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PERSPECTIVE

Top ten fundamental challenges of biomass pyrolysis for biofuels

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Pyrolytic biofuels have technical advantages over conventional biological conversion processes since the entire plant can be used as the feedstock (rather than only simple sugars) and the conversion process occurs in only a few seconds (rather than hours or days). Despite decades of study, the fundamental science of biomass pyrolysis is still lacking and detailed models capable of describing the chemistry and transport in real-world reactors is unavailable. Developing these descriptions is a challenge because of the complexity of feedstocks and the multiphase nature of the conversion process. Here, we identify ten fundamental research challenges that, if overcome, would facilitate commercialization of pyrolytic biofuels. In particular, developing fundamental descriptions for condensed-phase pyrolysis chemistry (i.e., elementary reaction mechanisms) are needed since they would allow for accurate process optimization as well as feedstock flexibility, both of which are critical to any modern high-throughput process. Despite the benefits to pyrolysis commercialization, detailed chemical mechanisms are not available today, even for major products such as levoglucosan and hydroxymethylfurfural (HMF). Additionally, accurate estimates for heat and mass transfer parameters (*e.g.*, thermal conductivity, diffusivity) are lacking despite the fact that biomass conversion in commercial pyrolysis reactors is controlled by transport. Finally, we examine methods for improving pyrolysis particle models, which connect fundamental chemical and transport descriptions to real-world pyrolysis reactors. Each of the ten challenges is presented with a brief review of relevant literature followed by future directions which can ultimately lead to technological breakthroughs that would facilitate commercialization of pyrolytic biofuels.

Paper body

As the world population grows, there is a need for new energy technologies that are domestic and sustainable. Achieving both objectives requires improving existing energy systems as well as utilizing renewable feedstocks, such as biomass. In addition to supporting agricultural economies, biomass is the only renewable source for liquid fuels and chemicals.[1,2] For this reason, the U.S. Department of Energy has made it a goal to replace 30% of all transportation fuels with biofuels.[3]

The 2005 ‘Billion-Ton Study’ (BTS) sponsored by the U.S. Department of Energy employed conservative assumptions to determine that more than a billion tons of biomass (unrestricted by price) is available annually for biofuels. This amount of biomass is capable of displacing 30% of U.S. petroleum consumption, as put forth in the government targets.[3] In 2011, an update to the BTS revisited the resource availability and confirmed the findings of the 2005 study.[4] Both government-

Broader context

Biomass pyrolysis is a promising technology for producing renewable fuels and chemicals from lignocellulosic feedstocks. This process utilizes moderate temperatures (400–600 °C) to depolymerize biomass to a mixture of oxygenates (or ‘bio-oil’) that are liquid at room temperature. The major benefit of this “next-generation” biofuel production process over traditional enzymatic approaches is that solid biomass is converted in only a few seconds (compared to hours or days for biological conversion). Despite the potential for pyrolysis as a future biofuel production platform, there is currently a lack of understanding of the fundamental processes which govern pyrolysis. In this perspective we reveal ten scientific challenges that we believe inhibit process design and optimization which in turn hinders commercial success of pyrolytic biofuels.

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supported studies underscore the importance and potential in utilizing biomass for fuels.

Widespread adoption of lignocellulose as a biofuel feedstock will require next-generation technologies (*e.g.*, fast pyrolysis, gasification) with superior performance compared to more mature biological processes (*e.g.*, enzymatic conversion). Thermochemical technologies employ high temperatures to convert biomass to fuels in a matter of seconds, which gives them an advantage over enzyme-catalyzed processes that require hours or days, especially for localized – close to the source – biomass utilization.

In techno-economic analyses, fast pyrolysis is typically competitive with biological and gasification technologies in terms of product fuel-cost.[5] While the fundamentals of fast pyrolysis are the focus of this perspective, all thermochemical technologies (*e.g.*, fast pyrolysis, gasification, combustion) involve pyrolysis chemistry as the initial step.[6,7] Fast pyrolysis processes utilize an array of reactor designs (*e.g.*, bubbling or circulating fluidized bed)[8,9] to rapidly heat mechanically processed biomass (such as wood fibers) to reaction temperature (400–600 °C). Once biomass reaches high temperatures (*i.e.*, >300 °C), it thermally depolymerizes to form small oxygenates (up to 80% yield) which are vapors in the reactor but condense to a liquid mixture (*i.e.*, bio-oil) at room temperature.[10] The ultimate benefit of pyrolysis is that solid biomass can be converted to a transportable liquid (bio-oil) while simultaneously increasing energy density (through deoxygenation).[11]

Despite these advantages, efficient utilization of bio-oils is non-trivial since transportation to regional biorefineries or immediate consumption in boilers/turbines is hindered by the poor fuel characteristics (highly oxygen content), chemical complexity (hundreds of compounds) and instability (due to oxygen content and acidity).[12–14] It is generally believed that commercialization of pyrolytic biofuels hinges on improving bio-oil quality and stability. Significant research has focused on the development of catalytic hydrogenation processes capable of upgrading bio-oil to fuels or chemicals.[15,16] One major impediment to the success of this approach is that hydrogen is expensive and therefore hydrogen-lean or hydrogen-free approaches to bio-oil upgrade are desirable.

We believe that directing condensed-phase chemistry could help improve bio-oil quality while simultaneously reducing the amount of hydrogen required for bio-oil upgrade which in turn minimizes operating costs. Fig. 1 shows that bio-oil composition (in terms of carbon-to-oxygen ratio) and yield can vary significantly depending on feedstock type, inorganic content and reaction conditions (*e.g.*, temperature). This information hints that it may be possible, with engineered feedstocks and optimized reaction conditions, to produce a bio-oil better suited for upgrade to a specific fuel or chemical. *The key to unlocking this potential is fundamental models capable of describing transport and reaction phenomena*.

Over the past five decades, biomass pyrolysis research has generally focused on three areas: (i) understanding the chemistry of individual biopolymers (*e.g.*, cellulose), (ii) developing reaction-transport models to describe conversion of complex lignocellulosic particles, and (iii) designing reactors. Many reviews, such as those by Di Blasi[19] and Bridgwater and Peacocke,[8] have nicely summarized these areas. It is generally believed that fundamental research will lead to a 'building-up' approach whereby chemical mechanisms are integrated into particle models (accounting for transport phenomena) which are capable of predicting global performance (*i.e.*, bio-oil yield and composition). However, each research area has garnered hundreds of publications and yet, a comprehensive understanding of any one area is not available today. For example, the slow progress in revealing pyrolysis chemistry and developing reaction-transport models results from two complexities which differentiate it from petroleum refining (which is better understood): (a) biomass feedstocks are multi-scale and (b) pyrolysis is multiphase (solid, liquid and gas). Understanding both multiscale and multiphase complexities represents a vital step forward in optimizing pyrolysis and developing next-generation biofuels' technologies.

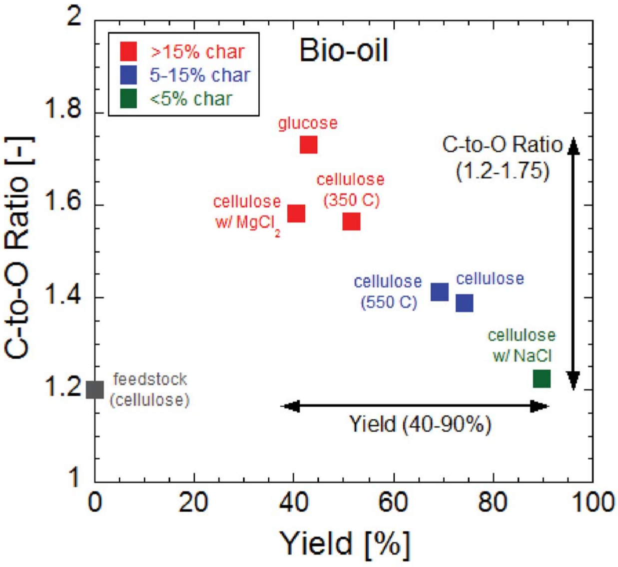

Fig. 1 Bio-oil composition (carbon-to-oxygen ratio) *vs.* yield for various feedstocks. Yield and carbon-to-oxygen (C-to-O) ratio are calculated from published experimental data and are based on a weight average of all volatile products and do not include char or permanent gases (CO and CO_2).[17,18] The reaction temperature is 500 °C unless noted otherwise.

Complexity 1: the multiscale nature of biomass feedstocks

Length scales within lignocellulosic biomass span eleven orders of magnitude (10^{-10} to 10^1 m) as shown in Fig. 2. While the precise structure and characteristics of biomass are still active areas of research,[20] much is known about biomass microstructure and the role it plays in plant function.[21] At the smallest length scale (angstrom, 10^{-10} m), biomass is comprised of C–C, C–H, C–O and O–H bonds as well as oxygenated and aromatic rings. These functional groups make up three biopolymers (10^{-9} to 10^{-8} m): cellulose (semicrystalline linear polymer comprised of β-linked glucose), hemicellulose (amorphous polymer made up mainly of 5-carbon sugar monomers), and lignin (3D polymer comprised of oxygenated phenylpropane units).[22] Additionally, minor amounts of small organics (or extractives)[23] and inorganic ions (*e.g.*, Mg^{2+} and Ca^{2+})[24] are present. Cellulose polymers are bound together *via* hydrogen bonding networks to form

