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Production of Biofuel via Hydrogenation of Lignin from Biomass

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Abstract

Historically, humans have been harnessing biomass as a source of energy since the time they knew to make a fire from woods. Even today, some countries still depend on woods as a main source of energy. Biologically, biomass contains carbon-, hydrogen- and oxygen-based matters that unify in a solid material and that are potentially to be converted to fuel. Lignin is one of the components present in lignocellulosic biomass and has been actively examined to be used for biofuel production. Issues arise with the chemical characteristic and rigidity of its structure, which a setback for its viability for biofuel conversion. However, such setbacks have been counteracted with the advances of lignin-based knowledge on its conversion to chemical precursors for biofuel conversion. Recently, investigations on hydrogenation as one of the chemical processes used can be potentially utilised for efficient and viable means for biofuel production.

Keywords: biofuel, chemical precursors, lignocellulosic biomass

1. Introduction

Biomass is a potential source of fuel consists of organic materials and considered as renewable and sustainable for energy development. With fossil fuel remaining unstable in terms of cost and sustainability, the need to generate biomass-based energy is becoming more imperative and feasible in economical point of view [1, 2]. One of the main benefits of biomass-based fuel (sometimes called as biofuel) is zero carbon dioxide release as compared to fossil fuel [3]. Furthermore, the dramatic rise of carbon dioxide concentration in the atmosphere has triggered researchers to find viable alternatives to fossil-based fuels.

One type of biomass which covers mostly of plant molecules is lignocellulosic biomass. Structurally, it composes of cellulose, hemicellulose and lignin. Cellulose and hemicellulose are mainly monomeric sugar linked to form polymer [4]. However, lignin consists of phenylpropane units, which cross-linked with tight and varied chemical bonds [4]. Thus, lignin complexity makes it difficult to be degraded as compared to almost unified type of bonding of cellulose and hemicellulose. Nonetheless, a few researchers have found ways to enhance degradability of lignin through recent pretreatment technologies [4, 5].

Lignin is separated from cellulose and hemicelluloses during kraft process, and only partial is utilised in combustion application as energy source [6]. In addition, through development of bioethanol production, it is expected that more lignin is produced as by-product which is also added to the mass number of lignin. Through advances of pretreatment technology and valorisation, lignin can be used as an alternative source for fine chemicals and raw material for fuel.

In the progress of lignin utilisation for fuel production, hydrogenation of lignin becomes one of viable methods. Lignin contains functional phenolic compounds, but the difficulties of extracting the compounds remain a bottleneck to unlock this potential material for fuel production. For example, the degree of interaction between monomers (phenolic compound) varied due to the heterologous nature of each individual monomers [7]. Another reason would be the feasibility of pretreatment technologies that are needed to be strategised and to fully utilise the monomers present [7]. In addition, the monomers have to be separated from the strong linkages within lignin structure, so that conversion to fuel can be executed efficiently.

In this chapter, lignin will be discussed of its structure and its different functional phenolic compounds. In addition, lignin depolymerisation or valorisation process to obtain individual monomers will also be presented. Further discussion will also include hydrogenation of lignin and the mechanism involved in the process. At the final part of this chapter, the future perspective of lignin hydrogenation that may lead to more innovative applications is discussed.

2. Biomass conversion to fine chemicals and fuels

The present development of biomass conversion to energy and chemicals together with individual types of abundant biomass in nature has been discussed in terms of its source, availability, types of biomass and chemical characteristics.

2.1. Historical background

In the abundance of biomass in the world's nature, traditional utilisation of biomass in order to survive has long been established. Primitively, when man knows how to create fire, biomass utilisation evolved from domestic usage to even larger application such as building houses, clothes production, paper making, etc. Yet the biomass utilisation seems endless and continues to produce more relevant products.

Henry Ford was the first to design a model car that runs using ethanol, and it was also reported that Rudolph Diesel intended on using vegetable oil to power his car engine [8]. However, at

the time of World War II, fossil fuels were more practical based on supply, price and efficiency which caused biofuel to be unpopular. In contrast, in the late 1990s, high intensity of research and investment were made to produce biofuel from biomass due to reverse effect on supply and price of fossil fuel which is unpredictable.

