



Views & Comments

Key Considerations on the Industrial Application of Lignocellulosic Biomass Pyrolysis toward Carbon Neutrality



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1. The importance of biomass in carbon neutrality

With the increasing urgency to mitigate climate change, over 100 countries have committed to net-zero carbon emissions by the mid-21st century [1]. For example, China has announced that it will reach a carbon peak and carbon neutrality by 2030 and 2060, respectively, with the rapid development of renewable energy undoubtedly playing a key role in achieving these goals. Compared with other renewable energy sources, such as wind energy, solar energy, and hydroelectric energy, biomass is the only renewable carbon-based option that can supply us with the carbon building blocks for the production of various chemicals while mitigating our dependence on fossil energy. One typical example is the production of bioethanol from biomass through a circular bio-economy approach [2]. Thus, biomass is commonly considered to be an irreplaceable, renewable, green, and zero-carbon material resource [3,4]. The conversion of biomass to green fuels or chemicals has received widespread attentions as society seeks to achieve carbon neutrality [5–8].

2. The current situation of biomass utilization

Biochemical and thermochemical conversion are the two main pathways for biomass valorization [9]. The former has the advantage of high product selectivity, but it is limited by a slow reaction rate and strict requirements for feedstock. By comparison, thermochemical conversion can rapidly convert biomass—especially lignocellulosic biomass, which has a relatively low water content—into solid (biochar), liquid (bio-oil), and gaseous products (e.g., CO and H₂) through a variety of thermal treatments such as carbonization, pyrolysis, and gasification [10,11]. Considering society's current reliance on liquid fuels, the pyrolysis of lignocellulosic biomass to produce bio-oil holds great significance, since bio-oil can be used as a replacement for petroleum-derived liquid fuels such as gasoline and diesel. Fig. 1 illustrates the concept of biomass utilization through pyrolysis. The Dutch company BTG Bioliqids has demonstrated the most successful commercialized

lignocellulosic biomass pyrolysis. Unfortunately, although biomass pyrolysis has been studied for about 150 years, its industrial applications remain limited due to the propensity of biomass to indiscriminately decompose and the low energy density and low stability of bio-oil (e.g., it is acidic, highly oxygenated, and thermally unstable) [12]. Therefore, bio-oil often requires upgrading before use, such as through catalytic cracking or catalytic hydrodeoxygenation.

3. Key challenges in lignocellulosic biomass pyrolysis

Although lignocellulosic biomass pyrolysis appears to be a very simple process, it presents some very challenging issues that must be tackled before it can be implemented widely.

3.1. Heterogeneity of raw materials

As the most abundant non-edible biomass, lignocellulosic biomass mainly comes from agricultural and forestry residues. Although cellulose, hemicellulose, and lignin are the three major components of all lignocellulosic biomass, the proportion of these three main components and even their specific structures vary largely among different lignocellulosic biomass species [12]. For example, woody biomass is rich in cellulose while nutshell biomass is dominated by lignin, resulting in significant differences in the composition of the resulting products. The heating value of bio-oil produced from lignin-rich biomass tends to be comparatively greater due to the aromatic-rich content. Furthermore, the chain length of cellulose [13], the ratio of pentose to hexose sugars in hemicellulose [14], the type of lignin structural unit (i.e., sinapyl, coniferyl, or *p*-coumaryl alcohols) [15], the binding mode and supramolecular configuration of the three major components [16], and the content/type of inorganics [17]—all of which are determined by the raw material—have a strong influence on bio-oil composition. The complicated composition of bio-oil that results from biomass heterogeneity hinders its long-term storage, downstream applications, and upgrading. To avoid biomass heterogeneity, strict