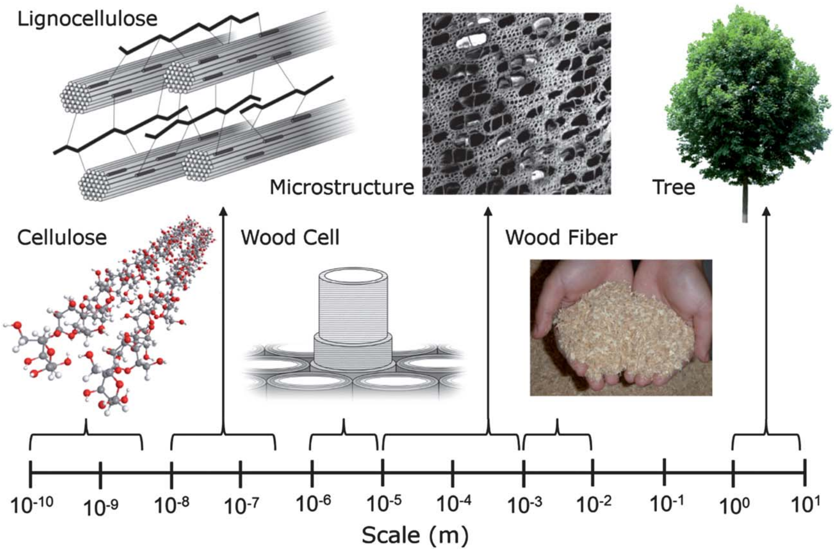

Fig. 2 Multiscale nature of lignocellulosic feedstocks. Lignocellulosic materials exhibit physical structures which span eleven orders of magnitude, from the atomic level of biopolymers (10^{-10} to 10^{-9} m) to the microstructured cellular network (10^{-5} to 10^{-3} m) to the macrostructure of trees and grasses (1–10 m).

semi-crystalline rods (microfibrils).[25] Groups of these microfibrils are connected by hemicellulose and lignin to ultimately produce nanometer-scale composites that make up plant cells (10^{-8} to 10^{-7} m).[26]

The cellular microstructure of biomass enables proper plant function. For example, tracheid cells form hollow tubular structures capable of transporting liquid water throughout the organism as well as providing structural support. Groups of adjacent cells form a multicellular porous structure comprised of smaller (lumen) and larger (parenchyma) cavities (10^{-5} to 10^{-4} m), which vary with the type of biomass (Fig. 3).[27] Multicellular structures then combine to form the plant macrostructure which is what is ultimately input into pyrolysis reactors. It is important to note that generally whole plants (10^{0} to 10^{1} m) are first mechanically processed to smaller fibers (10^{-3} to 10^{-2} m) which are then fed into pyrolysis reactors.[28–30] Unlike other energy feedstocks (*e.g.*, petroleum, natural gas, coal), lignocellulosic biomass feedstocks exhibit a multiscale (with variation over multiple orders of magnitude) structure, which is varying during degradation, rendering fundamental prediction of properties and product distributions a challenge.

Complexity 2: the multiphase nature of pyrolysis

Feedstock complexities are compounded by the multiphase nature of biomass pyrolysis. In recent years, it has been shown that solid biomass, upon heating, decomposes through an intermediate liquid before forming volatile products.[31–33] Intermediate liquids were first hypothesized to exist when woody biomass was shown to have a lubricating effect when pressed against moving high temperature surfaces.[33] Subsequent research demonstrated that rapid heating and cooling of cellulose produced solids (*e.g.*, char) with smooth surfaces, which is indicative of a liquid intermediate.[32] Finally, the existence of short-lived (<100 ms) intermediate liquids was confirmed by using high speed photography during ablative pyrolysis.[31] It was

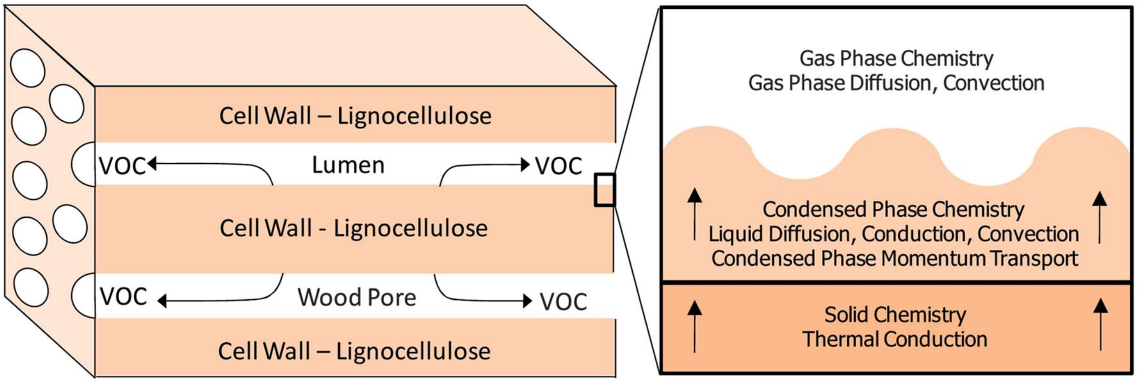

Fig. 3 Lignocellulose pyrolysis chemistry and transport phenomena. The decomposition of lignocellulosic materials such as wood fibers occurs through the thermal degradation of solid cellular wall material to form an intermediate liquid. Subsequent decomposition of the high temperature, non-equilibrium liquid generates volatile organic compounds (VOCs) which flow through the wood pore (cellular lumen) and exit the particle.

found that both cellulose (Fig. 4B) and lignin (Fig. 4C) pyrolysis proceed through an intermediate liquid, with the former exhibiting boiling and aerosol generation.[31,34]

The existence of the intermediate liquid implies that a comprehensive mechanism of pyrolysis must account for the chemistry of solid feedstocks and vapor products as well as chemical processes within the intermediate liquid. Solid-phase processes include phase changes in crystalline and amorphous polymers as well as breaking and forming of chemical bonds.[35,36] Within the intermediate liquid, species have significant functionality (*e.g.*, many O–H groups) leading to thousands of potential (elementary) reactions. Lignocellulosic materials have been shown to initially fracture to oligomers (*e.g.*, anhydroglucopyranose in cellulose pyrolysis) which are several monomers in size and capable of melting (Fig. 5).[35,36] Additionally, liquid species may be solvated by surrounding molecules, something that does not occur in gas and solid phases. Finally, both liquid-phase and interfacial mass transfer are present.[37] Eventually, the liquid phase reactions will produce small-molecules as products that either evaporate into the gas-phase, are ejected into the gas-phase as aerosols,[34] or polymerize to form char. Once products evaporate, thermal decomposition can still occur and these gas-phase reactions are typically not negligible in pyrolysis reactors.

Accurately describing the biomass transformation at the macroscopic scale requires integrating fundamental reaction mechanisms with transport models while accounting for the evolving structure of a multitude of scales. The resulting master pyrolysis model should be able to describe conversion of biomass particles in real-world reactors (*e.g.*, fluidized bed reactor). Ultimately, this all-encompassing model could be employed for optimization, which is especially crucial for fuels production since the world consumes over a billion gallons of gasoline per day.[38]

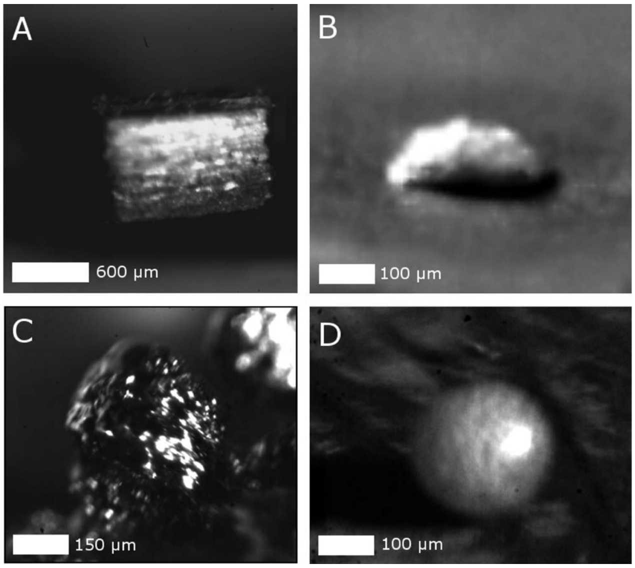

Fig. 4 Intermediate liquids in pyrolysis. (A) A hybrid poplar (*Populous tremuloides*) wood chip on a 700 °C alumina surface. (B) Cellulose decomposes through an intermediate liquid which appears to wet 700 °C alumina. (C) Lignin on 700 °C alumina decomposes through an intermediate liquid before reacting to form a second solid. (D) Liquid intermediate cellulose on 700 °C Fecralloy (Fe–Cr–Al alloy) exhibits dewetting.

Goal of this perspective

In this perspective, we identify ten fundamental research challenges that we believe will enable improved understanding, greater predictability and successful commercialization of biomass pyrolysis. Within the framework of the aforementioned complexities, the challenges outlined in this work relate to fundamental chemistry, species transport, and integrated particle models. Existing work is highlighted in the context of a given challenge, without a comprehensive review of the literature. Finally, these research challenges are restricted to upstream (condensed phase) processes dedicated to converting biomass to bio-oil. Downstream challenges related to catalytic upgrading of bio-oil are not considered here.

Challenge #1: what modern techniques can reveal pyrolysis chemistry?

Prior to addressing the pyrolysis puzzle, researchers must consider methods suitable for studying pyrolysis chemistry. New experimental techniques capable of providing molecular-level insight are needed to improve upon existing global kinetic schemes, such as the Broido–Shafizadeh mechanism.[39,40] In previous pyrolysis experiments, biomass samples are rapidly heated and then volatile products (*e.g.*, levoglucosan) are collected and quantified.[17,18,41–46] Characterization of solid and liquid phase intermediates has been largely avoided due to the short-lifetime and chemical complexity of condensed-phase species. Experimental information on condensed-phase intermediates, while largely unavailable in the literature, could facilitate the construction of solid- and liquid-phase reaction mechanisms.

While collecting and identifying condensed-phase intermediates is challenging, inroads have been made recently. Previous work using drop tube furnaces was employed to rapidly heat solid biomass particles and then quickly quench liquid and solid species.[32,42] These early efforts focused on characterizing short-lived condensed-phase intermediates, but analysis proved difficult because of the complexity of analytes. More recently, researchers have been able to capture aerosols ejected directly from the intermediate liquid.[34] Characterization of the aerosols using silyl-methylation[47] in conjunction with gas chromatography/mass spectrometry reveals that monomers, dimers and trimers exist in the intermediate liquid. Further analysis also shows that oligomers within an aerosol droplet have the same linkage type (β-1,4) indicating that they originate from the parent cellulose molecule rather than from repolymerization of monomers (such as levoglucosan or glucose). While these are important first steps in characterization of the liquid intermediate, future work with more advanced analytical techniques (such as H-NMR) could be utilized to better characterize these complex intermediates.

