



## Thermochemical Conversion of Biomass Components-Recent Research and Future Opportunity

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### Introduction

The overarching goal of biomass research is to develop innovative and pragmatic routes to exploit and utilize biomass resources [1,2]. These studies focused on both basic science and potential industrial applications [3] and have begun to address several challenges including the overall declining petroleum resources, increasing fuel demands and growing environmental concerns from the use of fossil fuels. In addition, the U.S. Department of Agriculture and U.S. Department of Energy have established a vision to derive 25% of chemicals and materials, and 20% of transportation fuels from biomass by 2030 [4] therefore, it is imperative to develop sustainable production of fuels, chemicals and bio-derived materials. Biomass is a readily available and low-cost material feedstock for biorefining operations that to date have been made primarily from fossil fuel resources [5]. The increasing global presence and growth of the integrated “biorefinery” concept has generated some of the most exciting and relevant technological topics in modern society [6].

Both biochemical and thermochemical conversion technologies have been developed for converting biomass to fuels and chemicals for several decades but some of the most translational results have occurred in the last ~10 years [3]. This short review will focus on recent studies the fundamental chemistry and the application of the thermochemical conversion platform, especially for the pyrolysis process.

Due to the complicated nature of biomass, understanding the biomass pyrolysis pathways calls for fundamental investigation of pyrolytic behaviors of various biomass components, which include cellulose, hemicellulose, lignin, tannin, lipid, protein, and chitin for normal lignocellulosic biomass, algae, and other bioresources [2,7]. This short review will primarily examine recent research for the pyrolysis process for these biomass components and the future opportunities.

### Pyrolytic Behaviours for Major Biomass Components

#### Cellulose

Cellulose is the most abundant terrestrial biopolymer. Generally, bio resources contain approximately 35-50% cellulose [8,9]. The major thermal decomposition product of cellulose has been reported [10,11] as levoglucosan, however, the detailed formation pathway(s) is still being developed. In addition, understanding the decomposition/transformation pathways of levoglucosan during the aging process of

pyrolysis oils is a crucial topic, since levoglucosan is often the most abundant component in whole biomass pyrolysis oils. The applications of levoglucosan, such as fermentation, modification and upgrading, will be a meaningful topic in the near future.

#### Lignin

Lignin is the second most abundant biomass component and the primary renewable aromatic resource in nature, and it's also one of the most complex natural polymers in regards to its chemical structure and composition [4,12-15]. Therefore, thermal deconstruction of lignin is an extremely complicated and crucial topic. The pyrolysis oil produced from lignin has been reported to be the most difficult one to upgrade [16-22]. The very complicated components of lignin pyrolysis oil bring a huge barrier to understand the fundamental chemistry of aging and upgrading processes. Due to the high average molecular weight, complex and unstable structures of lignin pyrolysis oil [23-25]. Many traditional analytical methods are challenged to fully analyze bio-oils. In contrast, advanced NMR methodology continues to improve the analysis of various lignin pyrolysis oils [4,7,8,26,27].

Several model structures, which could represent lignin pyrolysis oil, have been proposed in the literature [19,28] and some synthesized compounds based on these model structures have been used to further understand lignin pyrolysis oil. Future pyrolysis studies will continue to use model compounds to explore and define the fundamental chemical mechanisms of pyrolysis.

#### Hemicellulose

Hemicellulose is a polymer of several different sugars, including pentose such as xylose and arabinose and hexoses such as galactose, glucose and mannose. Typically, hemicellulose content in bioresources ranges ~25-30 wt% [29,30]. Surprisingly, there is very limited information about pyrolysis/torrefaction of hemicellulose in the literature. It has been reported [6,31-33] that hemicellulose is the very first component to decompose during the biomass torrefaction process generating a liquid and gas product stream.

In addition, select hemicelluloses are extracted and partially degraded during kraft pulping [34,35] and are byproduct of juice production [36]. Both of these industries and others may be a source of hemicelluloses in the future and hence the investigation of pyrolysis process of hemicelluloses will be very meaningful. The study of pyrolytic behavior of hemicellulose may well begin with mannose—the

most abundant sugar in softwood hemicelluloses, and xylose—the most abundant sugar in hardwood hemicelluloses [29,30].

