BIOMASS PYROLYSIS KINETICS: A REVIEW OF MOLECULAR-SCALE MODELING CONTRIBUTIONS

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Abstract - Decades of classical research on pyrolysis of lignocellulosic biomass has not yet produced a generalized formalism for design and prediction of reactor performance. Plagued by the limitations of experimental techniques such as thermogravimetric analysis (TGA) and extremely fast heating rates and low residence times to achieve high conversion to useful liquid products, researchers are now turning to molecular modeling to gain insights. This contribution briefly summarizes prior reviews along the historical path towards kinetic modeling of biomass pyrolysis and focusses on the more recent work on molecular modeling and the associated experimental efforts to validate model predictions. Clearly a new era of molecular-scale modeling-driven inquiry is beginning to shape the research landscape and influence the description of how cellulose and associated hemicellulose and lignin depolymerize to form the many hundreds of potential products of pyrolysis.
Keywords: Biomass; Cellulose; Pyrolysis; Molecular; Atomistic; Modeling.

INTRODUCTION

Advanced biofuels are considered the main renewable liquid fuel option to curb fossil fuel use, gain energy independence, and mitigate global climate changes due to greenhouse gas (GHG) emissions. Advanced biofuels, as defined by the RFS2, include cellulosic biofuels (renewable fuels derived from cellulose, hemicellulose, or lignin), which include cellulosic ethanol, biomass-to-liquid biodiesel (BTL) and green gasoline and biomass-based diesel or 'renewable diesel' produced from fats and oils not co-processed with petroleum products; excludes biofuels made from corn-starch ethanol (Argyropolous, 2010). A 2013 report published by the International Energy Agency (IEA) provides a global perspective on biomass use as an energy resource (Vakkilainem *et al*.,

2013). Currently, biomass resources account for approximately 10 percent of the global energy supply, of which two-thirds (66%) is used in developing countries for residential cooking and heating. The next largest use of biomass as an energy resource is by the industrial sector which weighs-in at a comparatively small fraction, 15%, of the total biomass usage. The top countries utilizing biomass as an industrial energy resource are Brazil, the U.S. and India. Brazil leads the list at 18% of the total industrial sector use globally as of 2009. The U.S. and India each had a 16% share of the global industrial biomass use for energy, with Nigeria, Canada, Thailand and Indonesia trailing far behind in the next group, each having about a 4% global share. In the transportation sector, the U.S. has by far the largest share of the global consumption of biofuels at 43% in 2011, of which ethanol was 94% of

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the U.S. total. Brazil's biofuel usage is also dominated by ethanol, at 94% of its total, with the country accounting for about 25% of the global usage.

In the U.S., for example, recent history shows that legislation in the mid-1970s, such as the Solar Energy Research, Development, and Demonstration Act, led to research and development for the conversion of cellulose and other organic materials (including wastes) into useful energy and fuel primarily in the form of ethanol (Payne, 2010). More recently, the Energy Policy Act of 2005 introduced the Renewable Fuels Standard (RFS) to ensure that gasoline sold in the U.S. would contain a minimum volume of renewable fuels, mainly corn ethanol, by 2012 (Payne, 2010). Yet, fluctuating world food prices and economic and environmental sustainability concerns have pushed the government to revise energy policy and move in the direction of alternative biomass feedstock for the production of biofuels. To this end, the Energy Independence and Security Act (EISA) of 2007 expanded the RFS regulations (RFS2) requiring the production of 36 billion gallons of ethanol blended gasoline, diesel, and jet fuel annually by 2022, of which 21 billion gallons of renewable fuels must be advanced biofuels, and of these advanced biofuels 16 billion gallons must come from cellulosic (or lignocellulosic) biofuels (Argyropolous, 2010). Just nine years away from the EISA deadline, 2013 Annual Energy Outlook (AEO2013) speculates that biofuels consumption growth will fall short of the RFS target based on projections relative to a baseline reference case which assumes an increase in production and consumption of domestic crude oil, natural gas, and diesel fuel, while the consumption of motor gasoline declines due to stringent fuel economy standards; the reference case and projections based on alternatives, in which current laws and regulations are not kept constant, are described in detail in the report until the year 2040 (five more years than in the AEO2012) (US Energy Information Agency, 2013). Demand for gasoline ethanol blend of E10 (10% ethanol blended gasoline) and E15 (15% ethanol blended gasoline) is expected to drop 0.6 million barrels per day from 2011 to 2022; however, domestic consumption of drop-in cellulosic biofuels (such as biomass-based diesel and green gasoline) is to grow from 0.3 to 9.0 billion gallons ethanol equivalent per year from 2011-2040 due to rising oil prices and lower production costs for biofuels technologies (US Energy Information Agency, 2013).

The conversion of biomass to heat, power, liquid fuels and bio-products involves complex reaction path mechanisms; thus, current research and development initiatives in this area are expansive and multi-disciplinary. There are two main routes to biofuels from cellulosic feedstock: biochemical and thermochemical. This paper focuses only on the thermochemical conversion of biomass by direct pyrolysis for the production of fuels and chemicals. Thermochemical methods include combustion, gasification, and liquefaction, all of which are well-established techniques due to a broad range of industrial applications. Biomass-based energy and chemicals production, pyrolysis, a thermal form of liquefaction involving decomposition of a material in an environment with no oxidizer, has emerged as a front-running technology. Pyrolysis offers a direct route from organic matter to renewable biofuels and chemicals. In essence, this approach is repurposing an old technology for a new application, and has gained considerable attention as a fundamental area of research in recent years.

Pyrolysis of cellulosic biomass generates biochar, a useful soil amendment; bio-oil, a viscous liquid product that can be upgraded to fuels and chemicals, and light permanent gases. Advancements in pyrolysis could lead to operational simplicity, and in turn, a much needed cost reduction in the overall thermochemical conversion process. Roadblocks presently facing the production of biofuels via pyrolysis include low liquid product yield (<80%), difficulty cleaning and stabilizing bio-oils, and developing catalysts to upgrade bio-oil into finished fuels (International Energy Agency, 2013, US Department of Energy, 2010). These issues require fundamental knowledge of the substrate and product chemistry, as well as kinetic and mechanistic information leading to the formation of products. Progress in pyrolysis research is further slowed due to a wide range of viable non-competitive biomass starting material, an essential component for maintaining sustainability, for which unique kinetic responses if not pathways must be defined. Furthermore, emerging research and technology are expected to *speak* to the economic, environmental, and societal issues at every step along the bioenergy production chain for next-generation biofuels.

EXTENDED BACKGROUND – The Historical Path Towards Kinetic Modeling

The present knowledge of biomass pyrolysis kinetics stems from extensive contributions by early researchers working in combustion, pyrolysis, and fire-proofing applications using carbohydrates and woody biomass (Fang and McGinnis, 1976, Hileman *et al.*, 1976, Shafizadeh and DeGroot, 1976, Antal Jr, 1985). Lignocellulosic plant matter comprises cellulose, hemicellulose and lignin as the main structural components of the plant cell wall (Shafizadeh, 1982, Antal

Jr, 1985). Much of the research efforts have focused on the structural and chemical properties of cellulose due to its widespread use in construction (wood) and industrial applications. And, while there is an extensive body of literature, leading back to a number of pivotal publications (Shafizadeh and Fu, 1973, Broido and Nelson, 1975, Antal Jr *et al*., 1980); yet, few comprehensive review papers on cellulose pyrolysis have been written (Anital Jr, 1982; Antal Jr and Varhegyi, 1995; Vinu and Broadbelt, 2012; Lede, 2012; and Burnham, Zhou and Broadbelt, 2015) in the past four decades or more of focused research. Notably, the paper by Vinu and Broadbelt, 2012, is technically not a review, but is summative in regard to its effort to bring together the state of knowledge on pyrolysis kinetic mechanisms for glucose-based carbohydrates including cellulose. Since 2000, however, pyrolysis of whole biomass, cellulose and lignin has been a fast-moving field of research, spawning extensive reviews, every 10 months (inclusive of the recent papers by Vinu and Broadbelt, 2012, Lede, 2012 and and Burnham, Zhou and Broadbelt, 2015) on the average in an effort to inform the research community and keep-up with the pace of advances. In addition to the earlier reviews on cellulose already mentioned, the following papers, listed chronologically, chronical the advances made in the 15 year period from 2000 to 2015 (Anital Jr, 1985; Sinha, *et al*., 2000; Bridgwater and Peacocke, 2000; Amen-Chen, Pakdel and Roy, 2001; Czernick and Bridgwater, 2004; Reale, *et al*., 2004; Branca, Albano and Di Blasi, 2005; Mohan, Pittman and Steele, 2006; Prakash and Karunanithi, 2008; Venderbosch and Prins, 2010; Slutter, *et al*., 2010; White, Catallo and Legendre, 2011; Pandey and Kim, 2011; Bridgwater, 2012; and Shen, *et al*., 2015). Short of the work by Vinu and Broadbelt, 2012, and Shen, *et al*., 2015, even the most recent reviews hardly mention the already large and rapidly growing body of literature on molecular-based modeling studies that are now a mainstream part of the effort to elucidate the complex process of lignocellulosic biomass pyrolysis. Furthermore, among the 19 reviews written since 2000, only three focus on lignin pyrolysis. Noting that there are a number of extensive review papers on classical experimental-based pyrolysis research and modeling, this paper, therefore, endeavors to summarize the classical works by quickly marching through the mentioned reviews, not necessarily chronologically, and then to move-on and detail the significantly newer and yet mostly un-reviewed body of literature on molecular-scale modeling.