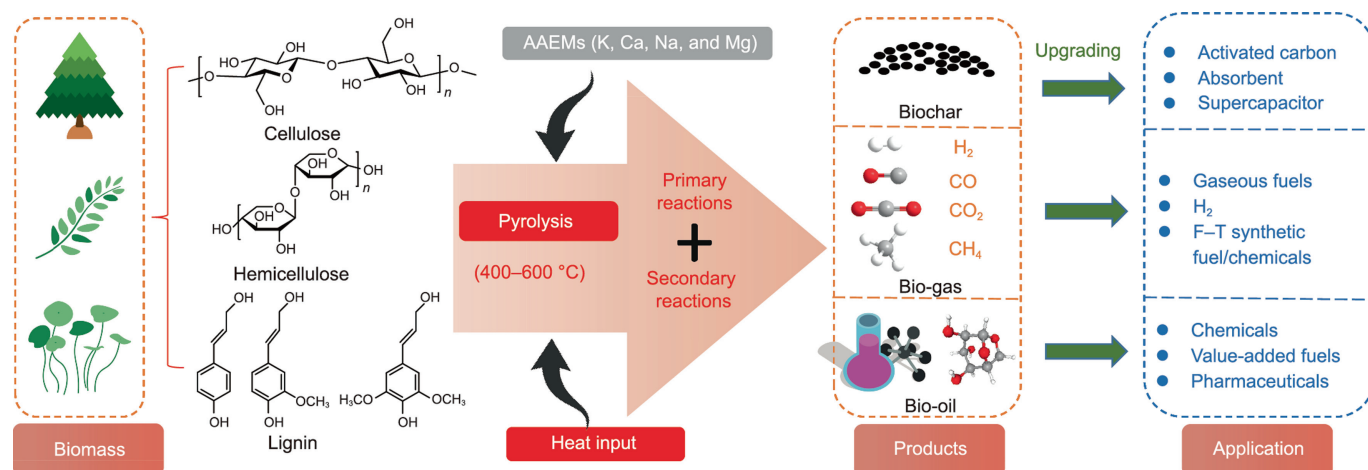


Fig. 1. Conceptual illustration of biomass utilization through pyrolysis. AAEMs: alkali and alkaline earth metallic species; F-T: Fischer-Tropsch.

requirements are imposed on the collection and pretreatment of raw materials, presenting challenges for the large-scale pyrolysis of lignocellulosic biomass due to the scattered biomass distribution [18]. Therefore, innovative pyrolysis technologies and systems, as well as novel pretreatment technologies with a broad compatibility with various raw materials, are urgently needed.

3.2. Complexity of reaction pathways and regulation of secondary interactions

Pyrolysis is an extremely complex reaction system involving the primary depolymerization of cellulose, hemicellulose, and lignin as well as secondary interactions among the primary reaction products [19]. In addition, inorganics act as inherent catalysts in the above-mentioned reactions. The primary reactions in biomass pyrolysis are highly dependent on the feedstock and temperature (generally around 500–600 °C), making it difficult to tune them using other external factors. The secondary interactions are almost ubiquitous in both the gaseous and solid phases, and include intramolecular electron transfer, volatile–volatile interactions, and volatile–solid interactions [20]. Depending on the sequence of the reactions, secondary interactions are probably more important in determining the final product distribution. Therefore, understanding and controlling the secondary reactions are especially critical for improving product selectivity and quality.

Regardless of the type, secondary interactions are largely influenced by the residence time of the volatiles, which provides an opportunity to control the secondary reactions and thereby control the outcome of the final products. As a typical example, the “internal recycling of bio-oil” has been proposed in order to intensify volatile–char interactions, which results in a significantly different bio-oil with less or even no coking behavior [21–23]. Based on our detailed analyses of the resulting bio-oil, we found that cellulose-derived anhydrosugars (e.g., levoglucosan) have been shown to be very reactive during the internal recycling of bio-oil, resulting in a significant improvement in the production of acetic acid and phenols. However, the internal recycling of bio-oil occurs at the expense of its yield, and the structure–activity relationship of char in volatile–char interactions is not yet well established, hindering further development toward commercial technology.

3.3. Migration of inorganics and formation of aerosol

Although the inorganics in biomass are present in small quantities, they are by no means inert or unimportant during the

pyrolysis process. The primary reaction pathways can be altered to yield different products via catalysis by inorganics. The inorganics can also vaporize and condense inside the reactor or in the bio-oil, causing plugging or accelerating the aging of the bio-oil. Moreover, the remaining inorganics in the char can interfere with the secondary volatile–char interactions [24]. Thus, understanding and controlling the migration of inorganics is important for the selective production of bio-oil. For example, alkali and alkaline earth metallic species (AAEMs; i.e., Na, K, Mg, and Ca) in biomass have been demonstrated to be powerful ring-fragmentation catalysts, so the presence of AAEMs during biomass pyrolysis significantly reduces the yields of sugars and increases the yields of light linear compounds [25]. To minimize the vaporization of inorganics, the pyrolysis of lignocellulosic biomass may be conducted at a lower temperature. However, further research is still required on improving the pyrolysis rate and adjusting the catalytic effect of inorganics in char.