### Tannin

Tannins are a commonly found biopolymer in the leaves and bark of most plants and can be more abundant than lignin in some plant structures [37]. There are two types of tannin—hydrolysable tannins, which are derivatives of gallic acid and esterified to polyols such as glucose. Condensed tannins are polymers of flavonoids and much more complicated than hydrolyzable tannins [37-39]. There are very limited references investigating the pyrolytic behaviors of tannins. Some preliminary studies [33,38] indicate that pyrolysis of tannin will produce catechol and methyl-catechol that makes this waste biopolymer a promising sustainable resource for these two chemicals. Several model compounds including gallic acid, flavonoid, and tannic acid can be employed to provide insights into the mechanisms of tannin pyrolysis

### Lipid

The research on algae has recently become important in view of its many advantages when compared to the lignocellulosic feedstocks [7,40]. The thermal treatments including liquefaction, pyrolysis and gasification of algae for production of biofuel have been reported as promising methods to utilize this sustainable resource [41,42]. Normally, algae contain carbohydrates, proteins and lipids. In some cases, lipid content in microalgae can reach as high as 70% of dry biomass weight [7]. Even after oil extraction, the residual biomass will still contain some lipids [40]. Therefore, the study of thermal decomposition of lipid will facilitate an understanding of the pyrolytic behavior of algae and its residue.

### Proteins

For algae, the protein content is ~30-50% on a dry matter basis [7]. The protein is also one of the major components of some agriculture wastes. However, there is very limited information about pyrolysis of protein. The fundamental exploration of the pyrolysis of this nitrogen containing natural resource will provide insight into the thermal conversion of algae which can exhibit a series of nitrogen contained pyrolysis products.

### Chitin

Chitin is another abundant polysaccharide in nature with a structure close to cellulose (i.e., replace C2-OH of cellulose with C2-NH-Ac). It is a major structural constituent existing in the exoskeleton or cuticles of crab and other invertebrates, as well as in the cell walls of some fungi [43-45]. Chitin is represented as a linear polysaccharide composed of N-acetyl-D-glucosamine. As the major by-product from the seafood industry, it is a natural future target for pyrolysis studies. Limited current applications of chitin include wound healing, drug release control, antimicrobial activity for food industry, and hair-care cosmetic additions [46-48]. Therefore, it will be of significant economic and environmental of interest if such sustainable chitin bio refining technologies could be developed. Due to its structural similarity cellulose and ~7 wt% of nitrogen contents, the conversion of chitin to nitrogen-containing chemicals or materials will be very attractive. Catalytic liquefaction is a promising method, which could depolymerize the chitin and also yield N-containing products.

The current annual stock of waste biomass is estimated as ~46 exajoules (EJ) from agricultural biomass and ~37 EJ from forestry biomass on a worldwide basis, which totals approximately 83EJ, which is around 20% of the total worldwide energy consumption. Based on the U.S. billion-ton update, the currently (2012) available forestry wastes, which typically are <\$60 per dry ton, is ~90 million dry tons in the U.S. Likewise, current available agricultural residues and waste resources at the same price range are ~240 million dry tons in the U.S. [49]. Certainly, the thermochemical conversion process is a promising approach to convert these waste bio resources to chemicals and biofuel precursors [50]. Future studies on the pyrolytic behavior of biomass components will facilitate the further application for the thermochemical conversion of waste biomass to fuels and chemicals.