Early papers on the kinetics of cellulose pyrolysis (Shafizadeh and Fu, 1973, Broido and Nelson, 1975) extoled a multi-step decomposition mechanism implying an intermediate form of cellulose, eventually to become known as "activated cellulose" or "intermediate activated cellulose (IAC)" as Lede (2012) would later call it. These works, and their follow-on efforts including Broido (1976) and Bradbury, Sakai, and Shafizadeh (1979), were *put to the test* by Antal and Varhegyi in 1995; who, further, criticized their own (Antal) support, in-part, of these models in an earlier review (Antal, 1982). Antal and Varhegyi (1995) define cellulose pyrolysis kinetics as a mathematical description of "the pyrolytic decomposition of a small homogeneous sample of pure cellulose (free of inorganic contaminants, with a well-defined degree of polymerization and crystallinity), which is uniform in temperature throughout the course of decomposition". Using this definition, the authors proceed to explain the thermal decomposition of cellulose assuming a first-order reaction with high activation energy ($E_a \approx 238$ kJ/mol). Varhegyi *et al*. (1994) critically assessed the most widely employed kinetic scheme for biomass pyrolysis, the multi-step Broido-Shafizadeh model, which suggests the formation of an "active" cellulose complex, that subsequently degrades to form char and volatile tar products. In an attempt to validate the Broido-Shafizadeh model, Varhegyi *et al*. (1994) performed prolonged thermal pretreatment experiments on small cellulose samples (0.5-3 mg), and found no evidence pointing to an initiation reaction at temperatures between 250 and 370 °C. However, their findings show that cellulose decomposition happens through two parallel reactions, of which only the tar-forming pathway is observed when the biomass substrate is not exposed to extended thermal pretreatment and thus rejecting the active cellulose concept. In his 2012 review on "the existence and role of intermediate active cellulose," Lede offers extensive, though in some cases indirect, evidence for the existence of IAC and encourages a range of experimental research needs, admitting to the difficulty in *isolation* of the IAC. Other researchers have adopted the intermediate activate cellulose concept as part of more discretely defined kinetic models, including that of Ranzi *et al*. (2008), Zhou *et al*. (2014a, 2014b), and Zhou (2016a, 2016b), for example.

The collective set of brief reviews: Sinha *et al*. (2000), Kersten *et al*. (2005), Branca *et al*. (2005), Demirbas and Balat (2007) and Prakash and Karunanithi (2008), all focus on the application of simple lumped kinetic models and unanimously call for more discretely defined models with better predictive ability over a wide range of pyrolysis conditions and for a wide range of raw materials. Statements such as "[there needs to be better] synergy between experiment and modeling," (Sinha, *et al*., 2000), and "[there

is a need for] generalized kinetic models which can be applied to… any particle," (Prakash and Karunanithi, 2008) are common themes in these reviews which at largely attempts to utilize simple existing models such as those reviewed above to predict pyrolysis outcomes from various experiments.

Possibly the most recent of review that exclusively focuses on classical kinetics research, White *et al*., is an extensive dissertation on biomass pyrolysis kinetics and the origins of the kinetic models up to about 2010 (White *et al*., 2011). Like many authors in the field of biomass pyrolysis, White *et al*. point out that the "pernicious persistence of substantial variations…irrespective of the kinetic model employed" poses a serious problem, and one that needs to be addressed soon if biomass pyrolysis is to become a proven technology for the commercialization of biofuels and bioproducts. Standardization of biomass pyrolysis techniques seems like the logical next step; however, standardization is a process not easily accomplished due to the many degrees of freedom involved. Factors ranging from the nature of the raw biomass substrate, to aspects of chemical and thermal processing of the feedstock can alter the kinetic data. White, *et al*. conclude with the following statement, "the chaos in solid state reaction kinetics has spilled over into the biomass pyrolysis community and continuation of the status quo is utterly unacceptable."

In the molecular-context of the present review, the papers by Vinu and Broadbelt (2012), Shen, *et al*. (2015) and Burnham, Zhou and Broadbelt (2015), deserve more discussion. Vinu and Broadbelt's 2012 work on pyrolysis of glucose-based carbohydrates assimilates decades of research on reaction pathways into a detailed kinetic schema with what appears to be 63 individual reactions – 25 Arrhenius-based rate constants along with activation energies and in some cases temperature exponents for modified Arrhenius equations – the constants of which were either obtained from among eight prior works or estimated by modeling fitting. Some constants were obtained using theoretically estimated activation barriers from quantum chemistry calculations. This work is among the first, if not the first to integrate molecularly-based kinetic parameters into a reaction model. The more recent Shen *et al*. (2015) review, while strictly descriptive, assesses the massive body of literature on reaction pathways for cellulose, hemicellulose and lignin. Calling almost exclusively upon experimentally-based literature, Shen *et al*. assemble pathways for whole biomass that include primary cellulose cracking and associated levoglucosan (LVG) production, secondary LVG fragmentation to lighter straight chain oxygenates, and furans, hemicellulose decomposition

via xylan-chain units and for O-acetyl-4-O-methyl-glucurono-xylan side-chain units and cleavage of typical lignin inter-unit linkages, formation pathways for the predominant aromatic products (guaiacol-type compounds) and suggested pathways for thermal transformation of guaiacol-type compounds to phenol-type compounds. Nonetheless, their thesis appears to cite few of the growing number of works that are now utilizing all-atom molecular-scale modeling to unravel the decomposition pathways for lignocellulosic materials. Finally, the very recent work by Burnham, Zhou and Broadbelt (2015) nicely ties classical methods and datasets used to discern global reaction kinetics, starting with the work of Broido and Shafizadeh, to recent molecular modeling efforts. This critical review finds computational molecular support for the concerted formation of a cellulose-based intermediate that decomposes into LVG with an activation energy in the neighborhood of 46 to 50 kcal/mole, confirmed by both experiment and molecular-scale computation.

The review by Amen-Chen, Pakdel and Roy (2001) on lignin pyrolysis focuses mainly on production of phenols, yet reviews the chemical basis units of lignin and thermoanlytical methods including thermogravimetric analysis and evolved gas analysis as they apply to the subject. The authors conclude that the transformation of biomass to phenols involves dehydration of OH groups of alkyl chains in the phenylpropan base unit followed by cleavage of the β-O-4 aryl ether bond and other interaromatic bonds. Focus on the importance and nature of catalysis to obtain desired products is also emphasized.

In a more recent review on lignin thermal degradation, Pandey and Kim, 2011 reviewed 112 paper on lignin research spanning a time frame between 1977 and 2010. This comprehensive review looks at the structure of lignin and its isolation from whole biomass as well as the primary routes to gas, liquids and char. It is clear that lignin is a complex material and that like cellulose, it has been extensively studied and characterized and that there is a broad diversity of processing alternatives through which to extract useful substances from this resource. Among the processing routes reviewed by Pandey and Kim are direct pyrolysis for which the authors review the kinetics, hydrogenolysis, base catalyzed depolymerization, hydrogen-donated solvation, hydrogenation (catalytic), oxidation and oxidative cracking, peroxide-based oxidative cracking, focused oxidative aldehyde production and supercritical depolymerization. While char is the major product from pyrolysis, biofuel, gases and focused chemicals are the primary products from other processing routes.

In addition to these reviews which specifically address chemical kinetics, there are a number of reviews that summarize process focused topics: (Bridgewater and Peaccocke, 2000; Czernick and Bridgewater, 2004; Mohan, Pittman and Steele, 2006; and Venderbosch and Prins, 2010). While these will not be addressed in this context, it seems appropriate to include mention of them in this rather inclusive review of reviews. Collectively, these tend to focus on reactor design and call for the need for more detailed and discrete forms of kinetic information and models.

Unique among reviews in the past 15 years is the paper by Slutter *et al.* (2010) who address the important issue of composition analysis of lignocellulosic feedstock. This paper tracks the lineage of the current sulfuric acid hydrolysis technique used to characterize the lignin and structural carbohydrate content of biomass. Accurate quantification of the composition of biomass will become increasingly important as computational models becomes increasingly distributed. As of 2010, the state-of-the-art was embodied in a series of laboratory analytical procedures (LAPs) developed by National Renewable Energy Laboratory (NREL) researchers.

The use of mass spectroscopy, particularly combined with gas chromatography, has been central in the study of biomass pyrolysis, both for investigation of component pyrolysis and whole biomass. In a unique review, Reale *et al.* (2004) review works associated with the application of mass spectroscopy to study lignin. This review is equally of value – though at this point somewhat dated since 12 years have passed since its publication – for the study of whole biomass, cellulose and hemicellulose depolymerization. The authors conclude that mass spectrometry is a powerful technique in terms of speed, specificity and sensitivity for the elucidation of structure in combination with chemical and thermal degradation methods available. Development of then new ionization technique in mass spectrometry (electrospray ionization and matrix laser desorption ionization) has provided new possibilities for analyzing lignins.

In summary, the vast body of literature on pyrolysis of lignocellulocis matter has been extensively reviewed by at least 20 teams of authors. These span a timeframe from 1982 to 2015 and primarily review experimental finding regarding reaction pathways, classical modeling methodologies based on continuity equations and experimental studies focusing on reaction-path mechanisms. And, while these reviews comprehensively cover these topics, they do not directly address the more recent and emerging body of literature on molecular-scale modeling. What follows appears to be the first such review.

REVIEW OF MOLECULAR-SCALE MODELING FOR STUDY OF BIOMASS PYROLYSIS

Classical kinetics experimentalists have contributed greatly in forming the available knowledge necessary for the pursuit of the multi-disciplinary venture that is biofuels. Yet, more than forty years after the proposed Broido-Shafizadeh model, contention remains among cellulose pyrolysis data within the literature. More recently, however, various nanoprobes such as XRD and NMR and, in particular, the more recent application of molecular-scale modeling, have greatly expanded the research domain. Early experiments using high-resolution ^{13}C NMR (CP-MAS) led to the confirmation of two distinct crystalline forms of native cellulose, I_α and I_β (Atalla and Vanderhart, 1984, VanderHart and Atalla, 1984). Cellulose I_α is predominantly found in the cell wall of some bacteria and algae, while cellulose I_β can be isolated from cotton, wood, and ramie fibers. Studies of this sort led to the reassessment of the crystal structure and the inter/intra-hydrogen bonding patterns of native cellulose (Isogai *et al.*, 1989, Nishiyama *et al.*, 2002, Nishiyama *et al.*, 2003). Fundamental questions regarding the molecular interactions at the micro- and nano-scale motivated the works of Wada *et al.*, wherein oriented thin-films of cellulose I_β and III_I were prepared and investigated using dynamic XRD studies heated from room temperature to 250 °C (Wada, 2002, Wada *et al.*, 2010). Results show that both cellulose polymorphs transition into a high-temperature phase when samples were heated above 200 °C. In addition, thermal expansion calculations for cellulose I_β and III_I demonstrated that anisotropic expansion in the lateral direction is closely related to the intermolecular hydrogen-bonding pattern of the system. This led to characterization and pyrolysis experiments related to cellulose crystallinity. Pyrolysis behavior of microcrystalline cellulose (MCC), and regenerated cellulose prepared from ionic liquids by varying the precipitation method, showed that in addition to having a higher degree of polymerization (DP) and crystallinity, the more crystalline form of cellulose resulted in higher onset, endset, and endothermic peak temperature, and a significantly higher enthalpy (365.4 J/g) than the precipitated cellulose samples. More importantly, the less crystalline cellulose samples showed higher yields of liquid products and favored the removal of oxygen via CO_2 when pyrolyzed in a fluidized bed reactor at 400 °C for one hour at a heating rate of 5 °C/min; gaseous and solid products were about the same for all three cellulose samples (Zhang *et al.*, 2010). These results may offer

evidence in support of the cellulose activation hypothesis, as the main result of this pre-processing is a drastic decrease in the degree of polymerization.