The first biomass used was in solid form—wood—which was used to produce fire and oil derived from plants and animals that has been turned to a useful medium to light up lamp [9, 10]. In the present day, biofuel is derived from food crops like sugar beets, grains and vegetable oils or, namely, first-generation biomass [11]. However, the impact on the global food supply and sustainability of land led to non-food stock for energy sources and the second generation of energy sources such as cellulosic biomass, inedible oil and algae-derived oil [11, 12]. Microalgae can reproduce in a mass rapidly per day and have been found enriched of high level of oil in total dry biomass [13]. However, regardless the high growth rates or high oil content, algae-derived oil production faces challenges that needed attention such as strain isolation, nutrient sourcing or availability, on-site management in production and handling and residual biomass or waste management [14].

Meanwhile, biobutanol, another type of fuel, has becoming popular in recent years that surpass bioethanol. Biobutanol is referred as the next generation of biofuels that offers many advantages. It can be produced directly with few combinations of physical, chemical and biological processes from food crops such as cereal crops, sugar beets and sugar cane. The first synthesis of biobutanol was achieved during 1912–1914 by acetone-butanol-ethanol (ABE) fermentation using *Clostridium* species as catalysts [15].

2.2. Trends in biomass conversion to fine chemicals and fuels

In developing technologies to fine tune biomass conversion to chemicals or fuels, many combinations of physical, chemical and biological approaches have been utilised. The strategy is to enhance accessibility to the main target component such as cellulose and hemicellulose or to separate main recalcitrant of the biomass which is lignin from the other component and treated individually as precursor for fuel.

For starter, all biomass should undergo pretreatment in order to achieve maximum conversion. During the past decades, the target is to produce fermentable sugar from complex ligno-cellulosic biomass which includes separating lignin from the complex biomass [16]. **Figure 1** shows a schematic flow of basic biomass conversion into value-added products.

During the course of chemical or biochemical conversion, an effective pretreatment is needed for maximum utilisation of the biomass. To summarise, a few criteria have been highlighted to achieve efficient pretreatment as indicated below:

- i. Preservation of hemicelluloses fractions, in order to have high yield of fermentable sugars;
- ii. Minimising the building up of inhibitors due to degradation;
- iii. Minimising the use of high energy in the process;
- iv. Cost-effective pretreatment processes.

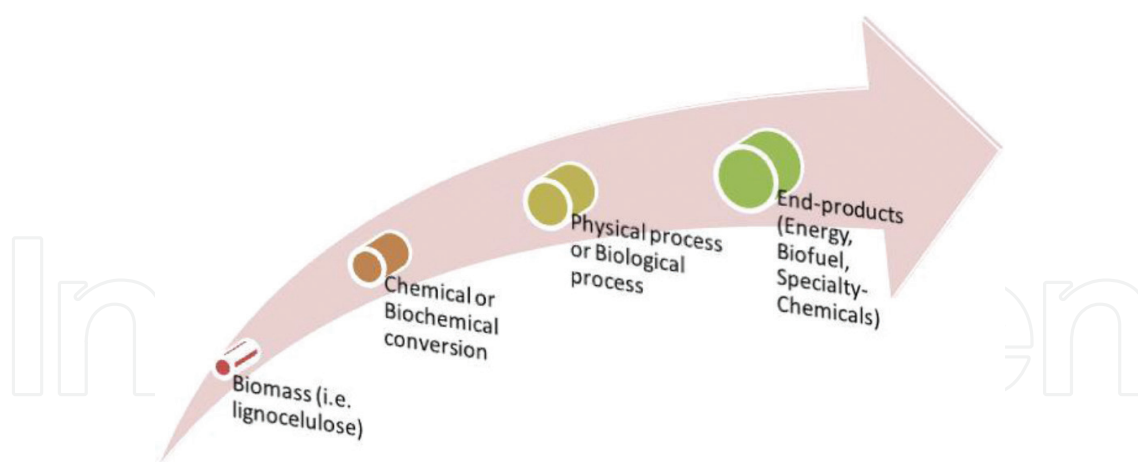


Figure 1. Schematic flow of general conversion of biomass to value-added products. Adapted from Ref. [17] with permission from Elsevier.

The above criteria become a basis for choosing the right method of pretreatment of biomass in order to maximise its efficiency. Further details on pretreatment will not be discussed here and can be found intensively discussed in other publications [18].

Meanwhile, as the complexity of the biomass dissolved through pretreatment processes, the next step is to choose the right method to directly convert the simpler form of the material to the desired product based on physical, chemical and biological processing methods.

