-relevant pathways of cellulose decomposition. Lack of confidence in calculating cellulose reaction pathways has been further compounded by the lack of a parallel experimental technique capable of measuring apparent kinetics/energetics for comparison.

In this work, we developed the experimental methods needed to characterize the products of cellulose conversion catalyzed by calcium. We evaluate conditions that lead to reaction-controlled catalytic chemistry absent transport limitations. The chemistry of calcium-catalyzed cellulose conversion is then evaluated by determining the distribution of chemical products as a function of catalyst loading and reaction temperature. Finally, the reaction rate is characterized using a temporally-controlled pulse-film reactor.

2.0 Background. High temperature cellulose chemistry has been studied for almost a century with only limited insight into the molecular-level mechanisms. Semi-global (lumped) mechanisms have been developed based on thermo-gravimetric analysis (TGA)[4,5,6] and utilize kinetics to grouped products organized by phases: (i) solids – char, (ii) vapors – tars, and (iii) gases[7,8,9]. Numerous lumped models have proposed the additional detail of an intermediate pathway of cellulose decomposition through a low degree

of polymerization including mechanisms by Piskorz, et al[10], Diebold[11],Banyasz et al.[12,13], and Liden et al.[14]. Other attempts to evaluate cellulose chemistry have implemented heat transfer models with lumped kinetics[15,16]. Substantial effort to elucidate molecular chemistry has pursued exhaustive characterization of pyrolysis products via GC/MS using a micropyrolyzer[17,18,19]. Additional work has mixed alkaline earth metals with carbohydrates and evaluated the product distributions under realistic conditions that consisted of both primary and secondary cellulose reactions[20]. These results have provided insight into the types of products produced, but **the absence of isothermal reaction kinetics (i.e. time resolved measurements) has prohibited insight into the molecular mechanisms** which produce the volatile products.

More recently, new advances in mass spectrometry by Ribeiro and co-workers have led to the identification of important reaction intermediates in cellulose pyrolysis chemistry such as ring-opened intermediates important for producing light oxygenates[21]. In addition, molecular-based mechanisms proposed by Broadbelt and co-workers offer the first ability to predict volatile product distributions[22,23]. These mechanisms are based on the hypothesis that all non-anhydrosugar products proceed through glucose, which is formed via hydrolysis of glucose[24]. It is not clear, however, whether free water is available within molten cellulose during reaction and if glucose is produced during reaction. Additional background is provided within the proposed work as needed.

Inorganic species within biomass range from less than 1% up to 15% of the total mass, depending on the biomass species and the content of the originating soil[25]. Inorganic ions such as potassium, calcium, and magnesium are the most abundant in biomass/lignocellulosic feedstocks[26]. At the operating temperatures of fast pyrolysis (400-600 °C), inorganic metals are retained within the char, indicating that they likely interacted with the biomass to catalyze biopolymer degradation[27,28]. Müller-Hagedorn et al.[29] studied the catalytic effect of both sodium and potassium chloride and showed that these metal ions lowered the decomposition onset temperature of biomass and decreased the production of levoglucosan (LGA). Liu et al.[30] investigated the catalysis of three potassium inorganic salts on cellulose pyrolysis using TGA–FTIR and found that the presence of potassium salts lowered the activation energy and increased the reaction rate of pyrolysis. Kawamoto et al.[31] reported that magnesium and calcium chlorides promoted char formation and suppressed the formation of levoglucosan under N_2 at 400 °C. Khelfa et al.[32] concluded that $MgCl_2$ promotes dehydration at low temperatures as observed both by TGA and pyrolysis analyzed by mass spectrometry. Patwardhan et al.[33] examined varying concentrations of inorganic salts and the following trends were observed in levoglucosan yield in the order of strongest to mildest influence: (a) cations—$K^+ > Na^+ > Ca^{2+} > Mg^{2+}$; (b) anions—$Cl^- > NO_3^- \approx OH^- > CO_3^{2-} \approx PO_4^{3}$.