These experiments provided vital chemical and structural information, paving the way for future work, yet a barrier of scales plagues many experiments. The mechanisms, by which a complex substrate such as lignocellulosic biomass pyrolyzes, can only be obtained by considering the events occurring at the molecular scale. Often, pyrolysis products can be observed only in their final state since reaction intermediates are difficult to study experimentally due to their short half-life. Studying pyrolysis reactions is further complicated by the presence of both condensed and gas phase intermediates and the fact that these phases can continue to interact and evolve with time. Therefore, researchers studying biomass pyrolysis are turning to molecular modeling for deeper insights.

Structure of Cellulose

A significant number of papers have recently appeared on the structure of cellulose, a large fraction of these focusing on the crystal structure, stability and consequently intermolecular forces between individual cellulose polymer chains. The plant cell wall is a network of cellulose microfibrils *covered* and interconnected by hemicellulose (Carpita and Gibeaut, 1993). The cellulose microfibrils do not self-associate in whole natural biomass because hemicellulose prevents the interaction (Hayashi *et al.*, 1987, Whitney *et al.*, 1999). However, by cross-linking with the microfibrils, the hemicellulose enables cell wall physical properties such as flexibility (Hayashi *et al.*, 1987, Whitney *et al.*, 1999). The cellulose micrifibrils are composed of a mixture of cellulose I_α and I_β, the single chain triclinic and two chain monoclinic unit cells respectively (Atalla and Vanderhart, 1984). Viëtor *et al.* (2000) established a computational procedure to predict the native crystal structure of cellulose microfibrils through packing and modelling of β-1, 4-glucopyronase chains, wherein the most favorable interchain distance and interactions at various helix-axis translations and mutual rotations were estimated by chain pairing. The MM3 force field was used. Two unit cells were found, a triclinic lattice symmetry (space group P_1) and a monoclinic form (space group $P2_1$) that correspond closely to the observed allomorphs of crystalline native cellulose I_α and I_β. Mathews *et al.* recently tested three united atom force fields (FF) for carbohydrates, CHARMM C35, GLYCAM06, and Gromos45a4 which are frequently used in molecular dynamics (MD) simulations of hydrated, 36-chain cellulose I_β microfibrils at room-temperature (Matthews *et al.*, 2012). Properties estimated using the C35 and GLYCAM were comparable, and these FFs simulated the high-temperature (500 K) behavior of celluloses I better than Gromos45a4, which gave very different results. GLYCAM06 shows sensitivity to the starting structure and electrostatic scaling factors. Overall convergence times were large (>800 ns) for all FFs yet varied by orders of magnitude depending on the properties of interest. Since the starting structure is an important parameter in molecular simulations, Mathews *et al.* pointed out that the bulk structure of cellulose determined using large diameter (10-20 nm) microfibrils from algae and tunicates, may not accurately represent cellulose microfibrils from plants, as the latter can be significantly smaller (2-3.5 nm) (Matthews *et al.*, 2011). Using the three-dimensional coordinates for cellulose I_β published by Nishiyama *et al.*, Mathews and co-workers conducted MD simulations using CHARMM C35 and the GLYCAM06 force fields to study the behavior of native cellulose at high temperatures (up to 500 K) (Whitney *et al.*, 1999, Nishiyama *et al.*, 2002). Significant observations include an "untwisting" due to the formation of a three-dimensional hydrogen bonding network near the center chains of the 36-chain model (DP 40), for which the authors suggest arise from conformational changes of the hydroxymethyl groups. Bergenstråhle *et al.* also studied the influence of temperature on the properties of the cellulose I_β crystal using molecular dynamics simulation with the GROMOS 45a4 force field and found that at room temperature, the crystal structure could be sufficiently reproduced in terms of crystal density, unit cell dimensions and packing, whereas above 450 K, changes in the orientation of the hydroxymethyl group caused a shift in hydrogen bonding patterns and unit cell dimensions(Bergenstråhle *et al.*, 2007).

In search for the "active cellulose" step that some researchers theorize initiates cellulose pyrolysis, Agarwal *et al.* performed molecular dynamics simulations of cellulose I_β. Although the authors do not state conclusively whether their findings corroborate or refute the emergence of an "active cellulose" intermediate they do explain that a three-dimensional hydrogen bond network emerges at high-temperatures (450-550 K) as a result of inter-chain hydrogen bonds; whereas at lower temperatures (300-400 K) the cellulose I_β structure is dominated by stronger intra-chain hydrogen bonds (Shafizadeh, 1982, Lin *et al.*, 2009, Agarwal *et al.*, 2011, Lédé, 2012). These temperature transitions in hydrogen bonding patterns of cellulose

provide a glimpse into the very early stages of pyrolysis, yet a link between reaction mechanism and reaction kinetics is still missing. Mazeau (2005) also studied structural micro-heterogeneties of the native I_β allomorphs of crystalline cellulose using molecular dynamics, starting from the coordinates of cellulose I_β published by Nishiyama *et al*. The native I_β-allomorph of cellulose reveals subtle but significant conformational differences between two different chains and a multiplicity of position of the hydrogen atoms of the HO_2 and HO_6 hydroxyl group (Mazeau, 2005). To check this, molecular dynamic simulations were done using the, Polymer Consistent Force Field (PCFF), a second generation force field, on 16 minicrystal and two macrocrystal models of cellulose which differed by initial orientation of the HO_2 and HO_6 hydroxyl groups. Results showed that only ten of the studied structures were stable and that the individual chain conformations of these retained crystal structures and remained stable at their equilibrium conformation during molecular dynamics simulation. Furthermore, stability was found to be sensitive to the initial position of the hydrogen atoms. Analysis of the hydrogen bonds reeal that in addition to inter-molecular hydrogen bonds, several inter-sheet (intra-molecular) hydrogen bonds were also present. These molecular modeling results suggest geometrical variability in the I_β allomorph of crystalline cellulose, corresponding to stable structural micro-heterogeneities.

Matthews, *et al*. 2005 considered the behavior of a small model crystal of $I\beta$ cellulose in water. Their work suggests that water becomes highly structures, forming at least a triple-layer around small cellulose microcrystals and may play a role in the observed slow hydrolysis of cellulose. While mainly of interest to the enzymatic hydrolysis community, the model structures and MD construct is of great value to researchers seeking to study cellulose pyrolysis as well. Following the work of Matthews *et al*. (2005), Yui, *et al*. (2006) also considered the MD simulation of $I\beta$ cellulose, in their case exposing model crystals to water and then heating the crystal model to 550 K. This work suggests various *phase* transformations at relatively low temperatures, at least for small crystals pretreated with water that support the activated cellulose concept. More recently, Zhang, *et al*., 2011 confirmed a phase transition between 475 and 500 K for $I\beta$ cellulose using MD simulation. In this case, however, a periodic crystal was used without water pre-treatment and the results are of direct importance for pyrolysis and tend to offer molecular-level support for the previously hypothesized and experimentally indicated transitions.

Similarly, Eichhorn, Young and Davies (2005 and 2006), considered the micromechanical analysis of cellulose fibers. This work establishes a basis for considering mechanically induced defects that may be of great importance in the interpretation of milled cellulose and milled whole biomass pyrolysis. Using Py/GC-MS, Murillo, Ware and Biernacki (2014) found systematic effects of milling on the composition of pyrolysis products from alfalfa and tall fescue.

Understanding and characterizing structure of biomass and its dynamics on a range of length and time scales is important for the development of cellulosic biofuels, both thermally and enzymatically generated. Recently, extensive synchrotron X-ray and neutron diffraction measurements on I_α and I_β cellulose and molecular simulation have provided detailed crystal and molecular structure information by revealing the hydrogen bonding network within each phase (Nishiyama *et al*., 2002, Nishiyama *et al*., 2003, Gross and Chu, 2010). To *stretch* the length and time scale vista for biomass, a slightly different approach was taken by Shen and Gnanakaran (2009) who used coarse-grained models to simulate a two-chain and a multiple-chain cellulose systems. They found that hydrogen bond networks vary with rising temperatures until the time of decomposition. Observations from the two-chain model suggests that different hydrogen bonding states dominate at different temperatures. Their method provides an accurate and constant-free approach to derive coarse-grain models for cellulose with a wide range of crystallinity, suitable for incorporation into large-scale models of lignocellulosic biomass. According to Srinivas *et al*. (2011), for the production of biofuels from lignocellulosic biomass, there is one obstruction, the efficient degradation of crystalline microfibrils of cellulose to glucose. To understand how different physical conditions affect the overall stability of the crystalline structure of microfibrils could facilitate the design of more effective protocols for the degradation of cellulose to glucose. One of the essential physical interactions that stabilize microfibrils is the network of hydrogen (H) bonds (Srinivas *et al*., 2011). Having recognized this, Srinivas *et al*. generated a coarse-grained strategy wherein they introduce a way to model cellulose fibrils with varying degrees of crystallinity, thereby enabling molecular dynamics simulations of cellulose with crystalline and amorphous characteristics (Srinivas *et al*., 2011). Their findings suggest that extensive inter- and intra-chain hydrogen bonds, as well as inter-sheet van der Waals interactions are suspected to be responsible for the recalcitrance of crystalline cellulose to enzymatic and chemical reactions (Gross and Chu, 2010, Beckham *et al*., 2011, Kim *et al*., 2011).

Both the chemical and physical (mechanical) properties of cellulosic materials are strongly dependent on the ratio of the crystalline and amorphous cellulose phases. This motivated Mazeau and Heux (2003) who performed molecular dynamics using the second generation force field PCFF (an augmented version of the ab initio consistent force field (CFF91)) on three cellulosic systems, the two native crystalline phase I_α and I_β and an amorphous phase, to study how crystalline and amorphous cellulose differs. The low value of the stress tensor components (an indication of approach to a local potential energy minimum and thus an equilibrium state) and bulk parameter results, such as unit cell dimensions, densities, Hildebrand solubility parameters, and hydrogen bonding for all three cellulosic systems, compared well with the corresponding experimental measures and the modelled microstructures were found to be mechanically stable. These results suggest that there are reasonable methods and strategies for modeling the amorphous phase of cellulose and that the conformational behavior of the amorphous state is very different than that of the crystalline cellulose phases (I_α and I_β). The amorphous phase model was also used by Mazeau and Heux (2003) to estimate the glass transition temperature of cellulose. In addition to the glass transition temperature, density and conformational behavior, the model amorphous cellulose could also be used to investigate other unknown properties including, permeation rates, surface interactions, etc.

