

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, bioresources 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.

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