Further complicating experiments, solid- and liquid-phase chemistries are convoluted with transport phenomena (conductive and convective heat transfer as well as liquid-phase

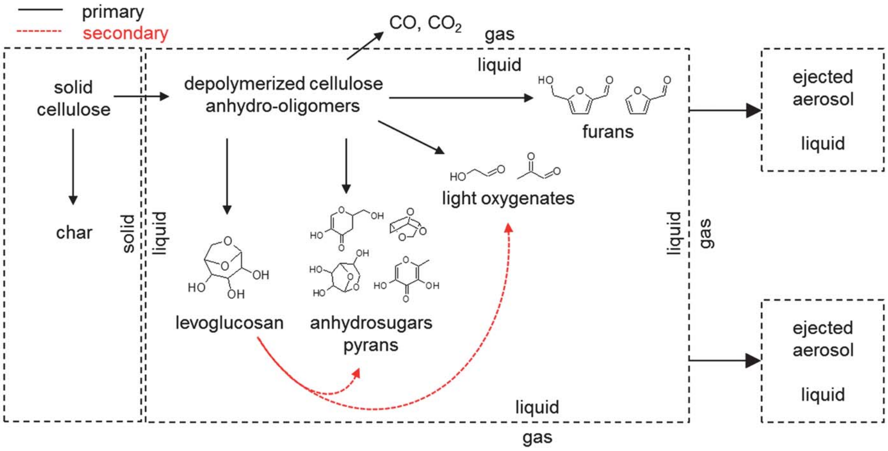

Fig. 5 Primary and secondary reactions in cellulose pyrolysis.

diffusion).[48] While intrinsic reaction rates can be obtained for low temperature slow pyrolysis (*i.e.*, temperature changes ranging from 1–100 °C min^{-1}),[43,49,50] kinetics from this process are not amendable to fast (100–1000 °C min^{-1}) or flash (>1000 °C min^{-1}) pyrolysis reactors since reaction temperatures are higher and product distributions are different in the latter processes.[11,48,51] Fig. 6 compares heat transfer and reaction kinetics and illustrates that four operating regimes exist in pyrolysis. These regions are defined by either the Pyrolysis number I ($Py^{I} = k/\rho C_{p}L^{2}k_{r}$) or II ($Py^{II} = h/\rho C_{p}Lk_{r}$) and the Biot number ($Bi = hL/k$).[52–55] Consideration of a wide range of thermal conditions ($h_{surface}$ and $k_{biomass}$) and particle sizes ($10^{-6} < L < 10^{-1}$ m) for both ablative reactors (A) and fluid bed reactors (F) indicates that only at relatively low temperatures (250 °C) is fluid-bed pyrolysis isothermal. This finding implies that these reactors are not suited for studying fast pyrolysis chemistry due to non-uniform thermal profiles within biomass samples (typical reaction temperatures ~500 °C).

As shown in the cellulose reaction-transport map in Fig. 6B, pyrolysis experiments can traverse several regimes by varying the characteristic length scale of the biomass sample. For experiments utilizing cellulose samples with characteristic lengths in the range of 10 μm to 1 mm, convection, conduction, and reaction rates are all within an order of magnitude of one another. At these length scales, heat transport is not much faster (*i.e.*, more than one order of magnitude) than reaction, and pyrolysis is not isothermal. As one possible solution to the lack of isothermal conditions, we have demonstrated a new experimental technique, thin-film pyrolysis (TFP), where heat transport (both conduction and convection) rates are much faster than reaction enabling isothermal pyrolysis. TFP utilizes microscale biomass thin-films which can be heated to reaction temperature (~500 °C) in only a few milliseconds. This rapid heating produces a temperature ramp in excess of 1 000 000 K min^{-1} with negligible temperature gradients during the heating process. TFP experiments have already demonstrated that cellulose glycosidic linkage type (α or β) does not affect pyrolysis chemistry whereas end group to monomer ratio is a critical descriptor.[17,56]

Experimental techniques can also be coupled with first principles simulations for enhanced understanding. Despite advances in computing power, direct simulation of the macromolecules that comprise biomass (such as lignocellulose) is all but impossible. State-of-the-art simulation techniques capable of predicting pyrolysis chemistry *a priori* (such as first principles molecular dynamics) require decades of CPU time to simulate one cellulose polymer (Fig. 7). However, recent experimental work has discovered a small-molecule surrogate for cellulose (*i.e.*, α-cyclodextrin).[17] This finding enabled the use of first principles simulations (Car–Parrinello Molecular Dynamics) to reveal how cellulose breaks down to form furans and light oxygenates, albeit at much higher temperatures than the experiments. While this work is a first step toward a comprehensive cellulose pyrolysis model, experimental confirmation of these pathways and intermediates has eluded researchers. The development of next-generation techniques similar to thin-film pyrolysis can lead to a deeper understanding of the underlying chemistry of pyrolysis. In parallel, advanced computational tools need to complement experimental studies to reveal key pathways in biomass degradation.

Challenge #2: how do anhydrosugars, pyrans and furans form from cellulose?

A first step in constructing a master pyrolysis model is to understand how major products form from cellulose, the least complex and most abundant component of biomass. It is generally accepted that the initial chemistry in cellulose pyrolysis is a series of depolymerization and dehydration reactions which produce an intermediate liquid and then volatile products (*i.e.*, bio-oil constituents).[57] High molecular weight volatiles, such as anhydrosugars (up to 65% yield from cellulose), pyrans (up to 10%), and furans (up to 15%), are of particular interest since they retain carbon–carbon bonds during pyrolysis giving them a higher energy density compared to the feedstock and smaller products (*e.g.*, formic acid, glycolaldehyde). Additionally, these relatively large products are abundant in bio-oil and may also be intermediates on the path to lower molecular weight products making them a logical starting point in mechanism construction.[44]

Pyrans and anhydrosugars retain the 6-member ring (containing 5 carbons and 1 oxygen) of the glucose monomer, but carbon functionalities are modified (cyclization to produce ether

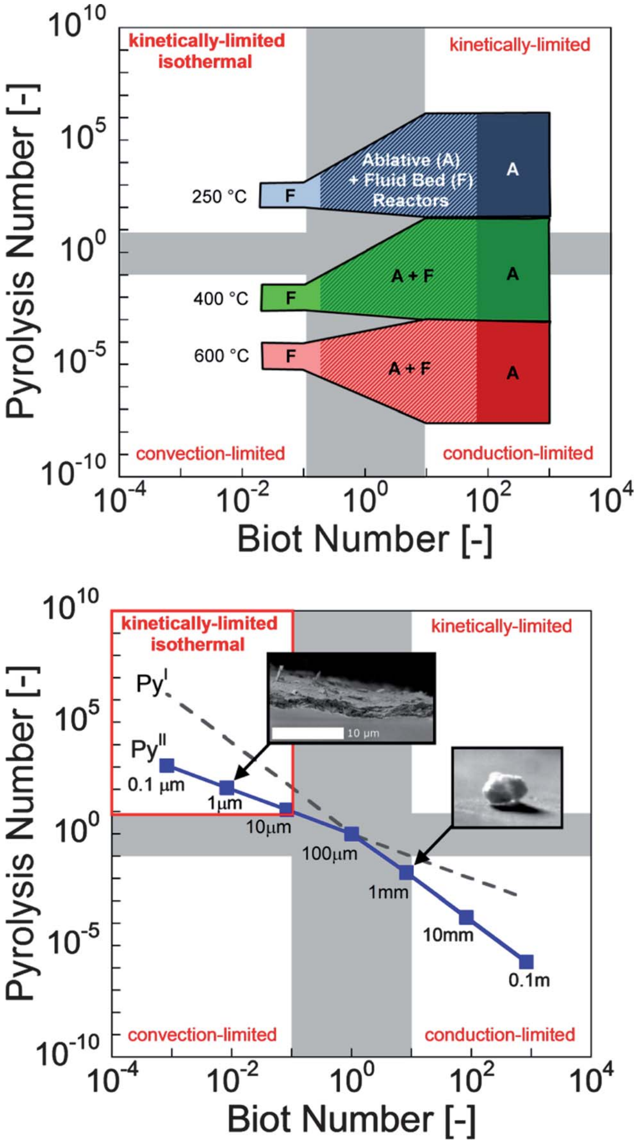

Fig. 6 Pyrolysis reaction-transport maps of lignocellulose and cellulose. Conversion of biomass is controlled by the relative rates of three phenomena: internal conduction (k_{cond}), external heat transfer (h), and chemical conversion (k_{rxn}). The ratios of these three time scales are defined by the Biot number (Bi) and Pyrolysis numbers (Py^{I}, Py^{II}). Four regions are shown (clockwise from top left): kinetically limited and isothermal, kinetically limited (nonisothermal), conduction-limited, and convection-limited. Top: particle reaction-transport map for fluidized bed (F) and ablative (A) biomass reactors (which exhibit different transport rates). Bottom: the pyrolysis of cellulose in contact with high temperature surfaces traverses two reaction/transport regions as particles shrink from 0.1 m to 0.1 µm. Thin-Film Pyrolysis (TFP) leads to isothermal cellulose pyrolysis chemistry for characteristic dimensions (film thickness) smaller than 10 µm.