3.0 Results. Prior work has focused on three predominant areas: (a) development of experimental methods for studying high temperature cellulose chemistry, sections 3.1 and 3.4, (b) evaluation of the major reaction pathways of cellulose, and (c) elucidation of the catalytic role of magnesium and calcium catalysts on reaction pathways.

Method Development #1 - Film Pyrolysis. The study of high temperature (>400 °C) chemistry of cellulose requires experimental methods that achieve reaction-limited conditions free of diffusion and/or heat transfer limitations. Initial work[34] established the method of 'Thin-Film Pyrolysis' whereby micron-scale samples of organic materials such as cellulose were prepared. As depicted in Figure 2A, dimensional analysis based on the relative rates of reaction and heat transfer indicate that isothermal samples must be on the order of 10 µm. Subsequent experiments[35] varied sample thickness and established the compositional variations resulting from isothermal and non-isothermal experiments. Most recently, the kinetics of furfural formation from cellulose was measured at 500 °C as a function of sample thickness as depicted in Fig. 2B. A reaction rate at constant value (~2.2 1/s) below 70 m definitively establishes that thin-film solid sample preparation is required to achieve chemistry-controlled reaction conditions necessary to evaluate mechanisms of reacting solids and catalytic solid systems[36].

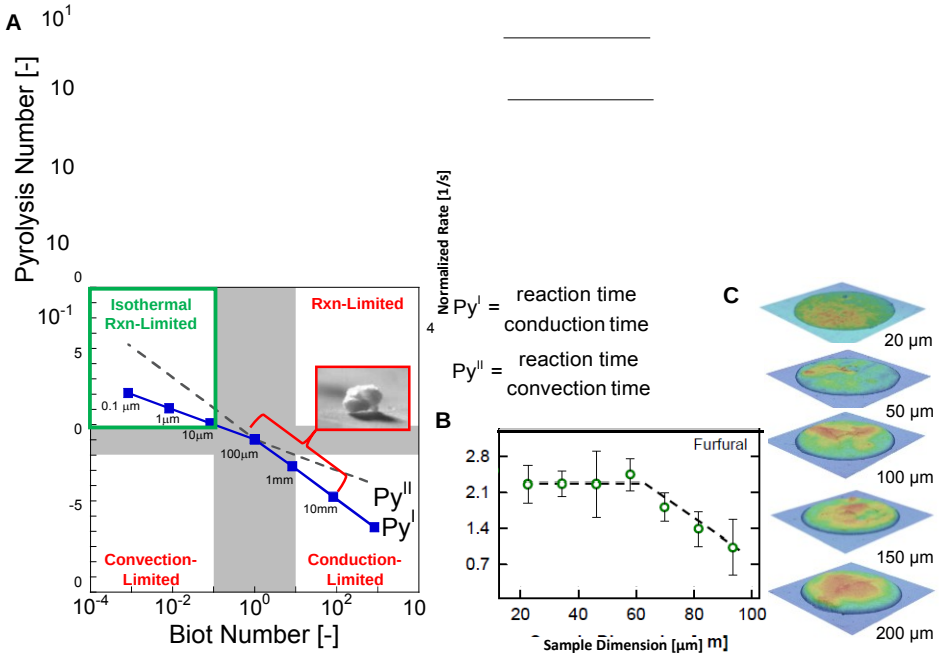

Figure 2. Thin-Film Pyrolysis – Method Development. A. Isothermal kinetics of cellulose reactions are obtained at low Biot number and high Pyrolysis numbers. **B.** The rate of furfural production from cellulose at 500 °C transitions from reaction-controlled to transport-controlled above 70 µm sample thickness. **C.** Optical profilometry of cellulose films characterizes variable cellulose sample thickness.

3.1 Elucidation of Cellulose Reaction Pathways. Utilization of film pyrolysis enabled the determination of the primary reaction pathways of cellulose, which were defined in this work as the sequential reaction steps leading to the first volatile component (green in Fig. 3). Variation of reaction temperature combined with high speed photography revealed that solid cellulose (β-1,4-glucopyranose) decomposes to a solid referred to as 'primary char,' while reactions at 500 °C or above led to the formation of a liquid intermediate phase[34]. The liquid was sampled and shown to consist of short-chain anhydro-oligomers of cellulose (β-1,4-glucopyranose chains with C1-C5 ether linkages)[37]. The kinetic competition between primary char formation and anhydro-oligomers is addressed in section 3.5.

