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Catalytic conversion of biomass

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Abstract: ***Resource scarcity and increasing climate change have brought attention to the need for sustainable and renewable resources. Biomass is an earth-rich material with great potential as a feedstock for alternative fuels and chemicals. In order to utilize biomass efficiently, such biopolymers must be depolymerized and converted into key structural units and/or target products, and biological or chemical catalysts are often used for fast and energy-efficient reactions. This paper presents recent advances in the catalytic conversion of biomass into biofuels and value-added products. Hydrodeoxygenation is an important and unique method for converting biomass and biomass-derived oxygenated chemicals into high value-added chemicals and fuels. However, the synthesis of catalysts with excellent hydrogenation and hydrodeoxygenation performance at the same time remains a great challenge.***

Keywords: Biomass; Catalytic; Resource; Hydrodeoxygenation.

1. Overview of biomass

Biomass is the only renewable source of organic carbon in nature[1], and catalytic upgrading of biomass into high value-added bio-based chemicals and biofuels is considered a promising strategy for the efficient use of biomass energy and is receiving increasing attention[2-5]. Biomass has three main components: lignin (15-20%), hemicellulose (25-35%) and cellulose (40-50%)[6]. Cellulose is a naturally occurring polymer compound characterized by the polydispersed or heterogeneous nature of natural polymers, which are stored in large quantities in nature. It uses C_5-C_6 sugars (e.g. glucose and fructose) as the basic and structural units, which are then linked by glycosidic bonds to form natural polymers. Hemicellulose is formed by the polymerization of different glycogen, it has short molecular chains and branched chains, it is not composed of a single glucose glycogen like cellulose. Lignin is composed of various methoxylated phenyl propane units with the main structures β-O-4, β-5, α-O-4, β-β, 5-5, 4-O-5 and β-linked, and is considered as a potential petroleum replacement resource for the preparation of aromatic chemicals[7]. Cellulose and hemicellulose can be converted into platform compounds such as alcohols, furfural and furan compounds. These platform compounds can then be further converted to bioaromatics through a series of reactions such as deoxygenation, dehydrogenation and cyclization. Compared with cellulose and hemicellulose, lignin can be directly converted to bioaromatics, which is considered as a promising technology. The inherent heterogeneity and recalcitrance of lignin are the main obstacles to its conversion into value-added compounds. Reduction depolymerization is the most widespread and efficient method for producing lignin monomers in recent years. Using H_2 or hydrogen donors (e.g. methanol, ethanol, 2-propanol, or even lignin itself) as hydrogen sources[8]·, lignin can be depolymerized to low molecular weight phenolic compounds over Ru, Pt, Pd, Ni, Rh, Co, and Cu-based catalysts by hydrolysis, hydrocracking, hydrogenation, hydrogenation, and hydrodeoxygenation processes[9]. By selective hydrodeoxygenation and precise control of reaction types (including hydrolysis, hydrogenation, dehydration and direct deoxygenation), a wide range of high value-added monomers (e.g. alkylphenols, phenols, cyclohexanone, cyclohexanol, cyclohexane, alkylbenzene, benzene, etc.) can be produced from phenolic oils depolymerized from different lignins. Therefore, there is an urgent need to shift from fossil fuels to renewable fuels[10].