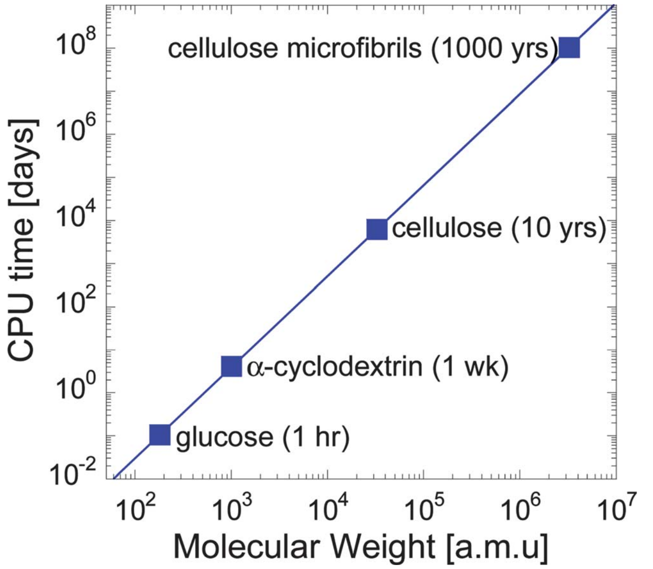

Fig. 7 Tractability of *ab initio* molecular dynamics simulation of carbohydrates and cellulose. CPU time of Car–Parrinello Molecular Dynamics simulations with 200 processors operating in parallel. Cellulose is assumed to have a degree of polymerization of 100 and microfibrils are taken to be bundles of 20 individual cellulose polymers. Calculation times for cellulose and cellulose microfibrils were extrapolated from CPU times of smaller carbohydrates (*e.g.*, glucose, cellohexaose, α-cyclodextrin) assuming CPU time is only a function of molecular weight.

bridges, elimination to form double bonds, *etc.*). Anhydrosugars are the most abundant product from cellulose pyrolysis and identifying these reaction pathways is a necessary component of any master pyrolysis model. Levoglucosan (1,6-anhydro-β-D-glucopyranose), the most abundant anhydrosugar product, has the same C-to-O ratio as cellulose but contains an additional ether bond in the form of an anhydro-bridge (^{1}C–^{6}O–^{6}C). Since levoglucosan is structurally similar to cellulose, it is likely that only a few reactions are involved in its formation. First, the ether glycosidic linkage (which connects glucose monomers) is cleaved followed by formation of an anhydro-bridge (an ether bond). Several mechanisms have been proposed to describe levoglucosan formation from low degree-of-polymerization (DP) anhydro-oligomers (*i.e.*, depolymerized cellulose). Numerous researchers claim that cellulose undergoes transglycosylation, whereby the ^{6}C hydroxyl group reacts with the ^{1}C–O glycosidic cleavage through a four-member pericyclic reaction[58–60] and that this depolymerzation (or 'unzipping') mechanism is likely dominant in cellulose pyrolysis. Alternatively, it has been proposed that heterolytic glycosidic cleavage results in the formation of a ^{1}C glucosyl cation end group.[45,61] If the ^{6}C hydroxyl group is free, the cationic intermediate is subsequently converted by the formation of a 1,6-anhydro-linkage which produces levoglucosan. Neither of these proposed mechanisms has been strongly supported by experimental or computational evidence in the literature.

Different from anhydrosugars and pyrans, furan formation from cellulose requires a ring opening step where the glucose monomer (6-membered ring) is converted to a five membered structure. Currently, there are two hypothesized mechanisms for furan ring formation from glucose monomers within cellulose (Fig. 8). 'Direct' mechanisms dictate that ring opening, rearrangement, and ring closure reactions occur while the intermediates are bound to the cellulose chain, whereas 'indirect' mechanisms indicate that cellulose conversion proceeds through a stand-alone pyran-ring intermediate (*e.g.*, glucose,

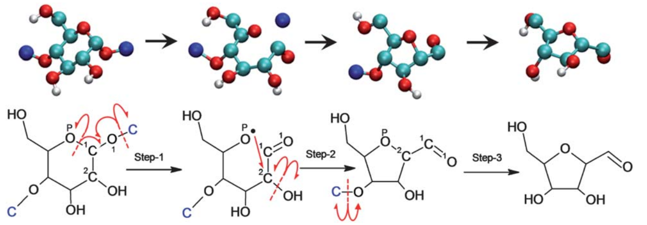

Fig. 8 A direct pathway of furan formation from cellulose. Direct mechanisms propose the opening of the pyran ring by homolytic or heterolytic cleavage and closure of the ring while still attached to the cellulose chain (dark blue atoms).[17] Alternatively, indirect mechanisms propose the formation of an independent intermediate such as levoglucosan (not shown).[43]

levoglucosan) which is subsequently converted to a 5-membered ring. From the 5-membered ring, dehydration reactions occur at ring carbons to generate volatile furans, such as hydroxymethylfurfural and furfural. One hypothesized indirect mechanism suggests that levoglucosan forms directly from cellulose, and then subsequently dehydrates to form furanoses, light oxygenates and char.[43] It has also been proposed that cellulose pyrolysis is analogous to low-temperature (<200 °C) carbohydrate chemistry. In these mechanisms, cellulose breaks down through heterolytic cleavage of glycosidic bonds to form small-molecule (*e.g.*, glucose) ionic intermediates which ring open (^{1}C–^{5}O cleavage) and then form furans. Alternatively, we have shown with first principles molecular dynamics at very high temperatures a fundamentally different mechanism for furan formation where glycosidic bonds are cleaved homolytically with simultaneous opening of the pyran-ring (^{1}C–^{5}O).[17] The linear intermediate then forms a furan ring by ^{5}O-radical attack at ^{2}C which is subsequently cleaved from the cellulose chain at ^{4}C. It is unknown which of these mechanisms is dominant under typical pyrolysis conditions.

While mechanisms have been suggested for furan and anhydrosugar formation, little has been postulated about how pyran products form from cellulose due to their relatively low abundance (∼5% yield from cellulose). Additionally, some pyran products are not present in National Institute of Standards and Technology (NIST) mass spectrometry libraries, and they are frequently not identified. For example, Shafizadeh and co-workers identified one major pyran product of cellulose pyrolysis as 1,5-anhydro-4-deoxy-D-glycero-hex-1-en-3-ulose (ADGH).[46] In their paper, the authors propose that ADGH forms from depolymerized cellulose oligomers through sequential elimination reactions at the ^{1}C and ^{4}C carbons. While this pathway has not been confirmed by experimental or computational evidence, it is a starting point in mechanism construction.

Challenge #3: how do products break down within the intermediate liquid?

Primary reactions within the condensed phase form numerous volatile components (*e.g.*, levoglucosan, furans) which can either evaporate or breakdown to form secondary products. Primary and secondary volatiles make up the final bio-oil product. As biomass samples become larger (and diffusion length scales increase) or reaction temperatures rise, volatile products are more likely to break down (*via* secondary reactions). To escape the intermediate liquid, volatiles must diffuse from liquid bulk to the gas–liquid interface. The extent of product breakdown within the condensed phase depends on the relative rates of secondary pyrolysis chemistry and mass transport.

The relevant reaction pathways must be identified in order to determine the contribution of secondary chemistry on the final bio-oil product. For example, levoglucosan (a primary product of cellulose pyrolysis) can break down within the intermediate liquid to form pyrans and light oxygenates.[44] Similarly, lignin can fragment to oxygenated aromatic monomers which can rapidly re-react to form oligomers or char.[62] Predicting the abundance and relative rate of secondary reactions is critical to developing master pyrolysis models as well as delineating transport- and reaction-controlled pyrolysis.

Evidence exists that transport controls the rate of primary and secondary pyrolysis reactions. A review by Milosavljevic and Suuberg demonstrated that volatilization in cellulose pyrolysis is kinetically limited (E_a = 200 kJ mol^{-1}) for slow temperature changes (<10 K min^{-1}) but not for high temperature ramps (>10 K min^{-1}). Additionally, they speculated that the latter process is transport limited due to the lower activation energy (E_a = 140 kJ mol^{-1}).[57,63]

By comparing yields for micrometer- and millimeter-scale cellulose samples, we have recently shown that transport-limitations can cause order of magnitude changes in the production of certain products.[17] Fig. 9 shows that when levoglucosan is co-pyrolyzed with a non-volatile carbohydrate (*e.g.*, fructose), it can break down within the intermediate through secondary pyrolysis pathways. However, the break down only occurs for millimeter-scale powder samples; secondary pyrolysis chemistry is not observed when micrometer-scale thin-films are employed. This is

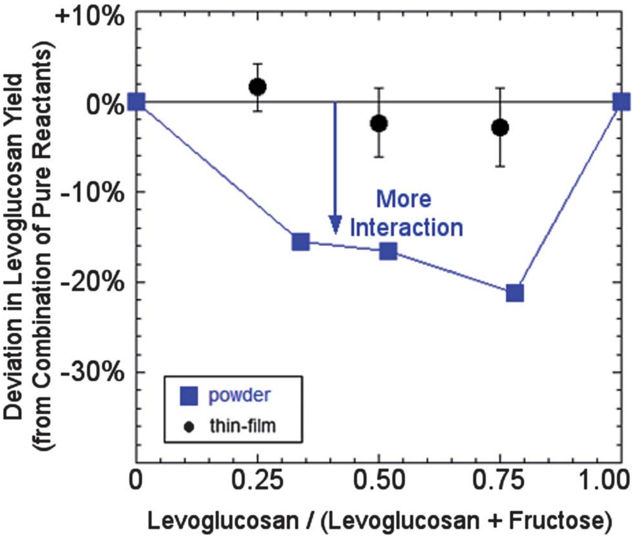

Fig. 9 The effect of residence time on secondary reactions. Combinations of levoglucosan and fructose are co-pyrolyzed at 500 °C in order to evaluate levoglucosan breakdown to form secondary products within the intermediate liquid. The effect of residence time in the intermediate liquid is evaluated by comparing levoglucosan breakdown in powder and thin-film co-pyrolysis which differ in characteristic diffusion length by two orders of magnitude.

largely due to the shorter residence time in thin-film experiments which enable levoglucosan to escape the intermediate liquid before reacting. However, the increased length-scale in powder experiments results in longer residence times which enable secondary pyrolysis of levoglucosan. Determining the residence time of volatiles within the intermediate liquid requires knowledge of both mass transport properties (*i.e.*, diffusivity) and the activities of condensed-phase products and intermediates. The vapor pressure of pyrolysis products, such levoglucosan or cellobiose, has been measured experimentally, but accurate volatility measurements are difficult because of their reactivity.[64] Additionally, applying experimental techniques or simulations to predict diffusion rates through the intermediate liquids is not straightforward. The intermediate liquid is extremely short-lived (<1 s) and the composition almost certainly varies with extent of reaction (larger oligomers early on and more volatile monomers near the end). For this reason, diffusivities and activity coefficients likely vary as the biomass particle pyrolyzes and developing expressions to predict them is non-trivial. This aspect also indicates a coupling of chemistry and transport; the chemistry determines the composition of the liquid and thus the transport properties, and in turn, transport properties control the fate of these intermediates toward escaping or further reaction.