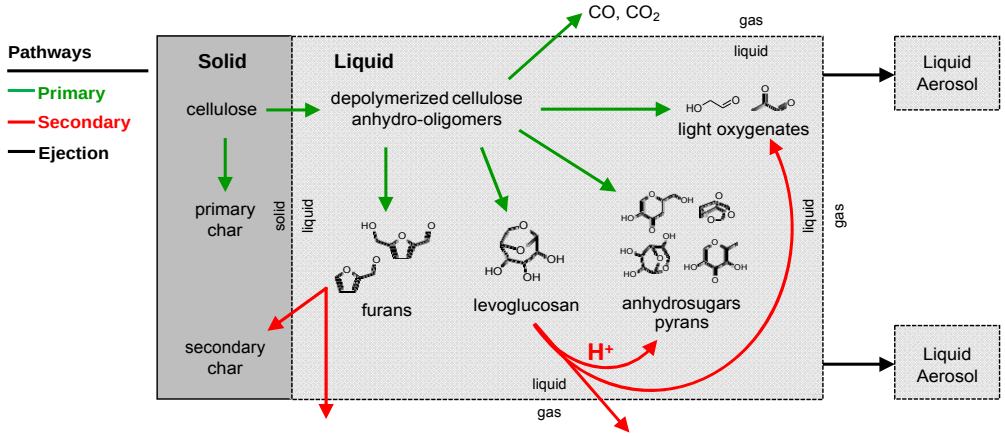

Figure 3. Experimentally-Determined Primary and Secondary Reaction Pathways of Cellulose.

Thin-film pyrolysis revealed that the primary reactions of cellulose (green in Fig. 3) produce five major classes of products: (i) furans, (ii) levoglucosan/anhydrosugars, (iii) pyrans, (iv) light oxygenates, and (v) permanent gases[34]. The distribution of these species varies with temperature, with maximum

anhydrosugars and light oxygenates produced between 450 and 500 °C[35]. More recently, we have shown that the distribution of primary products depends greatly on the ratio of intra-chain monomers to chain ends[38]. The yield of furans and light oxygenates increase with increasing quantity of chain ends (e.g. glucose-like end groups referred to as 'reducing end groups'), while the yield of anhydrosugars such as levoglucosan increase with increasing chain size[38]. The importance of the chain length effect on product distribution led to an important discovery that cellulose (long chains, 100-1000 monomers) exhibits chemistry consistent with zero chain ends. Identical product distributions and reaction rates were observed with both cellulose and cyclodextrin, a six-monomer α-glucopyranose ring[34]. Additionally, the stereochemistry of the glycosidic linkage was shown to exhibit no influence on the chemistry; α-1,4 and β-1,4-glycosidic linkages between monomers yielded identical product distributions[34].

Secondary reactions of cellulose were defined as the reactions that the volatile organic products undergo within the molten phase prior to evaporation as depicted in red in Fig. 3. While 'thin-film pyrolysis' was developed such that volatile species would evaporate at least an order of magnitude faster than reaction, it is also possible to prepare thicker samples whereby volatile products react prior to evaporation. By comparison between the two experiments, the extent of secondary reactions was determined. For example, furans including furfural and 5-hydroxymethylfurfural (HMF) were shown to evaporate in competition with formation of secondary char, a solid similar to humin formation[39].

The secondary reactions of levoglucosan within molten cellulose were also confirmed by combined isotope labeling ($^{13}C/^{12}C$ & $^{2}D/^{1}H$) and variation of sample thickness[40]. In these experiments, levoglucosan was prepared with varying mixture ratios of fructose; samples were prepared as both thin films (~2 μm thickness) and solid mixtures of powdered materials (~1 mm). Fructose was selected as a co-reactant with negligible volatility to simulate a molten carbohydrate due to its availability with ^{13}C and ^{2}D isotope exchange as well as its limited capability for forming anhydrosugars. By this method, levoglucosan products were identified as two pyrans (DHMP and ADGH) and two anhydrosugars (DAGP and anhydro-glucofuranose) as shown in Fig. 4A. Characterization of deuterium content post reaction indicated that reaction products of levoglucosan that required dehydration (e.g. pyrans) exhibited substantial H/D exchange, as shown in Fig. 4B. Significant H/D exchange was interpreted as an indication of acid-catalyzed dehydration, which was necessary for formation of pyran C=C π bonds.