More than 60% of the inorganics vaporized into volatiles are closely related to the aerosol emissions, which are the main air pollutants produced by biomass pyrolysis [26]. Two opposite routes—namely, the polymerization of small molecules and direct ejection from oligomeric intermediates—have been suggested to lead to the formation of aerosols [27]. The main reason for the controversy between these two possible routes is that the structures of the aerosols are unclear; thus, more research attention is required in this area.

3.4. The high coking tendency of bio-oil and anti-coking strategies

Applications of bio-oil are significantly hindered by the coking of bio-oil during thermal treatment, and almost all bio-oil upgrading processes require heating [28]. One exception is electrocatalytic upgrading, which can be conducted at room temperature [29]. Unlike the components in crude oil, the coking components in bio-oil originate not only from the heavy parts but also from some reactive light molecules featuring functional groups. For example, levoglucosan, whose molecular weight is only 162, has been found to be a typical coking component [19]. Identifying the coking components in bio-oil and further revealing the coking mechanism of bio-oil are critical for the development of anti-coking methods. However, it is difficult to collect coking components, since they are typically the most reactive compounds in the secondary reactions mentioned above. Moreover, identifying coking components is challenging, because a qualitative analysis of bio-oil usually relies on gas chromatography/mass spectrometry

(GC/MS), which cannot detect large amounts of coking components due to the formation of solids in the GC/MS inlet or separation column. Therefore, novel analytical methods including *in-situ* detection methods and *ex-situ* high-resolution detection methods need to be developed.

The identity of coking components and their corresponding coking mechanisms can also be deduced by characterizing the resulting coke. Nevertheless, although several studies have already been carried out in this field [30–32], the coking issue of bio-oil remains unsolved. The development of a novel anti-coking strategy for bio-oil processing is urgently needed in order to realize a sustainable carbon neutral fuel-development scheme.

3.5. Efficient utilization of solid and gaseous products

In addition to the liquid products of the pyrolysis of lignocellulosic biomass, roughly 15 wt%–30 wt% of solid biochar and 10 wt%–30 wt% of gaseous products can be obtained. To improve the economic competitiveness of biomass pyrolysis, the efficient utilization of these products is particularly important. Solid biochar is currently applied in the fields of catalysis, wastewater and atmospheric treatment, solid fuels, and so forth [33–35]. However, the properties of solid biochar are highly dependent on the raw material. For example, nutshell-derived biochar is more valuable than crop straw-derived biochar, while the latter is more abundant. Exploring new ways to utilize low-grade biochar and to improve the quality of biochar should be the focus of future research.

The gaseous products of biomass pyrolysis are usually dominated by carbon dioxide (CO₂), carbon monoxide (CO), and methane (CH₄), which have a lower heating value of around 5–10 MJ·Nm⁻³ [21]. In most cases, the gaseous products are burned for energy—a purpose that is limited by a high CO₂ content. Further research on the separation of gaseous components and the hydrogenation of CO₂ and CO to form various chemicals is needed in the future.

3.6. Providing a fast and efficient heat supply to the pyrolyzer in scaled-up operation

Due to the endothermic nature of biomass pyrolysis, it is necessary to provide the pyrolyzer with an external heat supply in order to sustain the pyrolysis temperature and further drive the thermolysis reactions. The heat supply mode is the key consideration in the design of a pyrolyzer. At present, heat is mainly supplied to biomass particles through gas/solid heat carriers and the pyrolyzer wall—a process that presents various issues in practical application due to its complex heat-exchange system, difficult operation, and low heat-transfer efficiency [36,37]. Heat transfer from the outside to the inside of a pyrolyzer becomes increasingly difficult when the pyrolyzer volume is scaled up. This issue is complicated by the fact that heat transfer is a volumetric phenomenon, while the heat supply originates from the surface. The realization of a fast and efficient heat supply to the pyrolyzer with a high heat flux is currently the bottleneck issue that limits the scaling up of pyrolysis technology. Therefore, the autothermal pyrolysis of biomass—including oxidative pyrolysis, which has not yet attracted enough attention—should be further developed in the future.

4. Conclusion

As a renewable, green, and zero-carbon resource, biomass is bound to play a key role in achieving carbon neutrality. However, the industrialization of biomass pyrolysis to produce high-quality fuels and value-added chemicals still has a long way to go, as chal-

lenging issues remain to be tackled in the whole process from raw materials to products. Researchers are encouraged to focus on the proposed key points in order to accelerate the world's carbon-neutrality goals.

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