2.2.1. Physical-based conversion

In this method, for some biomass, pretreatment sometimes will not be necessary. For example, woody biomass through combustion process will produce heat and electricity. The initial combustion will produce steam at high pressure and eventually the steam is used to activate turbine plants that in turn will generate electricity. Such biomass-fired steam turbine plants are located at the industrial sites that commonly where the biomass is produced. Another example is gasification process, where the biomass is directly heated and broken down into flammable gas. The gas or called 'biogas' will be drawn into filtration system to clean and refine before subjected to usage for electricity production.

The fact that major biomass components such as cellulose, hemicellulose and lignin can be fractionated based on different temperatures is exploited with the merging technology of pyrolysis [19–21]. The process involves three stages or heat-based degradation. The first stage includes water elimination, structural deformation and alkyl group formation which is also called pre-pyrolysis. The second stage involves decomposition of components and formation of pyrolysis products. Finally, the last stage produces carbon residuals and bio-oil from charred biomass. Mainly, pyrolysis dealt with cellulose and hemicellulose component conversion, but very little is known about the contribution of this process to lignin fraction. The lignin is merely converted to low concentration of phenolics and char. As it becomes more evident that large amounts of hydrolytic lignin will be produced in future bioethanol plants, lignin has gained interest as a chemical feedstock or aromatic compounds such as catechols, guaiacol, syringol, phenol, furfural, and acetic acid [22, 23].

2.2.2. Chemical-based conversion

In a chemical approach, cellulose in a raw biomass can be converted to biofuel. Another new process has been introduced to convert cellulose to chemical 5-hydroxymethylfurfural (HMF). Cellulose, through catalytic conversion, can be converted to HMF [24], and recently formation of HMF through catalytic conversion in ionic liquid produced more than 50% of HMF [25–28]. HMF is oxygen rich and hydrogen deficient that can be used for biofuel production through a reduction process that led to the production of 2,5-hexanedione (HD) [29]. Meanwhile, recently one report indicates that direct electrochemical method to convert HMF to HD without any means of catalysis or hydrogen. Instead HD is produced using water and metal electrode to open up furan ring in HMF and selectively in one-step mode [30].

There is another process called ‘thermochemical’ that involves thorough deconstruction of feedstock and develops the resulting intermediates into different types of fuels and fine chemicals. Thermochemical process consists of three processing parts which include gasification or devolatilisation to produce raw syngas, syngas conditioning and removal of other residual gases such as H_2S and CO_2 and finally conversion of syngas to fine chemicals such as olefins, aromatic mixed alcohols and fuel for transportation [31].

2.2.3. Biological process-based conversion

In general, biological process-based conversion involves cellulosic or hemicellulosic sugar conversion to fuel. Most popular ever known is biofuel such as bioethanol production using microorganism(s) as the catalyst in the bioconversion process. There are two-step processes which include fermentation and pretreatment to obtain the primary sugars [32]. In many publications, cellulose and hemicellulose conversion to biofuel production have been discussed thoroughly and can be read elsewhere [32, 33], and it is necessary to briefly discussed on lignin bioconversion.

Though it has inhibitory effect on any cellulose/hemicellulose conversion, if present, lignin can be converted to value-added products such as stand-alone feedstock. Recently, a *Rhodococcus* sp. can convert lignin into triacylglycerols under nitrogen-limiting conditions [34]. Furthermore, it was demonstrated that lignin valorisation can be channelled by different catabolic pathways of few aromatic catabolising bacteria to produce precursors for fuel production [3]. However, the thermal properties of each aromatic bonding in lignin need an integrated thermochemical process in order to penetrate the bonds [35].

2.3. Biomass types and characteristic

Biomass is usually derived from trees, forest residues, grasses, aquatic plants and crops. They are very important feedstock to produce valuable chemicals and fuel. These plants undergo photosynthesis process to convert carbon dioxide and water to primary and secondary metabolites. Primary metabolites include carbohydrates and lignin which presents in large concentration in biomass. The carbohydrates are simple sugar, cellulose and hemicellulose which take up more than 50% of the content of the biomass. However, some researchers divided the biomass in different moisture contents [36]. The high moisture content biomass includes aquatic plants and manures which have to undergo ‘wet’ processing techniques to convert it to energy. For example, conversion of these materials to biofuel

commonly involves degradation of the materials using microorganisms or fermentation. Meanwhile, woody plants or dry biomass involves physical techniques such as gasification, pyrolysis or physical combustion.