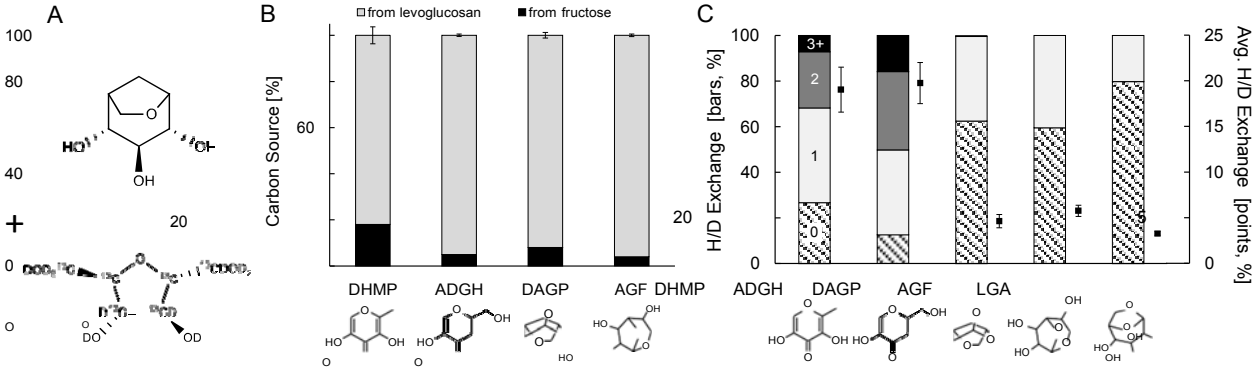

Figure 4. Secondary reactions of levoglucosan. A. Reaction of levoglucosan with isotopically-labeled fructose. **B.** ^{13}C labeling of reaction products of levoglucosan and fructose indicate that four major products are derived from levoglucosan. **C.** $^{1}H/^{2}D$ exchange between fructose and levoglucosan indicate substantial proton-exchange for dehydration products DHMP and ADGH.

3.2 Pathways of Metal Catalysis of Cellulose Chemistry. Initial work has focused on understanding the impact of single-metal atom catalysis and supported metals on the reaction pathways of cellulose. Supported Pt and Pd catalysts on carbon and silica supports were evaluated under thermally-thick conditions (L~0.5 mm) at 500 °C to evaluate the potential for tuning cellulose chemistry[41]. Conditions and catalysts were selected to evaluate the specific reaction of decarbonylation of furanic products. As shown in Fig. 5, uncatalyzed conversion of cellulose produces substantial quantities of aldehydic furans including furfural and 5-hydroxymethylfurfural. These particular species have been shown to be problematic tar-like compounds in downstream processes due to their proclivity to form coke. For this reason, selective decarbonylation to furan, and hydroxymethylfuran enhances product stability and improves fuel qualities. By evaluating a range of conditions, it was found that Pd/C and Pd/SiO_2 catalysts exhibit substantial capability for selectively decarbonylating furans with ~90% yield of stable furanic products, as shown in Fig. 5.

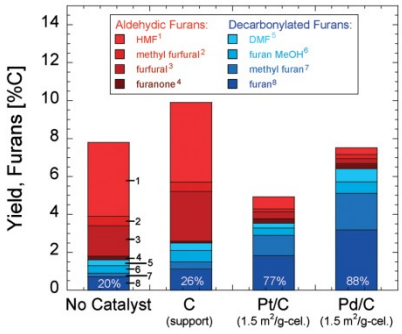

Figure 5. Impact of Metal Catalysts on Yield of Aldehydic Furans.