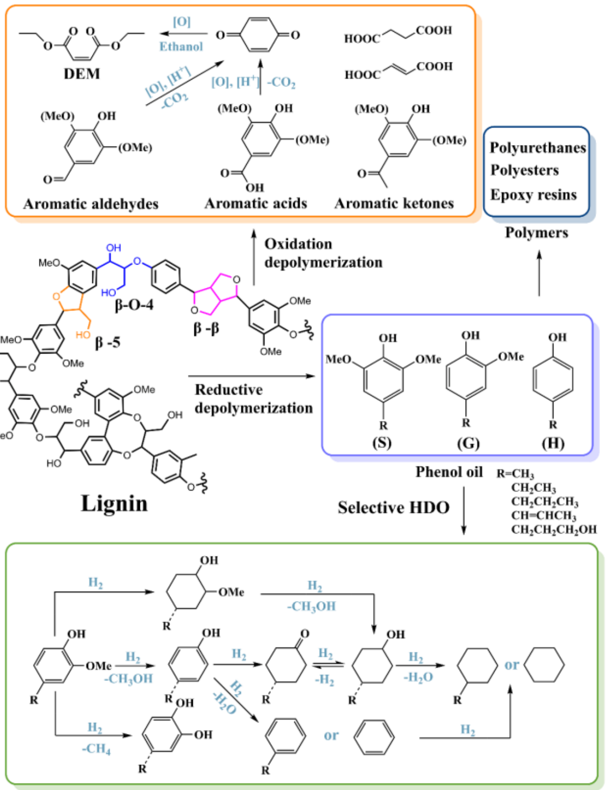

Fig.1. Lignin conversion route[11]

2. Catalytic depolymerization of biomass

Pyrolysis is one of the most promising methods for the utilization of biomass[11,12]. Biomass pyrolysis is the thermochemical transformation of biomass in an inert environment (usually produced by introducing inert gases or by evacuation) and under high temperature conditions (usually 400-550°C)[13,14]. It usually produces gases (CO_2, CO, H_2, CH_4, etc.), bio-oils (phenols, ketones, furans, aldehydes, alcohols, etc.) and biochar (insoluble solids with high carbon content) products[15]. Bio-oil, as its main product, has many disadvantages compared to fossil fuels such as high oxygen content, high water content, low calorific value, and low pH value. These drawbacks hinder its application and therefore some upgrading measures are needed to improve the quality of bio-oil.

One effective strategy to produce liquid biofuels is through rapid pyrolysis technology, where biomass is rapidly heated to approximately 500°C in an inert atmosphere to produce coke, light gas and pyrolysis oil[14]. Pyrolysis oil typically has a water content of 15-30 wt% that cannot be removed by conventional distillation because heating the pyrolysis oil leads to rapid coke formation. In addition, it has a high oxygen content, typically 35-50 wt%, resulting in a low calorific value (HHV=16-21 MJ/kg), which makes the utilization of pyrolysis oil challenging. Pyrolysis oil can in principle be upgraded by hydrodeoxygenation, which is carried out at high temperatures (250-400°C) and pressures (100-300 bar) in the presence of a catalyst. However, rapid catalyst deactivation and even reactor plugging due to coke formation are common problems. An alternative to fast pyrolysis is fast catalytic pyrolysis, where an acidic catalyst is present in the fast pyrolysis reactor or downstream reactor (called in situ catalytic pyrolysis), which reduces the oxygen content in the resulting organic phase.

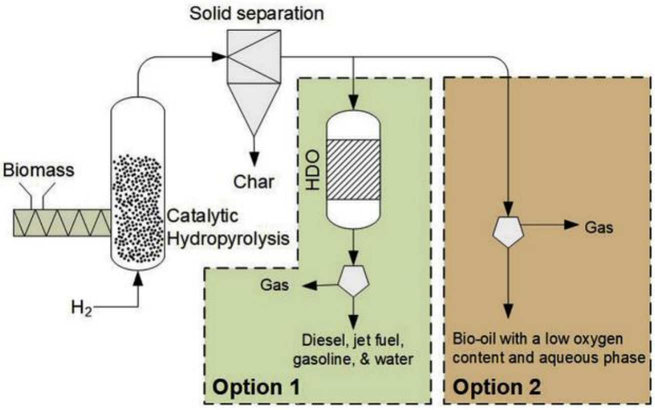

Fig. 2. Overview of catalytic hydropyrolysis with upgrading of the vapors in a fixed bed HDO reactor (option 1) and without upgrading of the vapors (option 2)[19]