Finally, Wohler and Berglund (2011) offer a cellulose structural model that may be a valuable starting-point for pyrolysis researchers since it is optimized to provide good interactions between the crystalline cellulose and surrounding molecules.

Cellulose Pyrolysis

More recent works have looked at transformations involving bond breaking and making in an effort to glean insights into pyrolysis reaction mechanisms. Agarwal *et al*. used Car-Parinello metadynamics simulations (CPMD) to uncover mechanisms that lead to precursors of levoglucosan, the main product of cellulose fast pyrolysis, and to minor compounds such as 5-hydroxy-methylfurfural (5HMF) and formic acid (Agarwal *et al*., 2012). At high-temperatures (873 K) Agarwal *et al*. observe the formation of pre-LVG compounds through a transition state stabilized by anchimeric effects and hydrogen bonding with a free-energy barrier of 36 kcal/mol. In addition, Agarwal and co-workers conclude that pre-LVG compounds are kinetically-favored over precursors of 5HMF and formic acid for the fast pyrolysis of cellulose when simulated at 873 K. Using isotopically-labeled levoglucosan and fructose, Mettler *et al*. illustrates how levoglucosan interacts with an intermediate liquid product during co-pyrolysis to form furans and oxygenates (higher energy products) through elimination and cyclization reactions (Mettler *et al*., 2012).

Mettler *et al*. also introduced a combined experimental-computational strategy using a thin-film experimental pyrolysis approach and molecular-scale modeling (Mettler *et al*., 2012). They suggest that their new thin film technique addresses common obstacles associated with biomass pyrolysis experiments such as slow heat transfer in isothermal conditions and the dependence of product yield on residence time of volatiles within the intermediate liquid phase. A comparison of products derived from cellulose and and various small oligomeric saccharides led the authors to suggest α-cyclodextrin (ACD) as a small molecule surrogate for cellulose. Using ACD rather than cellulose, Metler *et al*. performed *ab-initio* Car-Parinello molecular dynamics (CPMD) simulations and proposed that ACD decomposes through simultaneous reactions involving homolytic cleavage of glycosidic and pyran ring bonds; and so imply by virtue of experimental similarities that cellulose decomposes in the same manner as ACD, contrary to the hypotheses of heterolytic bond scissions as suggested by previous researchers (Shafizadeh, 1973, Varhegyi *et al*., 1988). In a more recent study, however, Murillo, *et al*. show that the reaction rate of the isomeric oligomeric saccharides maltose and cellobioe are not identical and that the α-bonded maltose thermal decomposition is initiated at a considerably lower temperature of 200 ºC, as compared to 225 ºC for cellobiose (Murillo *et al*., 2015). There results were supported by MD and DFT calculations which found that the higher stability of the cellobiose might be attributed to a greater degree of intra-molecular hydrogen bonding. These results suggest that the α-bonded oligomeric saccharide, ACD, may not be a suitable small molecule surrogate from which to predict absolute reaction rates or to infer reaction mechanisms.

Using quantum mechanics and density functional theory, Mayes and Broadbelt, 2012, proposed a lower energy pathway mechanism for glycosidic bond cleavage and levoglucosan formation than ionic or radical mechanisms. The simulations for glycosidic bond cleavage and levoglucosan formation were carried out using a polarized continuum model (PCM) for implicit tetrahydrofuran (THF) or water as solvents in an effort to accurately capture electrostatic effects at pyrolysis conditions so that ionic species could be properly stabilized. Their results suggest a mechanism with a 25 kcal/mol lower energy pathway for cellulose

glycosidic cleavage with a rate coefficient four orders of magnitude higher than for ionic cleavage. This mechanism for glycosidic bond dissociation and levoglucosan formation provides a basis for studying catalytic interventions in cellulose pyrolysis and is more in-line with experimental observations.

Mayes, *et al*. 2014 studied the effect of sodium ions on α-D-glucose and β-D-glucose thermal decomposition using density functional theory and verified the computational results with experimental outcomes for pyrolysis of α- and β-D-glucose with NaCl. Their results show that the presence of sodium ions changes the reaction rate coefficients for various pathways by different factors, with approximately 70% being catalyzed by Na^+ and 25% inhibited by Na^+ and others having no effects. This result provides an understanding of how inorganic salts effect the reaction network and act as a catalyst or in some cases an inhibitor in biomass pyrolysis.

Seshadri and Westmoreland, 2012 provide an extensive list of kinetic parameters for concerted reaction path of β-D-glucose, estimated using gas-pase quantum-chemistry and statistical-mechanics. Structure-identification and energy calculation were done using Gaussian 09 and thermodynamic properties estimated using the atomization method at a CBS-QB3 level of theory. Transition states were obtained and Arrhenius rate parameters estimated for a wide range of reactions between 300 and 1000 K. Parameters for isomerization of cyclic glucose products, reaction involving acyclic hexoses, formation of furanoses, and unimolecular and bimolecular rate reactions for the formation of levoglucosans and anhydrous-β-D-glucofuranos from β-D-Glucose and β-D-glucofuranose. This work clearly demonstrates a strategy for generation of such rate constants and enables development of highly distributed reaction schema for pyrolysis. While limited to the reaction pathways associated with β-D-glucose, such can be used along with either experimental or other computationally determined pathways for chain fragmentation to establish more comprehensive pathway models. In a very comprehensive work, Zhou *et al*. (2014a,2014b) (and more recently in Zhou *et al*., 2016a, 2016b, similarly) integrate the Seshadri dataset into a reaction pathway model involving 342 reactions and 103 molecular species.

Lignin Pyrolysis

Molecular modeling involving hemicellulose and lignin is less developed, and more difficult to find. An advantage of the extensive studies with cellulose is that the techniques being perfected for studying cellulose at the molecular and atomic level should be translatable to better understand thermal decomposition of hemicellulose and lignin polymers. What follows is a review of works related to lignin molecular modeling.

Besombes *et al*. (2003) studied the computational conformational properties of model β-O-4 lignin compounds using molecular modeling and compared the results with experimental data of X-Ray crystal structures and $^3J_{H\alpha H\beta}$ NMR coupling constant values of lignin. Their results provide an improved understanding of conformational forms of the β-O-4 dimer. Since their results show reasonable consistency between computational and experimental results, the CHARMM force field which they used for molecular dynamics simulations was validated for the study of β-O-4 lignin structures. Petridis and Smith, 2008 followed the work of Besombes, by further parameterizing a CHARMM molecular mechanics force field for lignin model compounds, anisole, supermolecular geometries (d_o, d_{120}) and *p*-hydroxyphenyl and validated it using a crystalline lignin dimer fragment.

Due to the difficulties related with experimental isolation of lignin, Elder (2007) calculated a Young's modulus for model β-O-4 lignin using quantum chemical calculations by subjecting a dimer compound to strain, coupled with determination of energy and stress. The computational results were compared with the experimental literature which shows that the computational Young's modules value agrees with experimental values. Furthermore, Elder predicted that at large strains, hemolytic bond scission may occur. Such may help explain variations observed in milled samples of whole biomass, refer to Murillo *et al*. (2014).

Beste and Buchanan (2009) studied the computational bond dissociation enthalpies of lignin by density functional theory using phenethyl phenyl ether (PPM) as the dominating β-O-4 ether linkage. The results shows that due to the oxygen substituents at the phenyl ring, the bond dissociation energy of the oxygen-carbon bond in PPM is 7.6 kcal lower than the carbon-carbon bond dissociation energy. Also, carbon-carbon bond dissociation shows little variation for addition of oxygen substituents at the phenyl ring. Elder (2010) subsequently studied the enthalpies of reaction in the pyrolysis of lignin (β-O-4 dilignols) using G3MP2 and CBS-4m levels of theory and compared the result with Beste and Buchman (2009). They show that bond dissociation enthalpy values were consistent with Beste and Buchman (2009) but resulted in lowered chemical kinetic selectivity resulting in more uniform product distributions. Parthasarathi *et al*. (2011) also studied the bond dissociation enthalpies in lignin, encompassing 65 lignin model compounds using density functional theory. The results

order the most prevalent carbon-oxygen and carbon-carbon bond linkages from weakest to strongest for the 65 model lignin compounds. Kim and co-workers took a further step forward in this direction by quantifying relative bond dissociation energies among common lignin bonds and the effect of native and oxidized substituents on the functional groups in lignin. The compiled data is vast, and should provide insight into lignin degradation and aid in the identification of catalytic cleavages. In a recent study, Sangha *et al*. use density functional theory to characterize radical coupling reactions in lignin synthesis using monolignol radicals. The enthalpies of 8-0-4, 8-8, 8-5 and p-coumaryl self- and cross-coupling reactions of lignin were found to be the most favorable, whereas 5-O-4, 5-5, and 8-1 linkages of lignin were less favorable. Sangha *et al*, have also reviewed the recent, relevant scientific literature on computational techniques useful for characterization of structural and energetic properties of biomass components and give their perspective on the role of molecular dynamics simulation in understanding lignin.

Finally, Liu and Zhang (2014) proposed five pyrolytic pathways for guaiacol pyrolysis based on their methoxyl group reactivity and studied their reactivity using by Gaussian 03 and density functional theory at B3LYP/6-31G++(d,p) level. From the standard thermodynamics and kinetic parameters at different temperatures, their five reaction pathways were ranked in descending order of reactivity. They concluded that coupling of a hydrogen radical to the carbon atom in the benzene rung at the methoxy group on guaiacol is effective at reducing the guaiacol demthoxylation energy barrier and that methoxy groups may be necessary to form o-quinonemethide, a known intermediate. Findings are consistent with some prior experimental studies.