3. Lignin: structural chemistry and route to conversion

Lignin is one of the major components in lignocellulosic biomass together with cellulose and hemicellulose. It intertwined with the cellulose-hemicellulose structural linkage that poses barriers for any physical or biological disturbance through the strong structure of lignin. The structural chemistry of lignin has been discussed and detailed of each of its monomers also presented. In addition, lignin conversion to fine chemicals and fuel has been added and mostly focuses on the present available data.

3.1. Lignin: structural chemistry

Through the binding of arrays of carbon-carbon and ether linkages, a single intermonomeric bonding scaffold was formed which is also known as lignin matrix [37]. This complex heterogenous structure of lignin consists essentially from three aromatic alcohols: p-coumaryl, coniferyl and sinapyl alcohols. These monolignols form phenolic substructures such as guaiacyl (G, from coniferyl alcohol), p-hydroxyphenyl (H, from coumaryl alcohol) and syringyl (S, from sinapyl alcohol) as shown in **Figure 2**. Each chemical structure confers a distinctive characteristic to lignin. Lignins composed mostly of G-units are usually softwood lignins, while lignins with different ratios of G- and S-units are hardwood lignins [37–40].

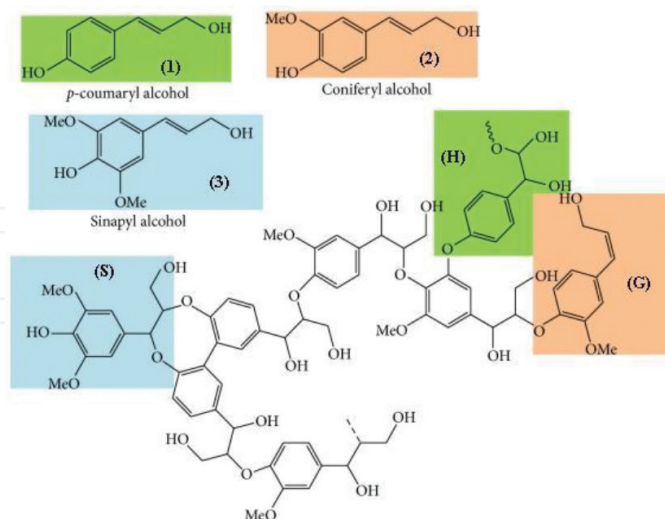


Figure 2. A segment of lignin polymer structure with monolignols involved in lignin biosynthesis: p-coumaryl alcohol (1), coniferyl alcohol (2) and sinapyl alcohol (3). Possible phenolic structures: guaiacyl (G), p-hydroxyphenyl (H) and syringyl (S). Reprinted from Ref. [38] with permission from Hindawi.

There are few types of native lignin substructures and interunit for different biomass sources as seen in **Figure 3**. The β -O-4' (aryl ether) interunit linkage has been identified as a major lignin substructure where it provides a foundation for polymeric framework deconstruction in industrial processes. Some are known to have some resistant to chemical degradation such as β -5', β - β' , 5-5', 5-O-4' and β -1' [37, 41]. Thus, lignin usually appears in a complicated macromolecule form due to the diversity functional groups and various kinds of linkage of lignin substructures [42]. Lignin usually exists in the form of lignin-carbohydrate complexes (LCCs) resulted from dehydrogenation of G, S and H monolignols. Hence, the covalently linked to hemicellulose lignin and the occurrence of lignin cross-linked to polysaccharides provide mechanical strength to plant cell wall and additional protection to other structures from external [37].