Catalytic pyrolysis is now becoming a major research direction in biomass conversion and utilization technology, which allows effective upgrading of bio-oil and targeted production of high value products compared to conventional pyrolysis[16]. In recent years, catalysts for catalytic pyrolysis of biomass mainly include molecular sieve-based catalysts (ZSM-5, HZSM-5, USY, etc.)[17], carbon based catalysts, metal oxides, hydrotalcite, and monolithic catalysts. A good catalyst is the key to ensure a smooth reaction, and different catalysts are oriented to produce different high-value products, so the correct choice of catalyst plays a major role in the quality improvement of bio-oil[18]. Currently, the mainstream catalysts used in this field are still molecular sieves and carbon based catalysts, where metal loading can give the advantages of both high specific surface area and access to metal active sites. A large number of studies have shown that secondary sintering can regenerate catalysts, and that higher temperatures can significantly reduce the amount of carbon build-up. Future research on catalyst regeneration can follow two general directions: changing the pore structure of catalysts and developing new continuous reaction regeneration systems. With the continuous development of microwave pyrolysis and the deepening understanding of microwave effect, microwave pyrolysis should be gradually combined with catalytic mechanism to explore the comprehensive mechanism of microwave effect coupled with catalytic effect to improve the quality of bio-oil and other high-value products from different directions.

3. Hydrodeoxygenation of biomass and its derivatives

In the beginning, researchers focused on direct hydrogenation of biomass[20]. As the research continued, it was found that direct hydrogenation would cause severe carbon build-up and rapid catalyst deactivation, which is not conducive to industrialization due to the complex composition of biomass. If biomass is first converted into active small molecule oxygenated compounds, and then it is further hydrogenated a series of high value-added chemicals can be synthesized[21].

Hydrodeoxygenation (HDO) is the most important reaction in the catalytic conversion of biomass, in which oxygen in organic matter reacts with hydrogen and forms water. HDO of aliphatic groups can be carried out by a dehydration followed by hydrogenation (HYD) step. HDO of oxygenated aromatics, especially phenols, can proceed by the direct deoxygenation (DDO) route, retaining the aromatics, or by the hydrogenation route (HYD), in which the aromatic rings are saturated prior to deoxygenation[22,23]. The important difference between HDO and decarboxylation/decarboxylation is that HDO removes oxygen without loss of carbon, thus leading to a higher carbon yield in the liquid at the cost of a higher hydrogen consumption[4]. The main reaction pathway depends on the type of catalyst.

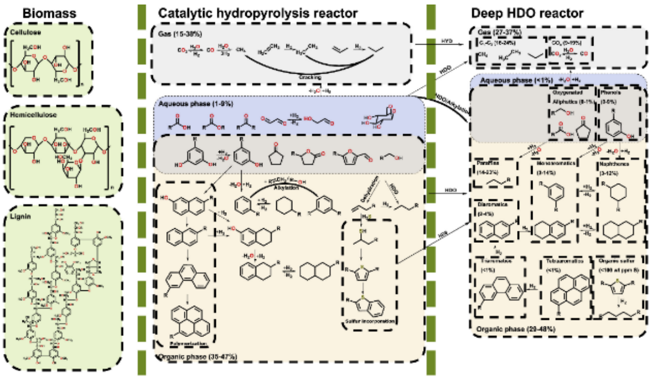

Fig. 3. Reaction scheme occurring in the catalytic hydrolysis reactor and the secondary deep HDO reactor used to lift the catalytic hydrolysis vapors[19]

In general, lignin-derived pyrolysis oils contain a large amount of oxygenated chemicals (oxygen concentration: 35-40 wt.%). The most dominant fraction is phenolics, obtained from the rapid pyrolysis of lignin at 25-40 wt.% (containing 7-11 wt.% monomer). Typically, lignin-derived monomeric phenols include mainly phenol[24,25], guaiacol, anisole[26,27], p-cresol, m-cresol and vanillin, which are widely used as model compounds for lignin to reduce the complexity of reactivity and mechanism studies[8]. The presence of oxygenated compounds leads to deteriorating properties such as severe corrosiveness (high acidity), low calorific value, thermal and chemical instability, and incompatibility with conventional fuels, making lignin-derived bio-oils unsuitable for direct use as liquid fuels in the petrochemical industry.