Mixed Systems and Whole Biomass

Early molecular modeling on the thermal stability of carbohydrates and lignin are scarce, and those related directly to the pyrolysis of lignocellulosic organic matter are virtually non-existent in the literature before the early 1990s (Elder, 1989, Vorwerg, 1990, Hardy and Sarko, 1993). However, the proliferation of, and advancements in software and computer technology, has equipped computational scientists with the tools to probe phenomena at length- and time-scales previously unattainable with experimentation alone. For instance, Houtman and Atalla (1995) searched for evidence of an associative interaction between polysaccharides and lignin oligomers that influences the course of lignin polymerization. Through molecular

dynamic simulations the authors found that the lignin precursors and oligomers can adsorb onto the surface of cellulose microfibrils, likely influencing the ability of the phenylpropanoid (C_9) precursors to participate in random polymerization reactions. Interactions of the polysaccharide-lignin network were experimentally observed in a study conducted by Wang *et al*. wherein the thermal decomposition of mixed biomass components (e.g. purified cellulose mixed with hemicellulose) showed that lignin-cellulose interactions enhanced the formation of levoglucosan; hemicellulose-lignin interactions have a positive influence on lignin-derived phenols, while lowering the formation of hydrocarbons; though, the interaction of cellulose and hemicellulose still remains ambiguous (Wang *et al*., 2011). Zhang *et al*. (2011) explored the molecular interactions of cellulose, hemicellulose, and lignin by examining the hydrogen-bond network of cellulose-hemicellulose, and the covalent-bonds between hemicellulose-lignin in woody biomass. Glucose and xylose monomers and dimers were used as model compounds for cellulose (amorphous) and xylan, respectively; in addition, α-linked monomers of D-mannose and D-glucose were used to simulate softwood hemicellulose. The monolignol guaiacyl (a G unit) and two β-O-4' linked G units are used to model the lignin polymer. Three levels of theory, semi-empirical AM1, Hartree-Fock, and density functional (DFT), were used to calculate bond lengths and angles revealing that the B3LYP method coupled with the 6-31G basis set is suitable for modeling hydrogen bonding in woody biomass, and the B3LYP method coupled with the 6-31G(d,p) basis set works well for simulating covalent bonds. Zhang *et al*. (2011) further noted that the model compound choice has a much larger effect on the hydrogen-bonding interaction between cellulose and hemicellulose than model compound choice on the hemicellulose-lignin interaction. It is difficult to capture the complete biomass matrix in a model, where many assumptions are made to simplify otherwise computationally expensive calculations. For this reason, much of the recent computational work in biomass pyrolysis has focused on understanding structural changes occurring at high-temperatures for model compounds, or for individual biomass components, most commonly cellulose.

Moving towards whole biomass MD structures, a series of recent works have explored the interaction of cellulose and other components including water, lignin and xylan chains. Mazeau and Rivet (2008) looked at wetting of water on cellulose while Khazraji and Robert (2013) explored the interaction between water and cellobiose chains of different lengths offering insights into the hydrated nature of cellulose.

Since plant matter is hydrated in its native state, such modeling insights are relevant, even to pyrolysis research, since the dehydrated states likely reflect the hydrated starting-points. Along the pathway to whole biomass MD models, Besombes, and Mazeau (2005) investigated the assembly of guaiacyl dimer (lignin component) onto Iβ cellulose, and Linder *et al.* (2003), Mazeau *et al.* (2005), Hanu and Mazeau (2006), Zhang, Agren and Tu (2011), and Mazeau and Carlier (2012) looked at adsorption of various hemicellulocic chains (xylans) on cellulose. Finally, Charlier and Mazeau (2012) present an entire MD cell wall structure model, see Figure 1, for a recreation of a whole cell wall based on molecular structures provided by Charlier and Mazeau (2012).

This pathway is critical to the study of pyrolysis since it paved the way for yet to be done studies on whole plant matter. Since the interactions between cellulose, hemicellulose and lignin has been demonstrated to be important to pyrolysis outcomes, it is likewise important to establish good whole biomass MD structures if MD is to continue to contribute to the discovery of the underlying mechanisms of whole biomass thermal degradation.

DISCUSSION AND CONCLUDING REMARKS

A huge body of literature spanning at least six decades exists on the pyrolysis of whole plant biomass and its component fractions, cellulose, hemicellulose and lignin. Nevertheless, there are still many unknowns and points of contention when it comes to the mechanistic details of the hundreds of reactions that occur when virgin biomass is pyrolyzed. Multi-step reaction mechanisms, such as the Broido-Shafizadeh and Diebold pathway, have been shown to work with a variety of kinetic models and reactor types, albeit with slight modifications and fast pyrolysis of model compounds (e.g. cellulose) has provided an understanding of the range of possible chemical and physical phenomena under a range of reaction conditions. However, to decipher the micro- and molecular-scale details of biomass decomposition molecular modeling has a unique contribution that is just now beginning to emerge with an increasing number of papers beginning to appear.

Early modeling efforts, for the most part, established baseline theory and methodologies for small organic-molecule computational-chemistry that would be later (more recently) extended to cellulose-like and finally cellulose and cellulosic networks (Elder, 1989, Vorwerg, 1992, Hardy and Sarko, 1993, Houtman and Atalla, 1995). Findings from early simulations with carbohydrates and other plant model compounds are still valid and insightful, and offer opportunities to improve molecular simulations by building upon what has been done with advanced technology and data processing methods.

Molecular-scale modeling has also made it possible to study the interaction between cellulose microfibrils, i.e. inter-sheet hydrogen bonds (Mazeau, 2005, Lin *et al.*, 2009, Agarwal *et al.*, 2011, Agarwal *et al.*, 2012). As opposed to intra- and inter-chain hydrogen
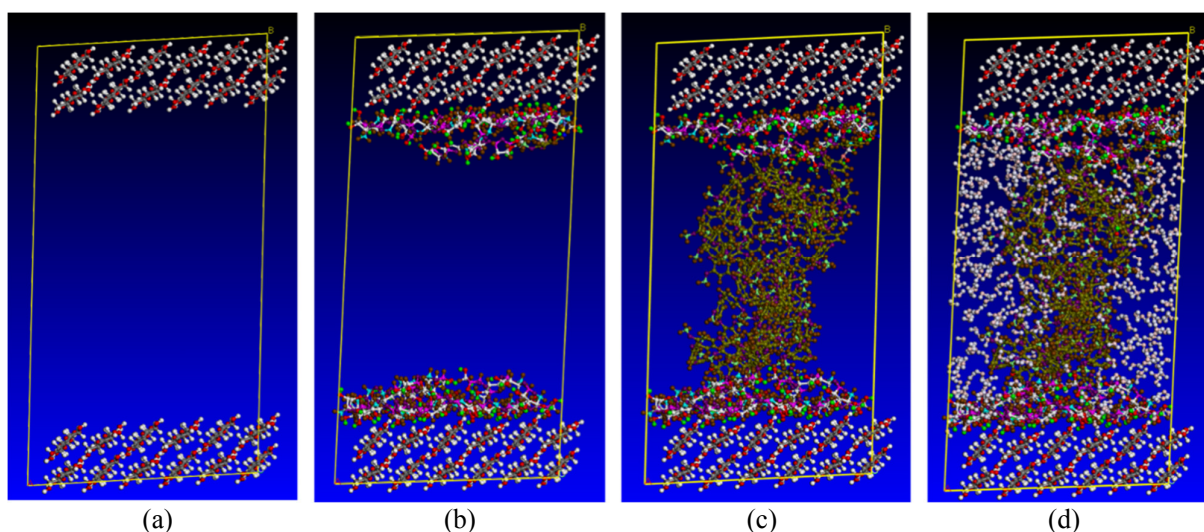

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| (a) | (b) | (c) | (d) |

Figure 1: Steps in the construction of the whole biomass (cell wall) molecular model: (a) cellulose chain layers; (b) cellulose/hemicellulose-ferulate complex; (c) cellulose/hemicellulose-ferulate/lignin, the lignin was modeled as 50 guaiacyl units with β-O-4 linkages; and (d) hydrated whole lignocellulosic biomass model. Structure recreated using coordinates given by Clarlier and Mazaue (2012).

bonds, inter-sheet hydrogen bonds were found to provide the crystalline structure with structural integrity and to be the origin of cellulose recalcitrance in solution and at high-temperatures as validated by simulations. Obtaining the most representative initial structure and configuration for the model under study is of paramount importance in molecular simulations, thus the recent discovery of the most accurate structure of cellulose Iα and Iβ, to date, by Nishiyama *et al*. (2002, 2003) has provided the foundation for reliable and relevant molecular modeling.

Within the context of biomass fast pyrolysis kinetics, molecular modeling has made strides in identifying feasible pathways from cellulose and lignin to viable products, while identifying transition states and reaction intermediates; though hemicellulose, due to its highly amorphous, variable and ambiguous structure has not been modeled as extensively. Among the most pressing needs and hopeful outcomes of theoretical molecular-scale modeling are the prediction of kinetic parameters for elementary reactions and the scaling of the same for use at relevant length-scales and the design and optimization of biomass pyrolysis reactors (Seshadri and Westmoreland, 2012; Zhou, *et al*., 2014a and 2014b; Shen, *et al*, 2015; and Zhou, *et al*., 2016a and 2016b). Finally, not covered hear to any extent, however, is the exploration of catalysts, especially for identifying new pathways to enhance selectivity among pyrolysis products; such would clearly enable and expand commercial opportunities for biomass pyrolysis.

Researchers at the National Renewable Energy Laboratory (NREL) are propelling molecular modeling capabilities forward with unprecedented computing power. They have recently revamped the code and algorithm in the CHARMM simulation program and combined it to run on a single peta-scale high-performance computer at NREL's Energy Systems Integration Facility (Scanlon, 2013). Although much of the application of this technology is focused on biochemical conversion of cellulosic biomass, the fact remains that NREL scientists have made it possible to perform MD simulations of thousands of nanoseconds in a matter of days – a calculation that would have previously taken several months.

Technological innovations across various disciplines and length scales will clearly be required to make bioenergy and bio-products as cost-competitive and efficient as the firmly established fossil fuel and petrochemical commodities. Clear explanations regarding pyrolysis chemistry, reaction mechanisms, kinetics, catalysis, reactor design and characterization are still being sought to make the much needed technological advancements in biomass pyrolysis.

Fundamental research at the molecular-scale will contribute at the longer length-scales associated with the much needed engineering advancements currently being sought globally for the expanding biofuels industry and development of associated technology for direct thermochemical conversion of biomass-to-liquid fuels (BTL) and chemicals. Molecular modeling opens up several new research paths to understand the biomass and polymer decomposition by peering into phenomena that would otherwise be unknown or inaccessible with experimentation alone.

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REFERENCES

Agarwal, V., Dauenhauer, P. J., Huber, G. W. and Auerbach, S. M., Ab initio dynamics of cellulose pyrolysis: Nascent decomposition pathways at 327 and 600 ºC. J. Am. Chem. Soc., 134, 14958-14972 (2012).

Agarwal, V., Huber, G. W., Conner Jr. W. C. and Auerbach, S. M., Simulating infrared spectra and hydrogen bonding in cellulose Iβ at elevated temperatures. J. of Chem. Phys., 135, 134506 (2011).

Amen-Chen, C., Pakdel, H. and Christian, R., Production of monomeric phenols by thermochemical conversion of biomass: A review. Bioresource Technology, 79, 277-299 (2001).