Challenge #4: how does solvation affect intermediate liquid chemistry?

Primary and secondary pyrolysis chemistries are impacted by the reaction environment within the condensed phase. The liquid intermediate may act as a pseudo-solvent altering both thermodynamics of products, intermediates and products as well as altering transition states thereby influencing activation energies. Since both thermodynamics and kinetics affect the final product distribution, understanding the role of solvation is critical to predicting the overall performance of pyrolysis processes.

Previous work has investigated glucose and cellobiose pyrolysis by assuming a gas-phase environment.[65,66] However, the problem with this approach is that in the aqueous-phase conversion of sugars to furans, it has been shown that not only is the electronic structure of reacting species altered,[67] but solvent/liquid molecules (in this case water) can actually act participate in the mechanism, can change the barrier by as much as 14 kcal mol^{-1}, and can solvate and potentially shield certain bonds.[96] Additionally, recent experimental work has indicated that hydrogen exchange occurs between intermediates and products within molten biomass.[97] In these experiments (Fig. 10), deuterated glucose was reacted with levoglucosan, and the extent of H/D exchange for each product was measured to reveal that significant exchange occurs in products that undergo dehydration. This phenomenon could be described by free protons within the intermediate liquid which could enable the formation of ionic species, which in turn selectively catalyze pyrolysis reactions (*e.g.*, anhydro-bridge formation). Therefore, understanding the free proton concentration (pH) of the intermediate liquid is crucial to resolving the solvation challenge. It is also possible Brønsted acids are readily available to catalyze other reactions such as hydrolysis which depolymerize cellulose. Undoubtedly, the reaction environment (pH, electronic state) changes with conversion, and characterizing the intermediate liquid could point towards the dominant type of chemistry (*e.g.*, homolytic *vs.* heterolytic; free ions *vs.* pericyclic reactions).

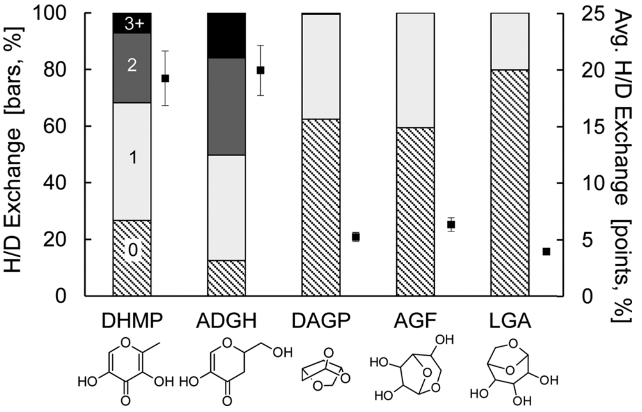

Fig. 10 Hydrogen exchange in pyrolysis products. Hydrogen exchange is shown in terms of total hydrogens exchanged in a product (bars) and percent (of total) hydrogens exchanged (squares). Hydrogen exchange was determined by co-pyrolyzing levoglucosan (the most abundant product of cellulose pyrolysis) and deuterated glucose (D12 – all hydrogens). Powder samples were pyrolyzed at 500 °C.[44]

Characterizing the intermediate liquid in pyrolysis could utilize the existing knowledge of low-temperature solvent systems. However, the high temperature, brief lifetime and chemical complexity of the solution make extracting detailed information difficult. While *in situ* experimental approaches to characterizing the liquid intermediate (such as infrared spectroscopy) would be useful, these approaches will be challenging due to the brief lifetime and chemical complexity of the reacting solution. *In situ* techniques would almost certainly require 10 ms or less temporal resolution in order to detect a particular property of the intermediate liquid. Determination of intermediate liquid properties as a function of time would require even faster responses, likely 1 ms or less. Future techniques capable of rapid collection of the intermediate liquid using millisecond sampling would enable separation of condensed phase components by molecular weight and/or polarity. This separation step could in turn allow for more advanced *ex situ* analytical techniques, such as NMR.

Challenge #5: how do inorganic catalysts influence condensed-phase chemistry?

The multiscale and multiphase nature of biomass pyrolysis makes it difficult to understand the role of catalysts. In general, pyrolysis catalysts can be classified in one of three groups, as shown in Fig. 11:

- *Natural catalysts (intraparticle)*: catalysts naturally exist within biomass in the form of ions such as Mg^{2+} and Ca^{2+} that are important to biological function of the organism.[24] During the pyrolysis process, these ions exist within the intermediate liquid and are converted to oxides such as MgO and CaO solids (ash) which also have catalytic activity.[18,61]
- *Primary catalysts (extraparticle)*: heterogeneous catalysts that exist outside of the particle could be used to influence pyrolysis chemistry once the intermediate liquid forms. Such extraparticle catalysts interact with biomass particles thermally

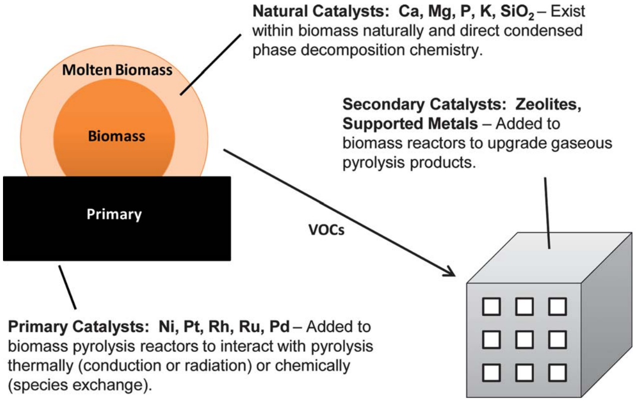

Fig. 11 Three classes of pyrolysis catalysts. Natural catalysts are native to biomass and are embedded within biomass nanostructures, while primary catalysts are non-native but can influence the chemistry through contact with the intermediate liquid. Secondary catalysts upgrade pyrolysis vapors and are commonly used in fluidized bed reactors.

(conduction or radiation) or chemically (chemical exchange and catalysis).[68,69]

- *Secondary catalysts (vapor)*: catalysts added to pyrolysis reactors that exist outside of the particle wherein vapor products could diffuse, adsorb and react to produce value-added products (also volatile). Secondary catalysts do not influence condensed-phase chemistry.[70–75]

A major research challenge is to determine how natural catalysts alter pyrolysis chemistry within the intermediate liquid. Inorganic materials are naturally embedded within solid biomass and although they make up a small weight fraction (<1%), these catalysts can drastically alter pyrolysis product distributions.[18,61] A brief analysis of the experimental literature shows that under certain reaction conditions, inorganics (*e.g.*, MgO, CaO, SiO, ash) can facilitate carbon–carbon bond cleavage to produce a bio-oil with an overall lower energy content due to increased light oxygenates and permanent gases and fewer furans and anhydrosugars.[18] While experimental data are limited, information seems to indicate that certain inorganics promote the formation of lower value products (light oxygenates and permanent gases) while others do not. For instance, calcium oxides seem to have negligible (<20%) effect on levoglucosan formation while others (*e.g.*, ash) appear to have a drastic (>60%) impact.[18] Inorganic catalysts have largely been viewed as an inhibitor to pyrolysis technology[18] but it remains open as to whether certain inorganics could promote a more desirable (*e.g.*, through deoxygenation) bio-oil product. Similar to the previous challenges, this is an opportunity for detailed models to explain the role of natural catalysts and direct the development of impregnated catalysts tailored to maximize bio-oil quality.

Challenge #6: how does char form in pyrolysis?

While biomass-derived char has notable energy content, it is generally accepted that char is an undesired by-product of pyrolysis for production of biofuels. Char can generally form through a number of mechanisms including gas-phase repolymerization of volatile products, polymerization of condensed-phase species, and dehydration of biopolymers (without depolymerization). The latter is the dominant mechanism at low temperatures encountered in slow pyrolysis where char products retain the superstructure of the biomass starting material.[76] In fast pyrolysis, char generally does not retain the structure of the original sample indicating that repolymerization may be the dominant mechanism for its formation.

Char yields vary significantly depending on the biomass feedstock. Recent work by our group[17,56] and others[45] has shown that long-chain cellulose produces much less char compared to glucose (5–13% *versus* 19–29%). This result is surprising since glucose has a much lower molecular weight, implying that fewer deoxygenation steps are required to generate a volatile product. Repolymerization of small molecule products and intermediates is the only possible formation route for glucose-derived char while cellulosic char can be produced from either repolymerization of volatiles or dehydration without depolymerization. The paths and fraction of char formation from small molecules is expected to depend on the functional groups of each molecule.

Mechanisms have been proposed for aqueous-phase humin formation, which may have analogies to pyrolysis-derived char. In the acid-catalyzed conversion of hydroxymethylfurfural (HMF), Patil and Lund suggest that humins form from polymerization of furans *via* aldol condensation.[77] This reaction produces a net dehydration and a carbon–carbon double bond and requires each of the two reactants to contain a carbonyl group (in form of an aldehyde or ketone).