Naturally occurring alkali and alkaline earth metals exist within lignocellulosic biomass as a requirement for biological function, but their impact on the chemistry at high temperature is not well described. While previous research has identified the variation in product distribution with impregnation of calcium and other materials[20], it was not determined if the metals acted primarily on the original polymer or the volatile organic products prior to evaporation (secondary reactions).

In this work[42], we compared the product distributions of calcium- and magnesium-catalyzed cellulose chemistry at conditions relevant to biomass energy applications. In particular, we varied the experimental conditions between isothermal (thin-film) and realistic (powder) to evaluate the catalysis of natural metals on cellulose. While magnesium and calcium were shown to significantly increase the rates of cellulose decomposition, their influence on the catalytic selectivity was small. Magnesium showed negligible impact on the distribution of primary cellulose products (Fig. 6D), while calcium only minimally reduced the yield of primary anhydrosugars (Fig. 6C). In comparison, under transport-limited conditions, it is clear that both calcium (Fig. 6A) and magnesium (Fig. 6B) extensively catalyze the secondary reactions of volatile organic products within molten cellulose.

Identification of specific compounds during catalytic conversion is depicted in Fig. 6E-6H. The formation of levoglucosan is suppressed for all catalysts and conditions, while calcium is the more active catalyst for conversion of hydroxymethylfurfural. Light oxygenates including glycoaldehyde and three-carbon oxygenated molecules such as hydroxyacetone are enhanced by calcium (not shown). Substantial enhancement in C1 products was observed with calcium including formation of carbon monoxide (Fig. 6G) and formaldehyde (Fig. 6H).

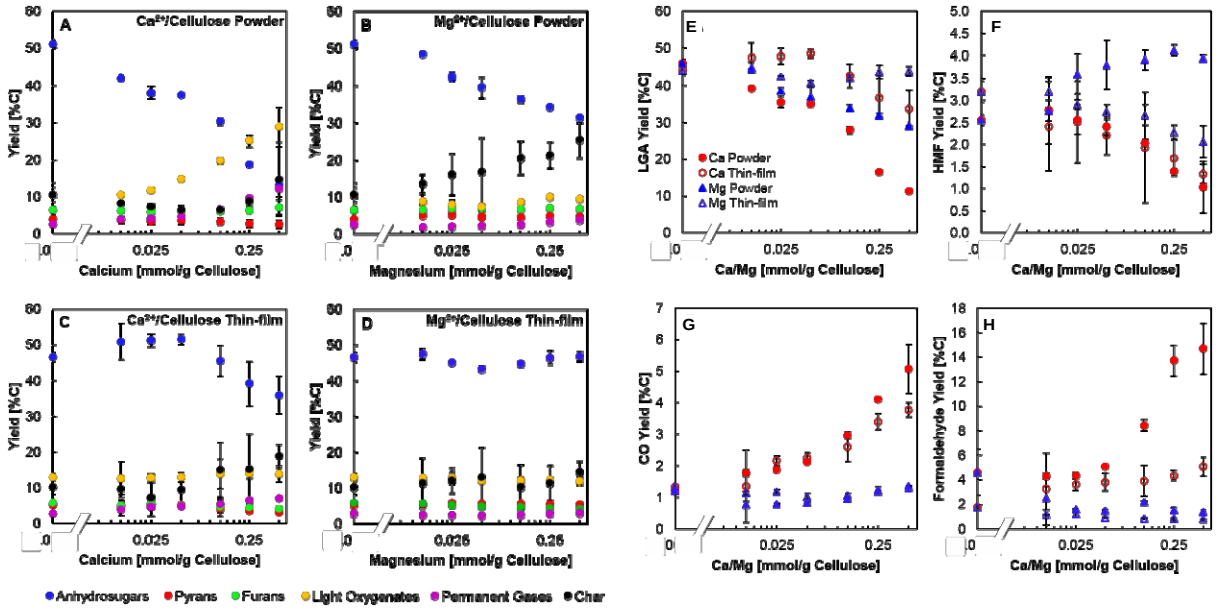

Figure 6. Alkaline Earth Metal Catalysis of Cellulose[42]. A/B. Yield of major product classes at industrial (powder) conditions. **C/D.** Yield of major product classes at isothermal (thin-film) conditions. **E/F/G/H.** Yield of specific product compounds levoglucosan, 5-hydroxymethylfurfural, carbon monoxide and formaldehyde.