Antal Jr, M. J., Friedman, H. and Rogers, F., Kinetics of cellulose pyrolysis in nitrogen and steam. Combust. Sci. Technol., 21, 141-152 (1980).

Antal Jr, M. J., Biomass Pyrolysis: A Review of the Literature. Part II. Lignocellulosic Pyrolysis. In: Advance in Solar Energy, Boer, K. W., Duffie, J. A., Eds., American Solar Energy Society, Boulder, CO (1982).

Antal Jr, M. J., Biomass Pyrolysis: A Review of the Literature Part 1 – Carbohydrate Pyrolysis. Adv. in Solar Energ., Springer, 61-111 (1985a).

Antal Jr, M. J., Biomass Pyrolysis: A Review of the Literature Part 2 – Lignocellulose Pyrolysis. Adv. in Solar Energ., Springer, 175-255 (1985b).

Antal Jr, M. J. and Varhegyi, G., Cellulose pyrolysis kinetics: The current state of knowledge. Ind. Eng. Chem. Res., 34, 703-717 (1995).

Argyropolous, P., National renewable fuel standard program. U.S. Energy Information Administration,

Washington (2010).

Atalla, R. H. and Vanderhart, D. L., Native cellulose: A composite of two distinct crystalline forms. Sciences, 223, 283-285 (1984).

Authier, O., Ferrer, M., Mauviel, G., Khalfi, A.-E. and Lédé, J., Wood fast pyrolysis: Comparison of lagrangian and eulerian modeling approaches with experimental measurements. Ind. Eng. Chem. Res., 48, 4796-4809 (2009).

Babu, B. and Chaurasia, A., Pyrolysis of biomass: Improved models for simultaneous kinetics and transport of heat, mass and momentum. Energy Convers. Manage., 45, 1297-1327 (2004).

Bahng, M.-K., Mukarakate, C., Robichaud, D. J. and Nimlos, M. R., Current technologies for analysis of biomass thermochemical processing: A review. Anal. Chim. Acta, 651, 117-138 (2009).

Barneto, A. G., Vila, C., Ariza, J. and Vidal, T., Thermogravimetric measurement of amorphous cellulose content in flax fibre and flax pulp. Cellulose, 18, 17-31 (2011).

Beckham, G. T., Matthews, J. F., Peters, B., Bomble, Y. J., Himmel, M. E. and Crowley, M. F., Molecular-level origins of biomass recalcitrance: Decrystallization free energies for four common cellulose polymorphs. J. Phys. Chem., B, 115, 4118-4127 (2011).

Bergenstråhle, M., Berglund, L. A. and Mazeau, K., Thermal response in crystalline Iβ cellulose: A molecular dynamics study. J. Phys. Chem., B, 111, 9138-9145 (2007).

Besombes, S. Robert, D., Utille, J-P., Taravel F. R. and Mazrau, K., Molecular modeling of syringyl and p-hydroxyphenyl β-O-4 dimers. Comparative study of the computed and experimental conformational properties of lignin β-O-4 model compounds. J. Agric. Food Chem., 51, 34-42 (2003).

Besombes, S. and Mazeau, K., The cellulose/lignin assembly assessed by molecular modeling, Part 1: adsorption of a threo guaiacyl β -O-4 dimer onto a Iβ cellulose wisker. Plant Physiology and Biochemistry, 43, 299-308 (2005).

Beste, A. and Buchanan III, A. C., Computational study of bond dissociation enthalpies for lignin model compounds. Substituent effects in phenethyl phenyl ethers. J. Org. Chem., 74, 2837-2841 (2009).

Boutin, O., Ferrer, M. and Lédé, J., Flash pyrolysis of cellulose pellets submitted to a concentrated radiation: Experiments and modelling. Chem. Eng. Sci., 57, 15-25 (2002).

Bradbury, A. G. W., Sakai. Y. and Shafizadeh, F., A kinetic model for pyrolysis of cellulose. J. Appl. Polym. Sci., 23, 3271-3280 (1979).

Branca, C., Albano, A. and Di Blasi, C., Critical evaluation of global mechanisms of wood devolatilization. Thermochim. Acta, 429, 133-141 (2005).

Bridgwater, A. V., Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy, 38, 68-94 (2012).

Bridgewater, A. V. and Peaccocke, G. V. C., Fast pyrolysis processes for biomass. Renew. Sust. Energ. Rev., 4, 1-73 (2000).

Broido, A. and Nelson, M. A., Char yield on pyrolysis of cellulose. Combust. Flame, 24, 263-268 (1975).

Broido, A., Kinetics of Solid-Phase Cellulose Pyrolysis. Thermal Uses and Properties of Carbohydrates and Lignins; Eds., Shafizadeh, F., Sarkanen, K. V., Tillman, D. A., Academic Press, New York, pp 19-35 (1975).

Brown, A. L., Dayton, D. C. and Daily, J. W., A study of cellulose pyrolysis chemistry and global kinetics at high heating rates. Energy & Fuels, 15, 1286-1294 (2001).

Brown, A. L., Dayton, D. C., Nimlos, M. R. and Daily, J. W., Design and characterization of an entrained flow reactor for the study of biomass pyrolysis chemistry at high heating rates. Energy & Fuels, 15, 1276-1285 (2001).

Burnham, A. K., Zhou, X. and Broadbelt, L. J., Critical review of the global chemical kinetics of cellulose thermal decomposition. Energy Fuel, 29, 2906-2918 (2015).

Calonaci, M., Grana, R., Barker Hemings, E., Bozzano, G., Dente, M. and Ranzi, E., Comprehensive kinetic modeling study of bio-oil formation from fast pyrolysis of biomass. Energy & Fuels, 24, 5727-5734 (2010).

Carpita, N. C. and Gibeaut, D. M., Structural models of primary cell walls in flowering plants: Consistency of molecular structure with the physical properties of the walls during growth. The Plant J., 3, 1-30 (1993).

Charlier, L. and Mazeau, K., Molecular modeling of the structural and dynamical properties of secondary plant cell walls: Influence of lignin chemistry. J. Phys. Chem., B, 116, 4163-4174 (2012).

Chaurasia, A. and Kulkarni, B., Most sensitive parameters in pyrolysis of shrinking biomass particle. Energy Convers. Manage., 48, 836-849 (2007).

Czernik, S. and Bridgewater, A. V., Overview of application of biomass fast pyrolysis oil, Energ. Fuel, 18, 590-598 (2004).

Demirbas, M. F. and Balat, M., Biomass pyrolysis for liquid fuels and chemicals: A review. J. Sci. Ind. Res., 66, 797-804 (2007).

Di Blasi, C., Numerical simulation of cellulose pyrolysis. Biomass Bioenergy, 7, 87-98 (1994).

Di Blasi, C., Kinetic and heat transfer control in the slow and flash pyrolysis of solids. Ind. Eng. Chem. Res., 35, 37-46 (1996).

Elder, T., Application of computational methods to the chemistry of lignin. Lignin, properties and materials. American Chem. Soc., Washington, D.C. 262-271 (1989).

Elder, T., Quantum chemical determination of Young's modulus of lignin. Calculations on a β-O-4 model compound. Biomacromolecules, 8, 3619-3627 (2007).

Elder, T., A computational study of pyrolysis reaction of lignin model compounds. Holzforschung, 64, 435-440 (2010).

Fang, P. and McGinnis, G., Flash Pyrolysis of Holo-cellulose from Loblolly Pine Bark. In: Thermal Uses and Properties of Carbohydrates and Lignins. Elsevier, New York, 37-47 (1976).

Fisher, T., Hajaligol, M., Waymack, B. and Kellogg, D., Pyrolysis behavior and kinetics of biomass derived materials. J. Anal. Appl. Pyrolysis, 62, 331-349 (2002).

Flynn, J. H. and Wall, L. A., General treatment of the thermogravimetry of polymers. J. Res. Nat. Bur. Stand., 70, 487-523 (1966).

Freeman, E. S. and Carroll, B., The application of thermoanalytical techniques to reaction kinetics: The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. J. Phys. Chem., 62, 394-397 (1958).

Glasser, W. G., Lignin. Fundamentals of Thermochemical Biomass Conversion. Elsevier, New York, 61-76 (1985).

Gomez, C. J., Manya, J. J., Velo, E. and Puigjaner, L., Further applications of a revisited summative model for kinetics of biomass pyrolysis. Ind. Eng. Chem. Res., 43, 901-906 (2004).

Grønli, M., Antal Jr, M. J. and Várhegyi, G., A round-robin study of cellulose pyrolysis kinetics by thermogravimetry. Ind. Eng. Chem. Res., 38, 2238-2244 (1999).

Gross, A. S. and Chu, J.-W., On the molecular origins of biomass recalcitrance: The interaction network and solvation structures of cellulose microfibrils. J. Phys. Chem., B, 114, 13333-13341 (2010).

Hanus, J. and Mazeau, K., The xyloglucan-cellulose assembly at the atomic scale. Biopolymers, 82(1), 59-73 (2006).

Hardy, B. and Sarko, A., Molecular dynamics simulation of cellobiose in water. J. Comput. Chem., 14, 848-857 (1993).

Hayashi, T., Marsden, M. P. and Delmer, D. P., Pea xyloglucan and cellulose VI. Xyloglucan-cellulose interactions in vitro and in vivo. Plant Physiol., 83, 384-389 (1987).

Hileman, F. D., Wojcik, L. H., Futrell, J. H. and Einhorn I. N., Comparison of the Thermal Degradation of α-Cellulose and Douglas Fir Under Inert and Oxidative Environments. In: Thermal Uses and Properties of Carbohydrates and Lignins. Elsevier, New York, 49-71 (1976).

Hoekstra, E., Hogendoorn, K. J., Wang, X., Westerhof, R. J., Kersten, S. R., van Swaaij, W. P. and Groeneveld, M. J., Fast pyrolysis of biomass in a fluidized bed reactor: In situ filtering of the vapors. Ind. & Eng. Chem. Res., 48, 4744-4756 (2009).

Houtman, C. J. and Atalla, R. H., Cellulose-lignin interactions (a computational study). Plant Physiol., 107, 977-984 (1995).

Hu, S., Jess, A. and Xu, M., Kinetic study of chinese biomass slow pyrolysis: Comparison of different kinetic models. Fuel, 86, 2778-2788 (2007).

International Energy Agency (IEA) Bioenergy, Task 34 pyrolysis: Annual report. http://www.pyne.co.uk/?id=69 (2011).