The development of effective catalysts to break down and convert woody biomass would be a paradigm shift towards achieving sustainable economic and environmental global goals through the use of cheap, highly abundant and renewable carbon resources. However, the development of lignocellulose is extremely challenging due to its complexity and the fact t+hat most biomass is currently treated simply as waste. The solution lies in the design of multifunctional catalysts that can effectively control substrate activity and product selectivity.

4. Catalysts in biomass catalysis

Acid catalysts are often required in biomass conversion processes. Homogeneous acid catalysts are effective, but product separation and catalyst recovery are difficult, so solid acid catalysts are receiving more and more attention. Solid acids such as molecular sieves, metal oxides, ion exchange resins, and heteropolyacids are used in biomass conversion reactions. Acid catalysts can obtain oxygenated liquid fuels and oxygenated organic chemicals mainly phenol derivatives with high yield and selectivity, therefore acid catalysts have received attention from many researchers. Frederick et al found that $ZnCl_2$ has good catalytic effect on biomass model compounds such as phenylbenzyl ether and diphenyl ether. Wang et al used concentrated sulfuric acid, concentrated hydrochloric acid, concentrated hydrochloric acid/phenol, concentrated sulfuric acid/phenol and phosphoric acid/phenol catalysts for the catalytic conversion of wheat straw fibers, respectively, and the results showed that the best catalytic effect was achieved in the mixed catalytic system of concentrated sulfuric acid/phenol.

The above homogeneous acidic catalysts, despite their advantages of good catalytic effect and high activity, are highly corrosive to the reaction equipment and therefore are limited in practical applications[28]. The development of active and environmentally friendly loaded acid catalysts is one of the current research hotspots in biomass conversion technology[29-31]. Narani et al. [32] investigated the depolymerization of sulfated lignin to alkyl-substituted phenolics under supercritical methanol using catalysts of NiW and NiMo loaded on acidic, neutral and basic carriers, respectively. Through a series of experiments, it was found that sulfated NiW loaded onto activated carbon at a reaction temperature of 320°C, pressure of 35 bar H_2 and time of 8 h could yield 28 wt% monomer yield, of which 76% were alkyl-substituted phenols and guaiacols. Extending the reaction time gave 35 wt% monomer yield and 26 wt% alkyl-substituted phenols. Junfeng Feng et al. [33] investigated the aqueous phase reforming of methanol and the in situ hydrodeoxygenation of phenolic compounds derived from biomass in a methanol-water solvent using Raney Ni and HZSM-5 or H-Beta bifunctional catalysts. The in situ hydrodeoxygenation process includes aqueous phase reforming of methanol, metal-catalyzed hydrogenation and acid-catalyzed hydrolysis/dehydration. The metal hydrogenation reaction is catalyzed by a Raney Ni catalyst, and the isolated acid-catalyzed hydrolysis/dehydration reaction is catalyzed by HZSM-5 or H-Beta. This in situ hydrodeoxygenation process with a bifunctional catalyst provides an efficient way to refine bio-oils containing high amounts of phenolic compounds into renewable hydrocarbon products.

Although acidic solid acid catalysts exhibit excellent catalytic effects, they are not very stable to water[34]. Water is often used as a solvent in biomass conversion or the reaction produces water, so a class of solid acid catalysts with excellent hydrothermal stability needs to be developed. The future research on solid acid catalysts should be deeply explored in the following research directions: 1) in-depth characterization of acidic sites and optimization of conditions; 2) how to make the substrate more accessible to acidic sites; 3) the effect of adding reducing metal components on catalyst acidity; 4) the interaction between catalyst and reaction medium, by-products and gases; 5) catalyst deactivation and regeneration.