3.3 Method Development #2: Pulsed-Film Kinetics. The research presented in sections 3.1-3.3 focused on the reaction pathways of cellulose by studying product distributions at complete conversion. However, mechanistic insight into the cellulose reactions to volatile products requires detailed information on the kinetics of formation and the intermediate species. ***The inability to measure the reaction kinetics of high temperature biopolymer chemistry is the primary limitation*** in this entire research field[39]. For example, it is unknown if cellulose is fully reacted with 0.1, 1.0 or 10 seconds. Without the capability for measuring rates, it has been impossible to compare calculated energetics of particular reactions (e.g. cellulose→furfural) with experiment, and the mechanisms remain unknown.

To address this key experimental issue, we have developed a new experimental technique called millisecond "Pulsed-Film Kinetics" (PFK) which enables measurement of temporal formation of the molecular products of cellulose pyrolysis. A challenge with measuring the kinetics of biopolymer conversion at high temperature has been the mismatch in timescales between the millisecond reaction (τ_{rxn}~10^{-3} s) and the time required for analysis of complex mixtures. While mass spectrometry (e.g. time-of-flight or electron impact) can achieve rapid temporal characterization of single masses or charge-to-mass ratios, the large distribution of chemical products (10^2-10^3 compounds) in pyrolysis products and fuels in general requires slow analysis methods such as gas chromatography (τ_{GC}~10^3-10^4 s). The mismatch in timescales of six-to-seven orders of magnitude was overcome by development of a high temperature thermal pulsing method which enables rapid heating and rapid quenching of solid reaction samples. Thus, the fast reaction and slow analysis methods are temporally decoupled.

The experiment is conducted in a two-chamber system depicted in Fig. 7A. A liquid silicon-based coolant continuously flows through a lower chamber comprised of a microstructured heat exchanger. The top chamber is a one-millimeter-thick gas channel through which helium continuously flows. The solid sample (e.g. cellulose) is a 5-100 μm film on a plate about the size of penny; this plate serves as a resistive heating element and attaches to two copper electrodes which pass through the top of the reactor. The heating element is thermally connected to the heat exchanger by a solid layer of aluminum nitride, which conducts heat well but serves as an electrical insulator. A 5.0 μm layer of indium is deposited between each solid layer to serve as a liquid thermal conductor to eliminate contact resistance.