Isogai, A., Usuda, M., Kato, T., Uryu, T. and Atalla, R. H., Solid-state CP/MAS carbon-13 NMR study of cellulose polymorphs. Macromolecules, 22, 3168-3172 (1989).

Kersten, S. R., Wang, X., Prins, W. and van Swaaij, W. P., Biomass pyrolysis in a fluidized bed reactor. Part 1: Literature review and model simulations. Ind. Eng. Chem. Res., 44, 8773-8785 (2005).

Kim, S., Chmely, S. C., Nimlos, M. R., Bomble, Y. J., Foust, T. D., Paton, R. S. and Beckham, G. T., Computational study of bond dissociation enthalpies for a large range of native and modified lignins. J. Phys. Chem., 2, 2846-2852 (2011).

Kissinger, H. E., Reaction kinetics in differential thermal analysis. Anal. Chem., 29, 1702-1706 (1957).

Koufopanos, C., Lucchesi, A. and Maschio, G., Kinetic modelling of the pyrolysis of biomass and biomass components. Can. J. Chem. Eng., 67, 75-84 (1989).

Koufopanos, C., Papayannakos, N., Maschio, G. and Lucchesi, A., Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal and heat transfer effects. Can. J. Chem. Eng., 69, 907-915 (1991).

Khazraji, A. C. and Robert, S., Self-assembly and intermolecular forces when cellulose and water interact using molecular modeling. Journal of Nanomaterials, 2013, 1-12 (2013).

Lédé, J., Blanchard, F. and Boutin, O., Radiant flash pyrolysis of cellulose pellets: Products and mechanisms involved in transient and steady state conditions. Fuel, 81, 1269-1279 (2002).

Lédé, J., Cellulose pyrolysis kinetics: An historical review on the existence and role of intermediate active cellulose. J. Anal. Appl. Pyrolysis, 94, 17-32 (2012).

Lee, S.-B. and Fasina, O., TG-FTIR analysis of switchgrass pyrolysis. J. Anal. Appl. Pyrolysis, 86, 39-43 (2009).

Lin, Y.-C., Cho, J., Tompsett, G. A., Westmoreland, P. R. and Huber, G. W., Kinetics and mechanism of cellulose pyrolysis. J. Phys. Chem., C, 113, 20097-20107 (2009).

Lv, P., Chang, J., Wang, T., Wu, C. and Tsubaki, N., A kinetic study on biomass fast catalytic pyrolysis. Energy & Fuels, 18, 1865-1869 (2004).

Linder, A., Bergman, R., Bodin, A. and Gatenholm, P., Mechanism of assembly of xylan onto cellulose surfaces. Langmuir, 19, 5072-5077 (2003).

Liu, C. and Zhang, Y., Study of guaiacol pyrolysis mechanism based on density function theory. Fuel Processing Technology, 123, 159-165 (2014).

Matthews, J. F., Skopec, C. E., Mason, P. E., Zuccato, P., Torget, R. W., Sugiyama, J., Himmel, M. E. and Brady, J. W., Computer simulation studies of microcrystalline cellulose Iβ. Carbohyd. Res., 341, 138-152 (2006).

Mamleev, V., Bourbigot, S. and Yvon, J., Kinetic analysis of the thermal decomposition of cellulose: The change of the rate limitation. J. Anal. Appl. Pyrolysis, 80, 141-150 (2007).

Mamleev, V., Bourbigot, S. and Yvon, J., Kinetic analysis of the thermal decomposition of cellulose: The main step of mass loss. J. Anal. Appl. Pyrolysis, 80, 151-165 (2007).

Manya, J. J., Velo, E. and Puigjaner, L., Kinetics of biomass pyrolysis: A reformulated three-parallel-reactions model. Ind. Eng. Chem. Res., 42, 434-441 (2003).

Matthews, J. F., Beckham, G. T., Bergenstråhle-Wohlert, M., Brady, J. W., Himmel, M. E. and Crowley, M. F., Comparison of cellulose Iβ simulations with three carbohydrate force fields. J. Chem. Theo. Comput., 8, 735-748 (2012).

Matthews, J. F., Bergenstråhle, M., Beckham, G. T., Himmel, M. E., Nimlos, M. R., Brady, J. W. and Crowley, M. F., High-temperature behavior of cellulose I. J. Phys. Chem., B, 115, 2155-2166 (2011).

Mayes, H. B. and Broadbelt, L. J., Unraveling the reactions that unravel cellulose. J. Phys. Chem., A., 116, 7098-7106 (2012).

Mayes, H. B., Nolte, M. W., Beckham, G. T., Shanks, B. H. and Broadbelt, L. J., The Alpha−bet(a) of salty glucose pyrolysis: Computational investigations reveal carbohydrate pyrolysis catalytic action by sodium ions. ACS Catal., 5, 192-202 (2015).

Mayor, J. R. and Williams, A., Residence time influence on the fast pyrolysis of loblolly pine biomass. J. of Energy Resources Technol., 132, 041801 (2010).

Mazeau, K. and Heux, L., Molecular dynamics simulations of bulk native crystalline and amorphous structures of cellulose. J. Phys. Chem., B, 107, 2394-2403 (2003).

Mazeau, K., Structural micro-heterogeneities of crystalline Iβ-cellulose. Cellulose, 12, 339-349 (2005a).

Mazeau, K., Moine, C., Krausz, P. and Gloaguen, V., Conformational analysis of xylan chains. Carbohydrate Research, 340, 2752-2760 (2005b).

Mazeau, K. and Rivet, R., Wetting the (110) and (100) surfaces of Iβ cellulose studied by molecular dynamics. Biomacromolecules, 9, 1352-1354 (2008).

Mazeau, K. and Charlier, L., The molecular basis of the adsorption of xylans on cellulose surface. Cellulose, 19, 337-349 (2012).

Meier, D. and Faix, O., State of the art of applied fast pyrolysis of lignocellulosic materials − a review. Bioresour. Technol., 68, 71-77 (1999).

Mettler, M. S., Mushrif, S. H., Paulsen, A. D., Javadekar, A. D., Vlachos, D. G. and Dauenhauer, P. J., Revealing pyrolysis chemistry for biofuels production: Conversion of cellulose to furans and small oxygenates. Energy Environ. Sci., 5, 5414-5424 (2012).

Mettler, M. S., Paulsen, A. D., Vlachos, D. G. and Dauenhauer, P. J., Pyrolytic conversion of cellulose to fuels: Levoglucosan deoxygenation via elimination and cyclization within molten biomass. Energy Environ. Sci., 5, 7864-7868 (2012).

Miller, R. and Bellan, J., A generalized biomass pyrolysis model based on superimposed cellulose, hemicelluloseand liqnin kinetics. Combust. Sci. Technol., 126, 97-137 (1997).

Milosavljevic, I. and Suuberg, E. M., Cellulose thermal decomposition kinetics: Global mass loss kinetics. Ind. Eng. Chem. Res., 34, 1081-1091 (1995).

Moghtaderi, B., The state-of-the-art in pyrolysis modelling of lignocellulosic solid fuels. Fire Mater., 30, 1-34 (2006).

Mohan, D., Pittman, C. U. and Steele, P. H., Pyrolysis of wood/biomass for bio-oil: A critical Review, Energ. Fuel, 20, 848-889 (2006).

Murillo, J. D., Moffet, M., Biernacki, J. J. and Northrup, S., High-temperature molecular dynamics simulation of cellobiose and maltose. AIChE J., (2015).

Nishiyama, Y., Langan, P. and Chanzy, H., Crystal structure and hydrogen-bonding system in cellulose Iβ from synchrotron X-ray and neutron fiber diffraction. J. Am. Chem. Soc., 124, 9074-9082 (2002).

Nishiyama, Y., Sugiyama, J., Langan, P. and Chanzy, H., Crystal structure and hydrogen-bonding system in cellulose iα from synchrotron X-ray and neutron fiber diffraction. J. Am. Chem. Soc., 125, 14300-14306 (2003).

Norinaga, K., Shoji, T., Kudo, S. and Hayashi, J.-i., Detailed chemical kinetic modelling of vapour-phase cracking of multi-component molecular mixtures derived from the fast pyrolysis of cellulose. Fuel, 103, 141-150 (2013).

Ohmukai, Y., Hasegawa, I. and Mae, K., Pyrolysis of the mixture of biomass and plastics in countercurrent flow reactor part I: Experimental analysis and modeling of kinetics. Fuel, 87, 3105-3111 (2008).

Olazar, M., Aguado, R., San José, M. J. and Bilbao, J., Kinetic study of fast pyrolysis of sawdust in a conical spouted bed reactor in the range 400–500 ºC. J. Chem. Technol. Biotechnol., 76, 469-476 (2001).

Orfao, J., Antunes, F. and Figueiredo, J., Pyrolysis kinetics of lignocellulosic materials – three independent reactions model. Fuel, 78, 349-358 (1999).

Ozawa, T., A new method of analyzing thermogravimetric data. Bull. Chem. Soc. Jpn., 38, 1881-1886 (1965).

Pandey, M. P. and Kim, C. S., Lignin depolymerization and conversion: A review of thermochemical methods. Cem. Eng. Technol., 34(1), 29-41 (2011).

Parthasarathi, R., Romero, R. A., Redondo, A. and Gnanakaran, S., Theortical study of the remarkably diverse linkages in lignin. J. Phys. Chem. Letters, 2, 2660-2666 (2011).

Payne, W., Are biofuels antithetic to long-term sustainability of soil and water resources? Advances in Agronomy, 105, 1-46 (2010).

Petridis, L. and Smith, J. C., A molecular mechanics force field for lignin. J. Comp. Chem., 30(3), 457-467 (2008).

Piskorz, J., Radlein, D. and Scott, D. S., On the mechanism of the rapid pyrolysis of cellulose. J. Anal. Appl. Pyrolysis, 9, 121-137 (1986).

Prakash N. and Karunanithi, T., Kinetic modeling in biomass pyrolysis – A review. J. Appl. Sci. Res., 4(12), 1627-1636 (2008).

Ranzi, E., Cuoci, A., Faravelli, T., Frassoldati, A., Migliavacca, G., Pierucci, S. and Sommariva, S., Chemical kinetics of biomass pyrolysis. Energy & Fuels, 22, 4292-4300 (2008).

Reale, S., Di Tullio, A., Spreti, N. and De Angelis, F., Mass spectrometry in the biosynthetic and structural investigation of lignins. Mass Spectrometry Reviews, 23, 87-126 (2004).

Sadhukhan, A. K., Gupta, P. and Saha, R. K., Modelling and experimental studies on pyrolysis of

biomass particles. J. Anal. Appl. Pyrolysis, 81, 183-192 (2008).