To examine if aldol condensation reactions are present in pyrolytic char formation mechanisms, we compare char yield for glucose-based carbohydrates and the fraction of carbonyl groups present in volatile products. As shown in Fig. 12, a large range of conditions for carbohydrate pyrolysis lead to a simple relationship: as the yield of carbonyl groups increases (in bio-oil products), the yield of char also increases. This relationship indicates that aldol

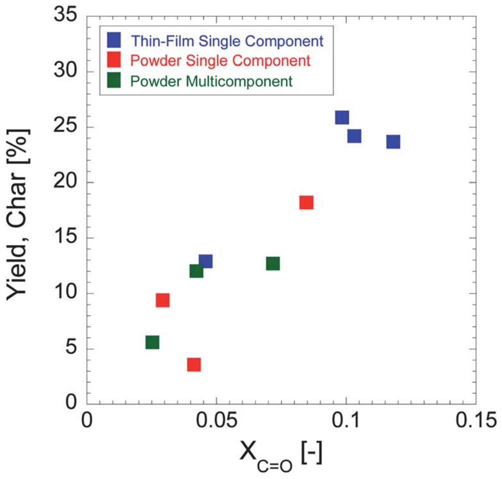

Fig. 12 Yield of char *versus* fraction of carbonyl carbons (C═O) within bio-oil products ($X_{C=O}$). Experimental data are shown for thin-film single component (glucose, cellobiose, cellotriose and cellulose),[17,56] powder single component (cellulose, cellulose + NaCl, cellulose + $MgCl_2$),[17,18] and powder multicomponent (mixture of levoglucosan and fructose) pyrolysis.[44] Only carbonyls in high molecular weight products (>4 carbons) are included in $X_{C=O}$ since polymerization of smaller products will still produce volatiles (rather than char). The reaction temperature for all experiments is 500 °C.

condensation chemistry may play a role in pyrolytic char formation. If true, this implies that a connection exists between the better-known aqueous-phase humin formation mechanisms which could enable simplification of pyrolytic char formation chemistry.

Challenge #7: how can heat transfer models be used to improve bio-oil yield and quality?

Heat transfer is important to consider when designing pyrolysis reactors. The rate at which samples are heated affects bio-oil yield and composition (or quality) and substantial differences in products are observed from rapid and slow heating. Over the past three decades, it has been conclusively shown that slow heating leads predominately to char, while higher heating rates (0.1–1.0 MW m^{-2}) produce higher yields of volatile organics (*i.e.*, bio oil).[18,39,40,68,69,78] This knowledge has led to a number of reactor designs where different heating methods are employed. Examples of pyrolysis vessels include fluidized bed reactors,[70,72,79] ablative reactors,[68,69] and focused radiation reactors.[32,42]

Predicting thermal profiles within a pyrolyzing lignocellulosic particle is a challenge since there is little experimental data available. During the initial heating, conduction transports thermal energy through the complex composite structure of the lignocellulosic particle. Biomass (*e.g.*, a wood fiber) is known to have anisotropic transport properties, such as thermal conductivity, as well as significant functionality with respect to temperature and composition. These complexities are due to many factors (which vary during the conversion process) such as density, composition, and inclination of the grain. Anisotropic functionalities result from the wood microstructure[80] as well as the orientation of the lignocellulose structure (*e.g.*, cellulose microfibrils) within cell walls.[81]

As the particle temperature exceeds 350 °C, pyrolysis chemistry accelerates and leads to the formation of the liquid intermediate. This phase change significantly complicates prediction of intra-particle heat transfer since the intermediate liquid can coalesce and interact with nearby structures.[31] Additionally, information is needed on the heat capacity, thermal conductivity and latent heats associated with the solid/intermediate liquid/vapor system. All of these parameters may be a strong function of composition and temperature. Heat transfer within this complex, three-phase system must also account for thermal convection from vapors driven from the intermediate liquid. Two approaches can be taken to address the aforementioned complexities: either these phenomena should be (i) investigated individually or (ii) system complexity should be reduced (*e.g.*, by identifying unimportant functionalities or parameters). The latter approach is certainly more tractable in the near term since experimental and computational techniques capable of characterizing solid and intermediate liquid properties are in their infancy. For example, simulations (such as molecular dynamics simulations) or experiments can be used to identify which structures are rate-limiting (*i.e.*, which have the lowest thermal conductivity) in a composite biomass particle.

Challenge #8: how are aerosols produced and how do they affect bio-oil properties?

While the dominant products of pyrolysis are evaporated vapors, some research has also focused on aerosols generated during fast pyrolysis. Previous work suggested that as much as 30% of bio-oil originates from aerosols and particulates,[41,82] and up to 60% of the inorganic content in bio-oil is connected to aerosol emissions.[83] Historically, these particles are thought to be produced from the nucleation and condensation of vapors.[84] However, it has been shown that both bio-oil and aerosols contain nonvolatile biomass-derived oligomers which retain their original linkages (*i.e.*, they were not formed by repolymerization) such as lignin tetramers and carbohydrate oligomers (with degree of polymerization up to nine).[85–87] The mysterious origin of these nonvolatile compounds led to speculation that aerosols were produced by a ‘thermo-mechanical ejection’ mechanism where lignocellulosic particles exhibit ‘explosive destruction’ and solid fragments are expelled into the gas-phase.[42,82]

We have recently described a new mechanism of primary aerosol generation directly from the intermediate liquid called ‘Reactive Boiling Ejection’ (RBE).[34] Fig. 13 shows spontaneous ejections of aerosol particles (<10 μm) from biomass with velocities of 0.1–0.5 m s^{-1}. Computational fluid dynamics simulations using the measured ejection velocities and experimental surface tension for the cellulose-derived intermediate liquid (10^{-6} to 10^{-5} N m^{-1}) reveal that interfacial bubble-collapse is the dominant mechanism for aerosol production. RBE occurs when the thin liquid film (at the droplet/bubble interface) fragments and the bubble collapses thereby leading to the formation of a liquid jet extending from the surface. The liquid jet subsequently fragments into aerosol particles which are ejected into the gas-phase. The composition of cellulose-derived aerosols was shown only to contain one of several possible carbohydrate dimers, solely cellobiosan. This finding indicates that aerosols have the same composition as the intermediate liquid, which is consistent with the RBE mechanism.

The RBE mechanism is only the beginning of addressing the aerosol generation research challenge. There are numerous potential aerosol generation mechanisms, and it is unknown if these alternative mechanisms occur within the intermediate liquid. Prediction of the RBE or other aerosol mechanisms in lignocellulosic materials will require detailed information on the properties of the intermediate liquid, such as surface tension and viscosity. Both of these properties are likely to vary over the lifetime of intermediate liquid since the composition changes with time. Additionally, it is also not known how the RBE mechanism can be implemented in a cellular environment typical of real biomass (*i.e.*, wood fibers). It has been shown that cellulose aerosols are small (10^{-8} to 10^{-5} m) and almost all ejected particles are smaller than the lumen ($\sim 10^{-5}$ m) and parenchyma (10^{-5} to 10^{-4} m) within woody biomass. A complete description of aerosol generation will require both an understanding of generation mechanisms and the process by which aerosols escape lignocellulosic microstructures.

Challenge #9: what experiments can validate particle pyrolysis models?

Integrating the aforementioned reaction and transport phenomena into a single model is non-trivial and validating the model is even more of a challenge. Future particle pyrolysis models should be capable of predicting volatilization as a function of time for various biomass feedstocks (necessary for reactor design) as

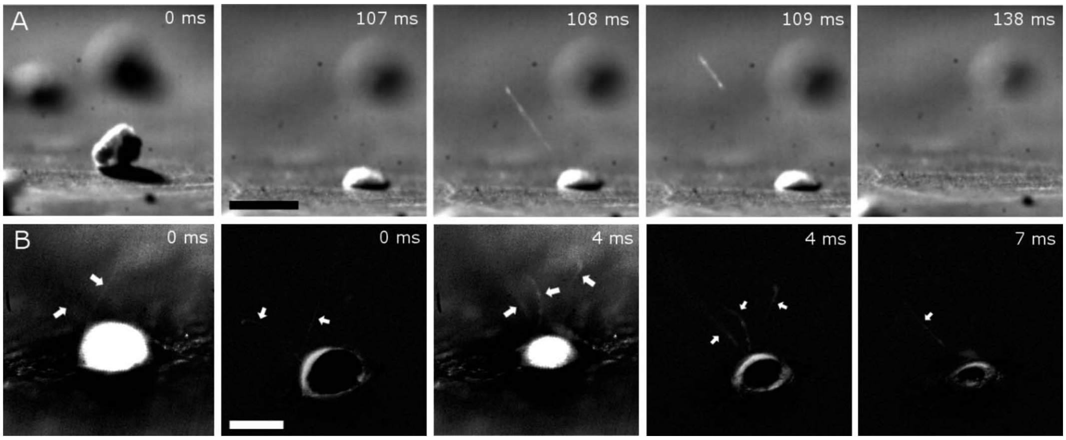

Fig. 13 Aerosol generation by reactive boiling ejection of molten cellulose. High-speed photography (one-millisecond resolution) reveals that a particle of microcrystalline cellulose thermally decomposes to an intermediate liquid on a 700 °C alumina surface which violently bubbles and evaporates. (A) Bubbles collapsing at the droplet interface can potentially form a liquid jet which extends from the surface and fragments to aerosol particles (<10 μm) moving at high speed (0.1–0.5 m s^{-1}). (B) A droplet of molten cellulose exhibits multiple aerosol ejections highlighted with white arrows (first and third panels). Subtraction of serial frames in the second, fourth, and fifth frames indicates moving objects (white) relative to stationary background (black). Scale bars = 300 μm.

well as the distribution of pyrolysis products. These models will be based on existing particle transport models, but with more detailed and fundamental methods for estimating transport parameters (*e.g.*, thermal conductivity, irradiative view factors, *etc.*), condensed-phase thermodynamics, and reaction kinetics.