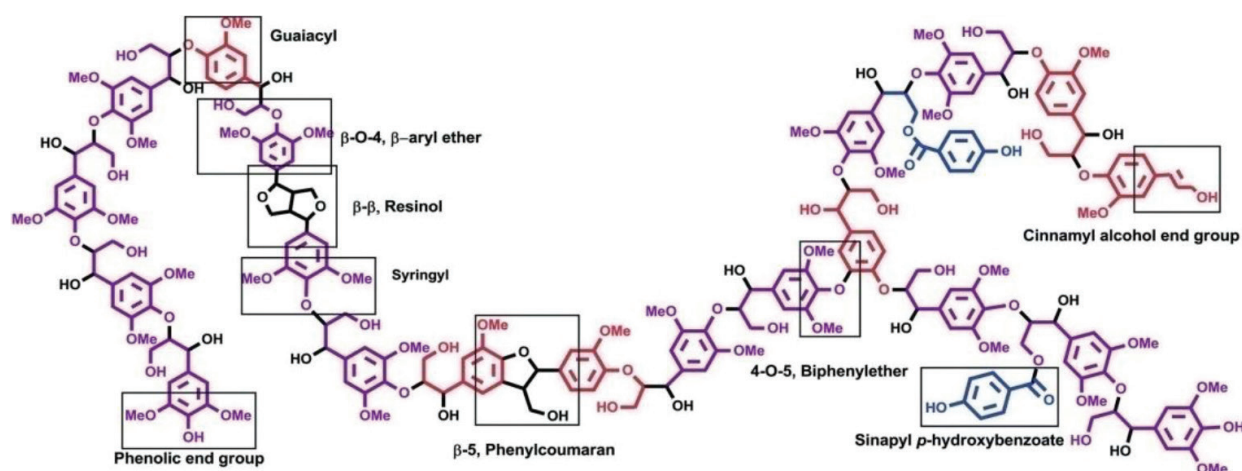


Figure 3. Common interunit linkages in lignin polymeric framework. Reprinted from Ref. [41] with permission of The Royal Society of Chemistry.

3.2. Lignin: chemical and biological conversion

High value compound can be produced through biological and chemical conversion of lignin. Processes such as gasification, hydrolysis, oxidation and pyrolysis are a well-known chemical conversion process. A wide range of polymers, chemicals and building blocks can be synthesised from chemically converted lignin [40]. Hydrodeoxygenation (HDO) is an example of chemical conversion method. It involves the removal of oxygen from oxygen-containing molecules in the presence of catalysts with high-pressure hydrogen at moderate temperature. Oxygen is removed to form water via hydrogenolysis reaction and then saturated by hydrogenation reaction [37]. Catalytic HDO of guaiacol (2-methoxyphenol), an oxygen-rich lignin model compound, has been investigated by Aqsha et al. for production of deoxygenated products. Guaiacol conversion products are mainly determined by methoxy, hydroxyl and benzene ring [43].

Alternatively, lignin converted from biological process such as enzymatic oxidation and microbial conversion involves living organisms [40]. Lignin-degrading microbes such as lig-

ninolytic peroxidase enzymes or laccase enzymes have been exploited to oxidise aromatic units within lignin complex molecules [44].

3.3. Examples of lignin to value-added materials

Yi-Lin Chung et al. developed a catalytic and solvent-free method for synthesis of a lignin-poly(lactic acid) copolymer. The g-type poly(lactic acid) (PLA) copolymer, synthesised from graft polymerisation of lactide onto lignin, is catalysed by triazabicyclodecene (TBD) as depicted in **Figure 4**. It displays a glass transition temperature range from 45 to 85°C with multiphase melting behaviour. It also can be used to enhance UV absorption and reduce brittleness without sacrificing its elasticity [45].

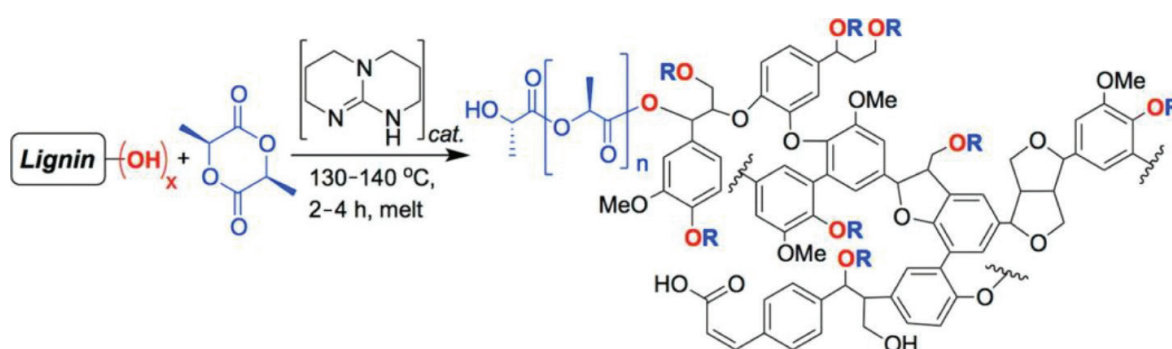


Figure 4. Ring-opening polymerisation of lactide (LA) on lignin using triazabicyclodecene (TBD) catalyst scheme. Reprinted with permission from Ref. [45]. Copyright (2013) American Chemical Society.