### References

1. Sannigrahi P, Ragauskas AJ, Tuskan GA (2010) Poplar as a feedstock for biofuels: a review of compositional characteristics. *Biofuels, Bioproducts and Biorefining* 4: 209-226.
2. David K, Ragauskas AJ (2010) Switchgrass as an energy crop for biofuel production: a review of its ligno-cellulosic chemical properties. *Energy Environ Sci* 3: 1182-1190.
3. Ragauskas AJ, Beckham GT, Biddy MJ, Chandra R, Chen F, et al. (2014) Lignin valorization: improving lignin processing in the biorefinery. *Science* 344: 1246843.
4. Perlack RD, Wright LL, Turhollow AF, Graham RL, Stokes BJ, et al. (2005) Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply.
5. Mu W, Ben H, Ragauskas A, Deng Y (2013) Lignin pyrolysis components and upgrading-technology review. *Bioenergy Res* 6: 1183-1204.
6. Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, et al. (2006) The path forward for biofuels and biomaterials. *Science* 311: 484-489.
7. Zhao C, Brück T, Lercher JA (2013) Catalytic deoxygenation of microalgae oil to green hydrocarbons. *Green Chem* 15: 1720-1739.
8. Ragauskas AJ, Nagy M, Kim DH, Eckert CA, Hallett JP, et al. (2006) From wood to fuels: integrating biofuels and pulp production. *Ind Biotechnol* 2: 55-65.
9. Huang F, Singh PM, Ragauskas AJ (2011) Characterization of milled wood lignin (MWL) in loblolly pine stem wood, residue, and bark. *J Agr Food Chem* 59: 12910-12916.
10. Shen DK, Gu S (2009) The mechanism for thermal decomposition of cellulose and its main products. *Biores Tech* 100: 6496-6504.
11. Ben H, Ragauskas AJ (2011) Heteronuclear single-quantum correlation-nuclear magnetic resonance (HSQC-NMR) fingerprint analysis of pyrolysis oils. *Energy Fuels* 25: 5791-5801.
12. Zakzeski J, Bruijninx PC, Jongerijs AL, Weckhuysen BM (2010) The catalytic valorization of lignin for the production of renewable chemicals. *Chem Rev* 110: 3552-3599.
13. Ben H, Ragauskas AJ (2011) Pyrolysis of kraft lignin with additives. *Energy Fuels* 25: 4662-4668.
14. Ben H, Ragauskas AJ (2012) One step thermal conversion of lignin to the gasoline range liquid products by using zeolites as additives. *RSC Adv* 2: 12892-12898.
15. Ben H, Ragauskas AJ (2013) Influence of Si/Al ratio of ZSM-5 zeolite on the properties of lignin pyrolysis products. *ACS Sus Chem Eng* 1: 316-324.
16. Ben H, Mu W, Deng Y, Ragauskas AJ (2013) Production of renewable gasoline from aqueous phase hydrogenation of lignin pyrolysis oil. *Fuel* 103: 1148-1153.
17. Ben H (2014) Upgrade of Bio-oil to Bio-fuel and Bio-chemical. *Mater Biofuels* 4: 229-266.
18. Ben H (2014) Pyrolysis of Biomass to Bio-oils. *Mater Energy* 4: 191-228.