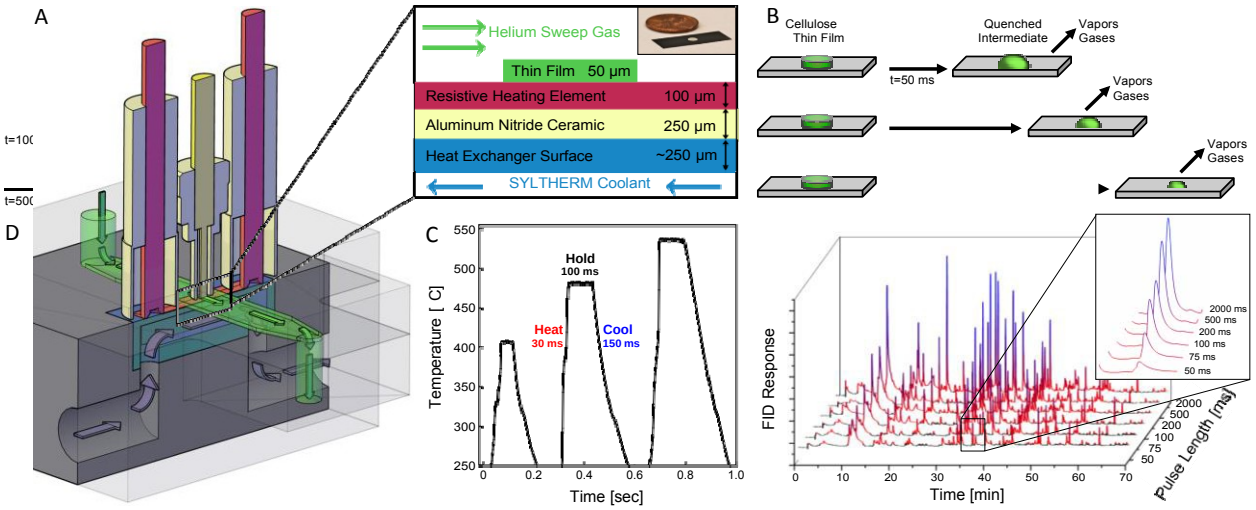

Figure 7. Pulsed-Film Kinetics of High Temperature Reactions of Cellulose. A. PFP Reactor. **B.** Tunable reaction time in ms of cellulose films. **C.** Reactor capability for kinetic pulses. **D.** Millisecond temporal characterization of ~100 organic compounds from cellulose at 500 °C.

The reactor allows for reaction pulses as short as 10 milliseconds at temperatures from 250 to 1000 °C as depicted in Fig. 7C. The temperature of the reaction sample is measured via an optical spectrometer capable of reading the temperature at 1000 Hz. The temperature reading is continuously logged and feeds back within a 2000 Hz PID control loop optimized for the PFK reactor. The design achieves the performance targets (e.g. heating/cooling rates) identified in Fig. 7C, such that <2% conversion of sample occurs during the combined heating and cooling phase. The method has been described within a manuscript submitted to *ACS Analytical Chemistry*[43].

3.4 Cellulose Transition Kinetics. The kinetics of cellulose chemistry at temperatures of 250-600 °C were measured by the method of pulsed-film kinetics. As shown in Fig. 7B, each thermal pulse (e.g. 500 °C, 50 ms duration) produced: (i) a GC chromatogram which separates and quantifies 50-100 organic compounds, and (ii) a liquid intermediate which is quenched for analysis via liquid chromatography, H-NMR, or infrared spectroscopy. The GC chromatograms were then stacked in sequence by pulse duration (τ_{pulse} = 50, 75, 100, 200, 500, 1000 ms), such that GC elution times and quantities of each separated compound could be determined. By this method depicted in Fig. 7D, the compositional evolution of single organic species could be tracked with millisecond temporal resolution; in this image, a single peak of furfural is depicted with reaction time.

Initial research has focused on the kinetics of furan formation from cellulose and shorter-chain polyglucans. As depicted in Fig. 8A, the temporal production of seven major furans was measured at 450 °C. Complete conversion of cellulose was achieved within 500 milliseconds. More interestingly, the formation kinetics for all of the furans appeared to be zero order in reactant concentration (i.e. a straight line); the rate of furan formation never varied until all reactant was consumed. This important observation was contrasted with the temporal production of the same seven furans at 500 °C as depicted in Fig. 8C. At this temperature, the formation kinetics for all of the furans were first order in reactant concentration with the signature first-order curve matching the experimental data.

The interpretation of variable kinetics between 450 and 500 °C was a transition from chain-end cellulose chemistry at low temperature to intra-chain glycosidic cleavage at high temperature. As depicted in the inset cartoon of Fig. 8A, a fixed reaction rate of furan production is consistent with the reaction occurring only at the chain end; the active site concentration of the polymer is fixed. This was confirmed by measuring the initial (differential) kinetics of furan production rates from short-chain polyglucans with β-1,4 glycosidic bonds. In Fig. 8B, the rate of formation of furans remained constant when normalized by the concentration of chain ends for cellobiose (G2), cellotriose (G3)…cellohexaose (G6) and even up to

short chain cellulose (G133). Different kinetics were observed above 500 °C; the formation rate of furans at high temperature was approximately constant when the measured rate was normalized to the concentration of monomers.