Fast pyrolysis of woody particles (characteristic length of millimeters) occurs at heating conditions which lead to internal compositional and thermal gradients consistent with a low Pyrolysis number (Py^{I} and $Py^{II} \ll 1$) shown in Fig. 6. For these conditions, it is generally understood that particles exposed to high heat transfer (10^{-1} to 10^{0} MW m^{-2}) initially undergo rapid heating by conduction and discharge of water vapor through the porous, cellular network of woody biomass. The remaining dried zone continues to increase in temperature before undergoing thermal degradation to produce solid char and gases/vapors, the latter of which move by pressure-driven flow through the porous particle to the surface. As observed by Di Blasi, this series of reaction events leads to four reaction zones which progress through the particle: virgin moist wood, a region of drying wood, the pyrolysis zone, and the char layer.[19]

Modeling of wood particle pyrolysis and accounting for each of the reaction zones requires detailed information as well as appropriate assumptions. Additionally, parameter values and functionalities strongly influence the predicted conversion conditions within the particle.[88] The pyrolysis chemistry will include the kinetic parameters necessary for prediction of the relative rates of competitive lumped or detailed chemistry pathways. Prediction of heat transfer must account for variable transport parameters in virgin biomass, dry biomass, reacting intermediate liquids, and the remaining char zone. Heat transfer by radiation is generally not significant for fast pyrolysis conditions and is typically not included.[89] Additionally, mass transfer of volatile products will vary with local conditions; diffusion rates depend on local porosity, density, and composition while convection depends on the extent of pressure driven flow through the particle pores.

The complexity of wood particle pyrolysis models has prompted a need for experimental validation techniques. For fast pyrolysis reaction conditions, most effort has been directed at characterizing the integral yields of gases, char and volatile components (bio-oil) from cellulose or woody biomass.[90–92] Validation of simplified reaction/transport pyrolysis models based on product phase has led to the capability for finding reaction conditions that optimize bio-oil yield. However, it has been recognized that, "…new experimental systems and extensive measurements are needed to provide the basis for process understanding and model formulation…".[19] The complex interdependence of transport and pyrolysis chemistry will require more detailed experimental data that will likely be based on *in situ* measurements of composition and temperature. Thus, new experimental techniques are required with pyrolysis-specific spatial and temporal resolution (micrometers to milliseconds), such as thin film pyrolysis and high speed photography.

Challenge #10: what causes particle shrinkage and how can it be predicted?

In addition to permanent gases and volatiles (i.e., bio-oil), fast pyrolysis of lignocellulosic particles also produces a solid char particle of reduced dimensions. Very simple experiments measuring the size of lignocellulosic particles such as wood before and after pyrolysis have shown that particles shrink by as much as 50% during conversion.[93] This change in physical structure during reaction has implications for predicting the conversion process such as variation in characteristic transport lengths for both heat transfer (*e.g.*, particle size) and mass transfer (*e.g.*, the internal microstructure/cell wall). Additionally, the change in porosity resulting from shrinkage alters the resistance to pressure driven flow through the particle and the convection of volatile species to the particle surface.

The importance of predicting particle shrinkage has led to a number of methods which relate dimensions to physical

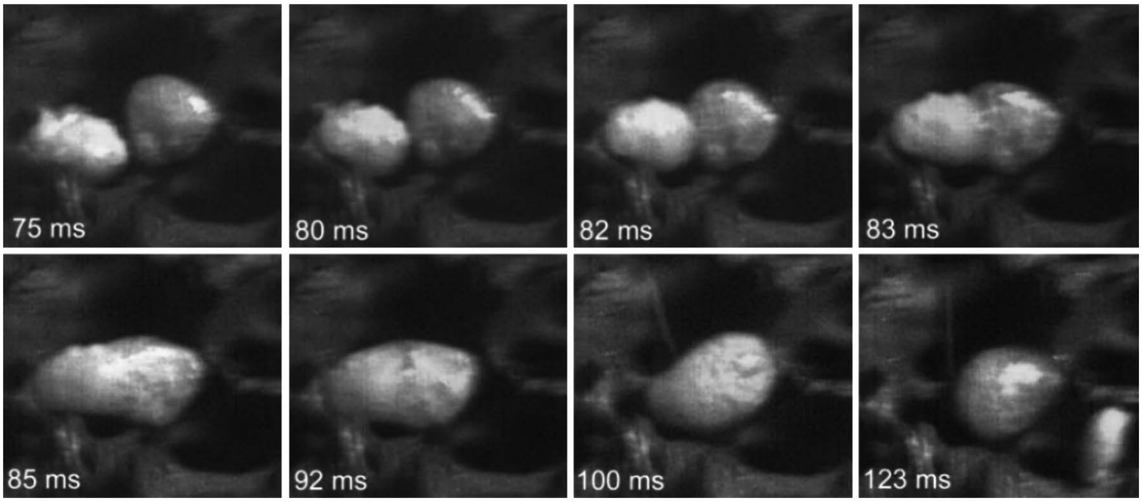

Fig. 14 Coalescence of liquid intermediate cellulose. Two particles of microcrystalline cellulose (250 μm in diameter) react on 700 °C structured alumina and form intermediate liquid cellulose. The two droplets rapidly coalesce within a few milliseconds (80–83 ms) to form a larger droplet which subsequently evaporates.

properties (*e.g.*, density). For example, researchers have proposed a one-dimensional model which assumes that wood microstructure collapse has a linear relationship with wood composition. This connection can be described by a shrinkage factor, α, in addition to several other parameters.[94] Alternatively, a two-dimensional model has compared the uniform shrinkage method throughout the particle with a shrinking shell model that assumes that microstructure collapse occurs locally with the reaction wave within the pyrolyzing particle.[95] Whatever shrinkage model is selected, an accurate predictor of particle shrinkage has been shown to be important for a complete prediction of conversion time.[19] A more detailed understanding of the role of shrinkage and how it affects product yields needs to be pursued.

An understanding of ‘structural changes’ (or particle shrinkage) during pyrolysis has previously been identified as an opportunity to improve understanding of pyrolysis fundamentals.[19] One proposed mechanism for shrinkage put forth by Mamleev *et al.* states that the cellular walls of the biomass microstructure can be likened to a ‘porous viscous suspension’ during reaction,[37] consistent with an intermediate liquid. The resulting forces of adhesion associated with the liquid are then proposed to lead to the local shrinkage of the sample. This proposed explanation is also consistent with droplets of intermediate liquid cellulose which have been observed to coalesce on the timescale of milliseconds as shown in Fig. 14. Further details regarding the properties of the fluid, local reaction chemistry and composition, and local shrinkage will be required to support this mechanism. *In situ* imaging and structural characterization methods will provide unprecedented and much needed information for developing a new generation of models.

Conclusions

In summary, we propose ten fundamental challenges that we believe will contribute to the path toward the successful commercialization of thermochemical biofuels. Solutions to each of the challenges will require in-depth understanding of the underlying phenomena and will ultimately lead to multiscale models of chemistry, particles and reactors. Armed with these tools, engineers can then accurately design and optimize next-generation pyrolysis processes. While these challenges are important, they are by no means comprehensive. For example, there is a significant interest in revealing lignin pyrolysis chemistry, for which we have only briefly addressed in these challenges. The challenges of lignin and numerous other problems follow analogously from the considered challenges of cellulose; it is almost certain that as our understanding of pyrolysis evolves, new problems will be revealed that alter the path forward to enhanced predictability and successful commercialization of biomass pyrolysis for biofuels production.

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References

1 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484–489.
2 K. Sanderson, *Nature*, 2006, **444**, 673–676.
3 R. D. Perlack, L. L. Wright, A. F. Turhollow, R. L. Graham, B. J. Stokes and D. C. Erbach, *Biomass as a Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*, Oak Ridge National Laboratory, Oak Ridge, TN, 2005.
4 R. D. Perlack and B. J. Stokes, *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry*, Oak Ridge National Laboratory, Oak Ridge, TN, 2011.
5 R. P. Anex, A. Aden, F. K. Kazi, J. Fortman, R. M. Swanson, M. M. Wright, J. A. Satrio, R. C. Brown, D. E. Daugaard, A. Platon, G. Kothandaraman, D. D. Hsu and A. Dutta, *Fuel*, 2010, **89**, S29–S35.
6 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.