19. Ben H, Ferguson GA, Mu W, Pu Y, Huang F, et al. (2013) Hydrodeoxygenation by deuterium gas—a powerful way to provide insight into the reaction mechanisms. *Phys Chem Chem Phys* 15: 19138-19142.
20. Ben H, Huang F, Li L, Ragauskas AJ (2015) In situ upgrading of whole biomass to biofuel precursors with low average molecular weight and acidity by the use of zeolite mixture. *RSC Adv* 5: 74821-74827.
21. Ben H, Sturgeon MR, Ferguson G, Beckham GT, Foust TD, et al. (2014) Aliphatic Model Compounds Ring Opening on Ir/Al<sub>2</sub>O<sub>3</sub>-A Mechanistic Study by Deuterium Tracing and NMR. *Am Chem Soc CATL*.
22. Wang H, Ben H, Ruan H, Zhang L, Pu Y, et al. (2017), Effects of Lignin Structure on Hydrodeoxygenation Reactivity of Pinewood Lignin to Valuable Chemicals. *ACS Sus Chem Eng* 5: 1824-1830.
23. Ben H, Ragauskas AJ (2013) Comparison for the compositions of fast and slow pyrolysis oils by NMR characterization. *Biores Tech* 147: 577-584.
24. Ben H, Ragauskas AJ (2011) NMR characterization of pyrolysis oils from kraft lignin. *Energy Fuels* 25: 2322-2332.
25. Ben H, Ragauskas AJ (2012) In situ NMR characterization of pyrolysis oil during accelerated aging. *ChemSusChem* 5: 1687-1693.
26. Ben H, Ferrell III JR (2016) In-depth investigation on quantitative characterization of pyrolysis oil by 31 P NMR. *RSC Adv* 6: 17567-17573.
27. David K, Ben H, Muzzy J, Feik C, Iisa K, et al. (2012) Chemical characterization and water content determination of bio-oils obtained from various biomass species using 31P NMR spectroscopy. *Biofuels* 3: 123-128.
28. Ben H, Jarvis MW, Nimlos MR, Gjersing EL, Sturgeon MR, et al. (2016) Application of a pyroprobe–Deuterium NMR system: deuterium tracing and mechanistic study of upgrading process for lignin model compounds. *Energy Fuels* 30: 2968-2974.
29. Willför S, Sundberg A, Hemming J, Holmbom B (2005) Polysaccharides in some industrially important softwood species. *Wood Sci Tech* 39: 245-257.
30. Willför S, Sundberg A, Pranovich A, Holmbom B (2005) Polysaccharides in some industrially important hardwood species. *Wood Sci Tech* 39: 601-617.
31. Ben H, Ragauskas AJ (2012) Torrefaction of Loblolly pine. *Green Chem* 14: 72-76.
32. Chen WH, Kuo PC (2010) A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. *Energy* 35: 2580-2586.
33. Chen WH, Kuo PC (2011) Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. *Energy* 36: 803-811.
34. Liu Z, Ni Y, Fatehi P, Saeed A (2011) Isolation and cationization of hemicelluloses from pre-hydrolysis liquor of kraft-based dissolving pulp production process. *Biomass Bioenerg* 35: 1789-1796.
35. Chakar FS, Ragauskas AJ (2004) Review of current and future softwood kraft lignin process chemistry. *Ind Crop Prod* 20: 131-141.
36. Chan JKC, Moy JH (1977) Hemicellulose from commercial pineapple juice underflow. *J Food Sci* 42: 1451-1453.
37. Hernes PJ, Hedges JI (2004) Tannin signatures of barks, needles, leaves, cones, and wood at the molecular level. *Geochimica et Cosmochimica Acta* 68: 1293-1307.
38. Ohara S, Yasuta Y, Ohi H (2003) Structure elucidation of condensed tannins from barks by pyrolysis/gas chromatography. *Holzforchung* 57: 145-149.
39. Gaugler M, Grigsby WJ (2009) Thermal degradation of condensed tannins from radiata pine bark. *J Wood Chem Tech* 29: 305-321.
40. Liu YQ, Lim LR, Wang J, Yan R, Mahakhant A (2012) Investigation on Pyrolysis of Microalgae *Botryococcus braunii* and *Hapalosiphon sp.* *Ind Eng Chem Res* 51: 10320-10326.
41. Kim SS, Ly HV, Choi GH, Kim J, Woo HC (2012) Pyrolysis characteristics and kinetics of the alga *Saccharina japonica*. *Biores Tech* 123: 445-451.
42. Chow MC, Jackson WR, Chaffee AL, Marshall M (2013) Thermal treatment of algae for production of biofuel. *Energy Fuels* 27: 1926-1950.
43. Chen X, Chew SL, Kerton FM, Yan N (2014) Direct conversion of chitin into a N-containing furan derivative. *Green Chemistry* 16: 2204-2212.
44. Wang Y, Pedersen CM, Deng T, Qiao Y, Hou X (2013) Direct conversion of chitin biomass to 5-hydroxymethylfurfural in concentrated ZnCl<sub>2</sub> aqueous solution. *Biores Tech* 143: 384-390.
45. Pierson Y, Chen X, Bobbink FD, Zhang J, Yan N (2014) Acid-catalyzed chitin liquefaction in ethylene glycol. *ACS Sus Chem Eng* 2: 2081-2089.
46. El Kadib A (2015) Chitosan as a sustainable organocatalyst: a concise overview. *ChemSusChem* 8: 217-244.
47. Lee KY, Mooney DJ (2001) Hydrogels for tissue engineering. *Chem rev* 101: 1869-1880.
48. White RJ, Brun N, Budarin VL, Clark JH, Titirici MM (2014) Always look on the “light” side of life: sustainable carbon aerogels. *ChemSusChem* 7: 670-689.
49. U.S. Department of Energy (2011) U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224. Oak Ridge National Laboratory, Oak Ridge, TN p: 227.
50. Mohan D, Pittman CU, Steele PH (2006) Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* 20: 848-889.