5. Summary and Prospects

Catalytic conversion of biomass is the primary route for production of high quality bio-based fuels and solving the energy crisis. Advances in biomass catalytic conversion technology hold promise for a greener future using renewable resources in clean energy and chemical production. Catalytic hydrolysis plays a dominant role in both biomass degradation and subsequent conversion of lignin derivatives to fuel additives and chemicals. Catalytic hydrolysis involves a complex series of chemical reactions, and an improved understanding of these reactions can be used to adjust the composition of the organic phase produced while minimizing operational challenges. Hydrodeoxygenation is an important and unique method for converting biomass and biomass-derived oxygenated chemicals into high value-added chemicals and fuels. However, the synthesis of catalysts with excellent hydrogenation and hydrodeoxygenation performance at the same time remains a great challenge.

As an important renewable resource, it is important to develop a green and efficient conversion process for biomass by mildly targeting and efficiently converting the vast majority of organic matter in biomass into high-value organic compounds as much as possible. At present, the application of biomass thermal cracking technology, the selection of suitable pretreatment methods and catalysts, the conversion of biomass resources to chemicals, has made certain research results, but to reach the level of industrial application still need to solve the following problems: (1) biomass conversion conditions are harsh, need to be high temperature, high hydrogen pressure reaction conditions. (2) Another challenge in biomass conversion technology is the poor stability of the catalyst and the fact that it is not easily recovered after the reaction. (3) low selectivity of biomass conversion products and low yield of high-value chemical products

In fact, the development of stable, efficient and economical multiphase catalysts capable of operating under mild and environmentally friendly conditions is essential to meet these targets. However, the following challenges need to be faced in the design and development of multiphase catalysts suitable for large-scale conversion of lignocellulose into value-added chemicals and fuels:

(1) Synthesis of stable and easily regenerated catalysts

When using biomass feedstock, most catalysts tend to deactivate within a short period of time due to the tendency of minerals and heteroatoms in biomass to irreversibly bind to the active site and poison the catalyst. In addition, catalytic conversion of lignocellulose usually involves high temperatures and pressures, which tend to produce coke or tar to cover the active sites. Heat treatment of the catalyst can regenerate some of the active sites, but this can also lead to sintering. Several strategies can address these issues, including exploring advanced catalyst preparation methods, such as stabilization of metal particles and carriers by enhanced metal-carrier interaction (SMSI), introduction of heteroatoms into metal catalysts, or development of multifunctional carriers that exhibit excellent stability under hydrothermal conditions.

(2) Precise design of multifunctional catalysts with high activity and selectivity

Tuning catalyst morphology and hydrophilicity/ hydrophobicity to improve the accessibility of reactants and intermediates to active sites. Precise adjustment of various active sites with desired adsorption or catalytic ability to modulate target reaction intermediates and reaction pathways. In addition, compared to monometallic catalysts, bimetallic or polymetallic and heteroatom-anchored catalysts have unique synergistic effects in addition to stability to generate new reaction sites and promote charge transfer, which can improve catalyst activity and selectivity. Geometric and electronic modification of the active sites by the above effects can enhance their catalytic performance.

(3) Deeper understanding of the reaction mechanism

Due to the complexity of the lignocellulosic conversion process, an in-depth understanding of the reaction mechanism, including the identification of key reaction intermediates, rate-limiting steps in the reaction pathway, surface/interfacial reaction kinetics and active sites involved in the catalytic cycle, is necessary. In situ or operational characterization studies of catalysts, combined with quantum chemistry or density flooding theory calculations, provide a more fundamental understanding of the reaction process, active sites and structure-activity relationships of catalysts, thus facilitating further optimization of catalyst structures for better catalytic performance.

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