7 NSF, *National Science Foundation. Chemical, Bioengineering, Environmental, and Transport Systems Division*, ed. G. W. Huber, University of Massachusetts Amherst, 2008, p. 180.
8 A. V. Bridgwater and G. V. C. Peacocke, *Renewable Sustainable Energy Rev.*, 2000, **4**, 1–73.
9 A. V. Bridgwater, *J. Anal. Appl. Pyrolysis*, 1999, **51**, 3–22.
10 A. V. Bridgwater, D. Meier and D. Radlein, *Org. Geochem.*, 1999, **30**, 1479–1493.
11 D. Mohan, C. U. Pittman and P. H. Steele, *Energy Fuels*, 2006, **20**, 848–889.
12 A. Oasmaa and S. Czernik, *Energy Fuels*, 1999, **13**, 914–921.
13 A. Oasmaa and D. Meier, *J. Anal. Appl. Pyrolysis*, 2005, **73**, 323–334.
14 S. Czernik and A. V. Bridgwater, *Energy Fuels*, 2004, **18**, 590–598.
15 T. P. Vispute, H. Y. Zhang, A. Sanna, R. Xiao and G. W. Huber, *Science*, 2010, **330**, 1222–1227.
16 S. P. Zhang, Y. J. Yan, T. C. Li and Z. W. Ren, *Bioresour. Technol.*, 2005, **96**, 545–550.
17 M. S. Mettler, S. H. Mushrif, A. D. Paulsen, A. D. Javadekar, D. G. Vlachos and P. J. Dauenhauer, *Energy Environ. Sci.*, 2012, **5**, 5414–5424.
18 P. R. Patwardhan, J. A. Satrio, R. C. Brown and B. H. Shanks, *Bioresour. Technol.*, 2010, **101**, 4646–4655.
19 C. Di Blasi, *Prog. Energy Combust. Sci.*, 2008, **34**, 47–90.
20 D. J. Cosgrove, *Methods Mol. Biol.*, 2001, **715**, 291–303.
21 D. Fengel and G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, New York, 1984.
22 H. Mark, *J. Phys. Chem.*, 1940, **44**, 764–788.
23 W. A. Kenney, L. Sennerbyforsse and P. Layton, *Biomass*, 1990, **21**, 163–188.
24 L. S. Levitt, *Science*, 1954, **120**, 33–35.
25 Y. Horikawa, T. Itoh and J. Sugiyama, *Cellulose*, 2006, **13**, 309–316.
26 E. M. Rubin, *Nature*, 2008, **454**, 841–845.
27 R. M. Rowell, *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Boca Raton, FL, 2005.
28 M. T. Holtzapple, A. E. Humphrey and J. D. Taylor, *Biotechnol. Bioeng.*, 1989, **33**, 207–210.
29 P. Stockburger, *Tappi J.*, 1993, **76**, 71–74.
30 P. Bajpai, *Biotechnol. Prog.*, 1999, **15**, 147–157.
31 P. J. Dauenhauer, J. L. Colby, C. M. Balonek, W. J. Suszynski and L. D. Schmidt, *Green Chem.*, 2009, **11**, 1555–1561.
32 O. Boutin, M. Ferrer and J. Lede, *J. Anal. Appl. Pyrolysis*, 1998, **47**, 13–31.
33 J. Lede, H. Z. Li and J. Villermaux, *J. Anal. Appl. Pyrolysis*, 1987, **10**, 291–308.
34 A. R. Teixeira, K. G. Mooney, J. S. Kruger, C. L. Williams, W. J. Suszynski, L. D. Schmidt, D. P. Schmidt and P. J. Dauenhauer, *Energy Environ. Sci.*, 2011, **4**, 4306–4321.
35 F. Shafizad and Y. L. Fu, *Carbohydr. Res.*, 1973, **29**, 113–122.
36 J. Piskorz, P. Majerski, D. Radlein, A. Vladars-Usas and D. S. Scott, *J. Anal. Appl. Pyrolysis*, 2000, **56**, 145–166.
37 V. Mamleev, S. Bourbigot, M. Le Bras and J. Yvon, *J. Anal. Appl. Pyrolysis*, 2009, **84**, 1–17.
38 E.I. Administration, *International Energy Outlook 2011*, 2012, http://www.eia.doe.gov/oiaf/ieo/world.html, accessed 28 February 2012.
39 A. Broido and M. A. Nelson, *Combust. Flame*, 1975, **24**, 263–268.
40 A. G. W. Bradbury, Y. Sakai and F. Shafizadeh, *J. Appl. Polym. Sci.*, 1979, **23**, 3271–3280.
41 D. S. G. Radlein, A. Grinshpun, J. Piskorz and D. S. Scott, *J. Anal. Appl. Pyrolysis*, 1987, **12**, 39–49.
42 J. Lede, F. Blanchard and O. Boutin, *Fuel*, 2002, **81**, 1269–1279.
43 Y. C. Lin, J. Cho, G. A. Tompsett, P. R. Westmoreland and G. W. Huber, *J. Phys. Chem. C*, 2009, **113**, 20097–20107.
44 M. S. Mettler, A. D. Paulsen, D. G. Vlachos and P. J. Dauenhauer, *Energy Environ. Sci.*, 2012, DOI: 10.1039/c2ee21305b, in press.
45 P. R. Patwardhan, J. A. Satrio, R. C. Brown and B. H. Shanks, *J. Anal. Appl. Pyrolysis*, 2009, **86**, 323–330.
46 F. Shafizadeh, T. T. Stevenson, T. G. Cochran and R. H. Furneaux, *Carbohydr. Res.*, 1978, **67**, 433–447.
47 J. D. Nicholson, *Analyst*, 1978, **103**, 193–222.
48 C. Di Blasi, *Ind. Eng. Chem. Res.*, 1996, **35**, 37–46.
49 J. M. Cho, J. M. Davis and G. W. Huber, *ChemSusChem*, 2010, **3**, 1162–1165.
50 C. J. Gomez, G. Varhegyi and L. Puigjaner, *Ind. Eng. Chem. Res.*, 2005, **44**, 6650–6660.
51 O. Onay and O. M. Kockar, *Renewable Energy*, 2003, **28**, 2417–2433.
52 D. L. Pyle and C. A. Zaror, *Chem. Eng. Sci.*, 1984, **39**, 147–158.
53 J. Lede and J. Villermaux, *Can. J. Chem. Eng.*, 1993, **71**, 209–217.
54 J. Lede, *Biomass Bioenergy*, 1994, **7**, 49–60.
55 O. Authier, M. Ferrer, A. E. Khalfi and J. Lede, *Int. J. Chem. React. Eng.*, 2010, **8**, A78.
56 M. S. Mettler, A. D. Paulsen, D. G. Vlachos and P. J. Dauenhauer, *Green Chem.*, 2012, **14**, 1284–1288.
57 I. Milosavljevic, V. Oja and E. M. Suuberg, *Ind. Eng. Chem. Res.*, 1996, **35**, 653–662.
58 R. J. Evans and T. A. Milne, *Energy Fuels*, 1987, **1**, 123–137.
59 F. Shafizadeh, *Adv. Carbohydr. Chem.*, 1968, **23**, 419–474.
60 F. J. Kilzer and A. Broido, *Pyrodynamics*, 1965, **2**, 151.
61 G. R. Ponder, G. N. Richards and T. T. Stevenson, *J. Anal. Appl. Pyrolysis*, 1992, **22**, 217–229.
62 M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer and C. Roy, *Biomass Bioenergy*, 2007, **31**, 222–242.
63 I. Milosavljevic and E. M. Suuberg, *Ind. Eng. Chem. Res.*, 1995, **34**, 1081–1091.
64 V. Oja and E. M. Suuberg, *J. Chem. Eng. Data*, 1999, **44**, 26–29.
65 R. S. Assary and L. A. Curtiss, *ChemCatChem*, 2011, **4**, 200–205.
66 M. H. Zhang, Z. F. Geng and Y. Z. Yu, *Energy Fuels*, 2011, **25**, 2664–2670.
67 R. S. Assary, P. C. Redfern, J. R. Hammond, J. Greeley and L. A. Curtiss, *J. Phys. Chem. B*, 2010, **114**, 9002–9009.
68 P. J. Dauenhauer, B. J. Dreyer, N. J. Degenstein and L. D. Schmidt, *Angew. Chem., Int. Ed.*, 2007, **46**, 5864–5867.
69 J. L. Colby, P. J. Dauenhauer, B. C. Michael, A. Bhan and L. D. Schmidt, *Green Chem.*, 2010, **12**, 378–380.
70 A. Aho, N. Kumar, K. Eranen, T. Salmi, M. Hupa and D. Y. Murzin, *Fuel*, 2008, **87**, 2493–2501.
71 P. T. Williams and N. Nugranad, *Energy*, 2000, **25**, 493–513.
72 T. R. Carlson, T. R. Vispute and G. W. Huber, *ChemSusChem*, 2008, **1**, 397–400.
73 T. R. Carlson, G. A. Tompsett, W. C. Conner and G. W. Huber, *Top. Catal.*, 2009, **52**, 241–252.
74 T. R. Carlson, J. Jae, Y. C. Lin, G. A. Tompsett and G. W. Huber, *J. Catal.*, 2010, **270**, 110–124.
75 M. C. Samolada, W. Baldauf and I. A. Vasalos, *Fuel*, 1998, **77**, 1667–1675.
76 M. Kumar and R. C. Gupta, *J. Mater. Sci.*, 1995, **30**, 544–551.
77 S. K. R. Patil and C. R. F. Lund, *Energy Fuels*, 2011, **25**, 4745–4755.
78 G. Varhegyi, E. Jakab and M. J. Antal, *Energy Fuels*, 1994, **8**, 1345–1352.
79 F. A. Agblevor, S. Beis, O. Mante and N. Abdoulmoumine, *Ind. Eng. Chem. Res.*, 2010, **49**, 3533–3538.
80 B. M. Suleiman, J. Larfeldt, B. Leckner and M. Gustavsson, *Wood Sci. Technol.*, 1999, **33**, 465–473.
81 J. R. Barnett and V. A. Bonham, *Biol. Rev.*, 2004, **79**, 461–472.
82 J. Piskorz, P. Maherski and D. Radlein, *Biomass, a Growth Opportunity in Green Energy and Value-Added Products*, Amsterdam, 1999.
83 N. Jendoubi, F. Broust, J. M. Commandre, G. Mauviel, M. Sardin and J. Lede, *J. Anal. Appl. Pyrolysis*, 2011, **92**, 59–67.
84 P. R. Patwardhan, R. C. Brown and B. H. Shanks, *ChemSusChem*, 2011, **4**, 1629–1636.
85 B. Scholze, C. Hanser and D. Meier, *J. Anal. Appl. Pyrolysis*, 2001, **58**, 387–400.
86 E. Fratini, M. Bonini, A. Oasmaa, Y. Solantausta, J. Teixeira and P. Baglioni, *Langmuir*, 2006, **22**, 306–312.
87 J. A. Lomax, J. M. Commandeur, P. W. Arisz and J. J. Boon, *J. Anal. Appl. Pyrolysis*, 1991, **19**, 65–79.
88 C. Di Blasi, *Prog. Energy Combust. Sci.*, 1993, **19**, 71–104.
89 L. J. Curtis and D. J. Miller, *Ind. Eng. Chem. Res.*, 1988, **27**, 1775–1783.
90 C. Di Blasi, *Ind. Eng. Chem. Res.*, 1996, **35**, 37–47.
91 C. Di Blasi, *Chem. Eng. Sci.*, 2000, **55**, 5999–6013.
92 C. Di Blasi, *AIChE J.*, 2002, **48**, 2386–2397.
93 D. Y. Kim, Y. Nishiyama, M. Wada and S. S. Kuga, *Wood and Cellulose: Building Blocks for Chemicals and Fuels and Advanced Materials*, Syracuse, New York, 2000.
94 C. Di Blasi, *Chem. Eng. Sci.*, 1996, **51**, 1121–1132.
95 M. Bellais, K. O. Davidsson, T. Liliedahl, K. Sjostrom and J. B. C. Pettersson, *Fuel*, 2003, **82**, 1541–1548.
96 S. H. Mushrif, S. Caratzoulas and D. G. Vlachos, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2637–2644.
97 M. S. Mettler, A. D. Paulsen, D. G. Vlachos and P. J. Dauenhauer, *Energy Environ. Sci.*, 2012, DOI: 10.1039/C2EE21305B, in press.