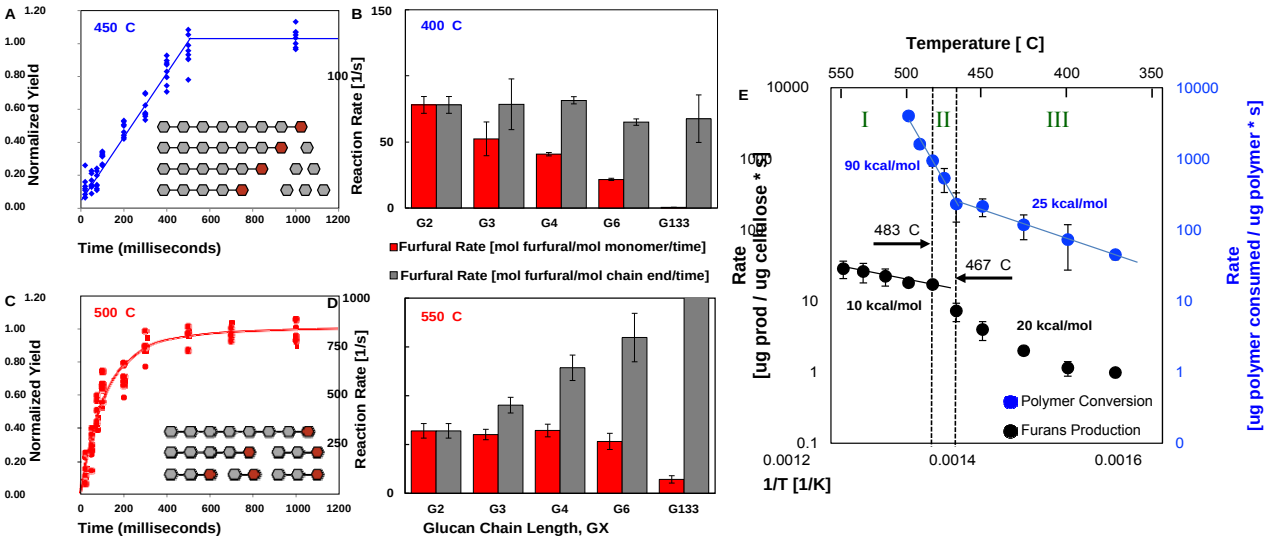

Figure 8. Kinetics of Cellulose (PolyGlucan) Chemistry. A. Temporal normalized yield of seven major furans at 450 °C. **B.** Differential reaction rate ($X_{cellulose}$<20%) of furfural production at 400 °C with respect to mass of monomers (grey) and chain ends (red). **C.** Temporal normalized yield of seven major furans at 500 °C. **D.** Differential reaction rate ($X_{cellulose}$<20%) of furfural production at 550 °C with respect to mass of monomers (grey) and chain ends (red). **E.** Differential kinetics cellulose conversion (blue) and lumped furans formation (black).

The cellulose chemistry kinetic transition at ~475 °C was interpreted by the differential kinetics depicted in Fig. 8E. Using cyclodextrin (α-1,4-cyclohexaglucan) as a surrogate for cellulose, the conversion kinetics of cellulose was measured from 400-525 °C. Previous work has shown that cyclodextrin exhibits identical reaction kinetics and product distributions as cellulose, but it was easier to quantify by liquid chromatography. Above 475 °C, the reaction rate of cellulose was observed to rapidly increase such that a 10 ms pulse at 525 °C achieved 20% conversion; this was the maximum measurable rate of the PFK reactor. The rapid increase in rate and change in apparent slope (Fig. 8E) is consistent with the cellulose polymer reacting only at the polymer end at low temperature to transitioning to thermal conditions that also activate internal glycosidic bonds. The calculated activation barrier of 90 kJ/mol appears to be consistent with the C-O bond dissociation energy of 86 kcal/mol which would suggest that the transition is due to the thermal C-O-C bond rupture. This transition also coincides with the formation of liquid intermediate cellulose[44], which has been shown to consist primarily of short-chain anhydro-oligomers which derived from cellulose randomly breaking internally[37]. The kinetic transition at 475 °C also explains the importance of conducting pyrolysis at 500 °C; cellulose glycosidic cleavage occurs too rapidly to volatile products at this temperature for dehydration of the cellulose polymer to occur to form char.

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