Sangha, A. K., Petridis, L., Smith, J. C., Ziebell, A. and Parks, J. J., Molecular simulation as a tool for studying lignin. Environmental Progress & Sustainable Energy, 31 (1), 47-54 (2012).

Sangha, A. K., Parks, J. M., Standaert, R. F., Ziebell, A., Davis, M. and Smith, J. C., Radical coupling reactions in lignin synthesis: a density functional theory study. J. Phys. Chem., B, 116, 4760-4768 (2012).

Scaiano, J. C., Berinstain, A. B., Whittlessey, M. K., Malenfant, P. R. L. and Bensimon, C., Lignin-like molecules: Structure and photophysics of crystalline a-guaiacoxyacetoveratrone. Chem. Mater., 5, 700-704 (1993).

Scanlon, B., Makeover puts CHARMM back into biofuel business. Renewable Energy World, http://www.renewableenergyworld.com/rea/news/article/2013/05/makeover-puts-charmm-back-in-biofuels-business?cmpid=BioNL (2013).

Seshadri, V. and Westmoreland, P. R., Concerted reactions and mechanism of glucose pyrolysis and implications for cellulose kinetics, J. Phys. Chem., A, 116, 11997-12013 (2012).

Shafizadeh, F., Introduction to pyrolysis of biomass. J. Anal. Appl. Pyrolysis, 3, 283-305 (1982).

Shafizadeh, F. and DeGroot, W. F., Combustion Characteristics of Cellulosic Fuels. In: Thermal Uses and Properties of Carbohydrates and Lignins. Elsevier, New York, 1-17 (1976).

Shafizadeh, F. and Fu, Y., Pyrolysis of cellulose. Carbohydr. Res., 29, 113-122 (1973).

Shen, D., Jin, W., Hu, J., Xiao, R. and Luo, K., An overview on fast pyrolysis of the main constituents in lignocellulosic biomass to valued-added chemicals: Structures, pathways and interactions. Renew. Sust. Energ. Rev., 51, 761-774 (2015).

Shen, T. and Gnanakaran, S., The stability of cellulose: A statistical perspective from a coarse-grained model of hydrogen-bond networks. Biophys. J., 96, 3032-3040 (2009).

Sinha, S., Jhalani, A., Ravi, M. R. and Ray, A., Modeling of pyrolysis in wood: A review. Sol. Energy Soc., India, 10(1), 41-62 (2000).

Sluiter, J. B., Ruiz, R. O., Scarlata, C. J., Sluiter, A. D. and Templeton, D. W., Composition analysis of lignocellulosic feedstock. 1. Review and description of methods. J. Agric. Food Chem., 58, 9043-9053 (2010).

Soravia, D. R. and Canu, P., Kinetics modeling of cellulose fast pyrolysis in a flow reactor. Ind. Eng. Chem. Res., 41, 5990-6004 (2002).

Srinivas, G., Cheng, X. and Smith, J. C., A solvent-

free coarse grain model for crystalline and amorphous cellulose fibrils. J. Chem. Theo. Comput., 7, 2539-2548 (2011).

Teng, H. and Wei, Y.-C., Thermogravimetric studies on the kinetics of rice hull pyrolysis and the influence of water treatment. Ind. Eng. Chem. Res., 37, 3806-3811 (1998).

Theander, O., Cellulose, Hemicellulose and Extractives. Fundamentals of Thermochemical Biomass Conversion. Elsevier Applied Science, New York, 35-60 (1985).

Trinh, T. N., Jensen, P. A., Dam-Johansen, K., Knudsen, N. O., Sørensen, H. R. and Hvilsted, S., Comparison of lignin, macroalgae, wood, and straw fast pyrolysis. Energy & Fuels, 27, 1399-1409 (2013).

Tsamba, A. J., Yang, W. and Blasiak, W., Pyrolysis characteristics and global kinetics of coconut and cashew nut shells. Fuel Process. Technol., 87, 523-530 (2006).

U. S. Department of Energy, Using heat and chemistry to make fuel and power: Thermochemical conversion. Energy Efficiency and Renewable Energy Biomass Program, http://www1.eere.energy.gov/biomass/pdfs/thermochemical_four_pager.pdf (2010).

U. S. Energy Information Agency, Annual energy outlook 2013. http://www.eia.gov/forecasts/aeo/pdf/0383(2013).pdf (2013).

Vakkilainen, E., Kuparinen, K. and Heinimo, J., Large industrial users of energy biomass. International Energy Agency (IEA) Bioenergy, Task 40: Sustainable International Bioenergy Trade, 55 (2013).

van de Velden, M., Baeyens, J., Brems, A., Janssens, B. and Dewil, R., Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. Renewable Energy, 35, 232-242 (2010).

Vanderhart, D. L. and Atalla, R., Studies of microstructure in native celluloses using solid-state carbon-13 NMR. Macromolecules, 17, 1465-1472 (1984).

Varhegyi, G., Antal Jr, M. J., Szekely, T. and Szabo, P., Kinetics of the thermal decomposition of cellulose, hemicellulose, and sugarcane bagasse. Energy & Fuels, 3, 329-335 (1989).

Varhegyi, G., Antal Jr, M. J., Szekely, T., Till, F. and Jakab, E., Simultaneous thermogravimetric-mass spectrometric studies of the thermal decomposition of biopolymers. 1. Avicel cellulose in the presence and absence of catalysts. Energy & Fuels, 2, 267-272 (1988).

Varhegyi, G., Antal Jr, M. J., Szekely, T., Till, F., Jakab, E. and Szabo, P., Simultaneous thermogravimetric-mass spectrometric studies of the thermal decomposition of biopolymers. 2. Sugarcane bagasse in the presence and absence of catalysts. Energy & Fuels, 2, 273-277 (1988).

Varhegyi, G., Jakab, E. and Antal Jr, M. J., Is the broido-shafizadeh model for cellulose pyrolysis true? Energy & Fuels, 8, 1345-1352 (1994).

Venderbosch, R. H. and Prins, W., Fast pyrolysis technology development. Biofuels Bioprod. Bioref., 4, 178-208 (2010).

Viëtor, R. J., Mazeau, K., Lakin, M. and Perez, S., A priori crystal structure prediction of native celluloses. Biopolymers, 54, 342-354 (2000).

Vinu, R. and Broadbelt, L. J., A mechanistic model of fast pyrolysis of glucose-based carbohydrates to predict bio-oil composition. Energy Environ. Sci., 5, 9808-9826 (2012).

Vorwerg, W., Computer modelling of carbohydrate molecules (ACS Symposium Series 430). Am. Chem. Soc., Washington, D. C. 36, 620 (1990).

Wada, M., Lateral thermal expansion of cellulose Iβ and IIII polymorphs. J. Polym. Sci., Part B: Polym. Phys., 40, 1095-1102 (2002).

Wada, M., Hori, R., Kim, U.-J. and Sasaki, S., X-ray diffraction study on the thermal expansion behavior of cellulose Iβ and its high-temperature phase. Polym. Degrad. Stab., 95, 1330-1334 (2010).

Wang, S., Guo, X., Liang, T., Zhou, Y. and Luo, Z., Mechanism research on cellulose pyrolysis by PY-GC/MS and subsequent density functional theory studies. Bioresour. Technol., 104, 722-728 (2012).

Wang, S., Guo, X., Wang, K. and Luo, Z., Influence of the interaction of components on the pyrolysis behavior of biomass. J. Anal. Appl. Pyrolysis, 91, 183-189 (2011).

White, J. E., Catallo, W. J. and Legendre, B. L., Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies. J. Anal. Appl. Pyrolysis, 91, 1-33 (2011).

Whitney, S. E., Gothard, M. G., Mitchell, J. T. and Gidley, M. J., Roles of cellulose and xyloglucan in determining the mechanical properties of primary plant cell walls. Plant Physiol., 121, 657-664 (1999).

Yu, J., Yue, J., Liu, Z., Dong, L., Xu, G., Zhu, J., Duan, Z. and Sun, L., Kinetics and mechanism of solid reactions in a micro fluidized bed reactor. AlChE J., 56, 2905-2912 (2010).

Yui, T., Nishimura, S., Akiba, S. and Hayashi, S., Swelling behavior of the cellulose Iβ crystal models by molecular dynamics. Carbohyd. Res., 341, 2521-2530 (2006).

Zhang, C., Zhang, R., Li, X., Li, Y., Shi, W., Ren, X. and Xu, X., Bench-scale fluidized-bed fast pyrolysis of peanut shell for bio-oil production. Environ. Prog. Sus. Energy, 30, 11-18 (2011).

Zhang, J., Luo, J., Tong, D., Zhu, L., Dong, L. and Hu, C., The dependence of pyrolysis behavior on the crystal state of cellulose. Carbohydr. Polym., 79, 164-169 (2010).

Zhang, X., Li, J., Yang, W. and Blasiak, W., Formation mechanism of levoglucosan and formaldehyde during cellulose pyrolysis. Energy & Fuels, 25, 3739-3746 (2011).

Zhang, X., Yang, W. and Blasiak, W., Modeling study of woody biomass: Interactions of cellulose, hemicellulose, and lignin. Energy & Fuels, 25, 4786-4795 (2011).

Zhang, Q., Agren, H. and Tu, Y., The adsorption of xyloglucan on cellulose: Effects of explicit water and side chain variation. Carbohydration Research, 346, 2595-2602 (2011).

Zhou, X., Nolte, M. W., Mayes, H. B., Shanks, B. H. and Broadbelt, L. J., Experimental and mechanistic modeling of fast pyrolysis of neat glucose-based carbohydrates. 1. Experiments and development of a detailed mechanistic model. Ind. Eng. Chem. Res., 53, 13274-13289, (2014).

Zhou, X., Nolte, M. W., Mayes, H. B., Shanks, B. H. and Broadbelt, L. J., Fast pyrolysis of glucose-based carbohydrates with, added NaCl part 2: Validation and evaluation of the mechanistic model. AIChE, J., 62, 778-791 (2016).

Zhou, X., Nolte, M. W., Shanks, B. H. and Broadbelt, L. J., Experimental and mechanistic modeling of fast pyrolysis of neat glucose-based carbohydrates. 2. Validation and evaluation of the mechanistic model. Ind. Eng. Chem. Res., 53, 13290-13301 (2014).

Zhou, X., Nolte, M. W., Mayes, H. B., Shanks, B. H. and Broadbelt, L. J., Fast pyrolysis of glucose-based carbohydrates with, added NaCl part 1: Experimental and development of a mechanistic model. AIChE, J., 62, 776-777 (2016).