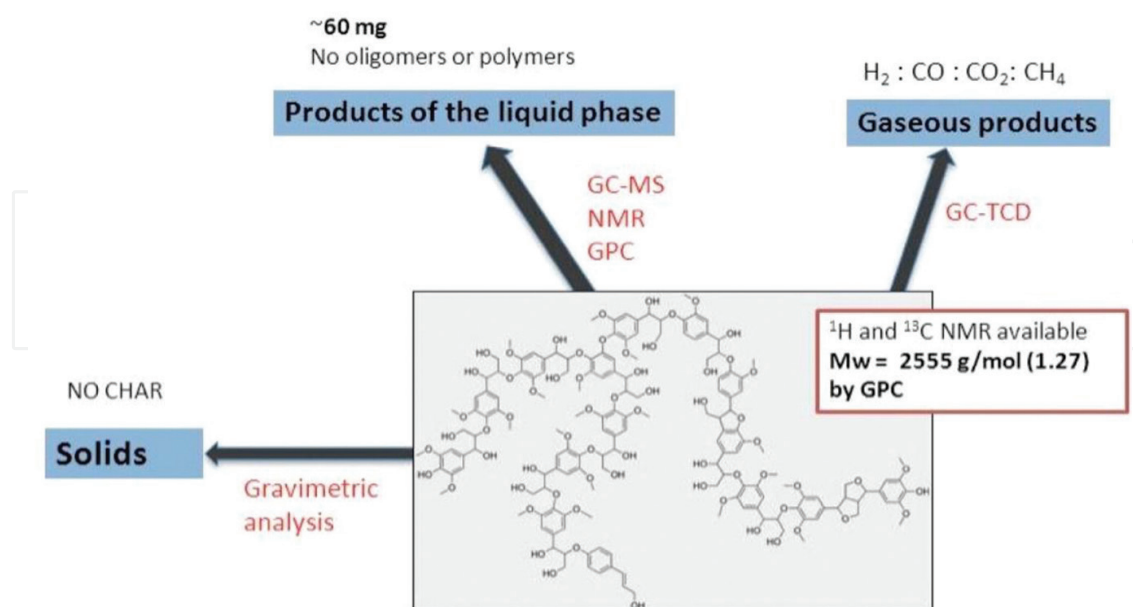


Figure 5. Quantitative analysis of product streams from organosolv lignin substrate. Reprinted with permission from Ref. [46]. Copyright (2014) American Chemical Society.

Barta and Ford devised a novel catalytic system to produce organic liquids from renewable lignocellulose feedstock. Supercritical methanol was used as reaction medium in a single-stage reactor at operating temperature of 300–320°C at 160–220 bar using copper-doped porous metal oxide. This system was tested on organosolv lignin solution (deep brown colour). As summarised in **Figure 5**, no char was formed during reaction, and the gaseous products were mainly hydrogen gas. The average molecular weight of liquid-phase product is within range of the monomer, and dimer units indicate that organosolv lignin was fully converted [46].

4. Hydrogenation of lignin

It is a continuation of previous section, but in this section, the focus is more on hydrogenation process of lignin. In this section, examples of recent literatures reported so far on the hydrogenation of lignin and details on the methods will be discussed.

4.1. Lignin valorisation

Lignin valorisation is an approach or strategy to convert lignin obtained from any sources, especially biomass, into value-added products as shown in **Figure 6** [47]. Scientists have studied this strategy for many decades through variation of thermal, catalytic and biological approaches in order to break lignin down into its constituent monomers and oligomers as well as upgrading the resulting monomers to fuels or chemicals [48].

The strategy usually involved one or more processes in order to achieve maximum lignin conversion. For example, Gianpaolo Chieffi et al. studied the efficiency of integrating smart recycle and upcycle of biomass-derived waste stream with strategies for the preparation of functional carbonaceous and composite materials using Fe and Ni (cheap and abundant metal precursors) [49].

Lignin valorisation can be roughly categorised into two sections: (1) upstream which involved separation and isolation process of lignin (e.g. pyrolysis, hydrogenolysis and hydrolysis) and (2) downstream, where valorised products are obtained through depolymerisation and chemical modification of the isolated lignin (e.g. hydrodeoxygenation, catalytic cracking, hydrogenation and dehydrogenation) [50]. In this section, we focus on the downstream process which is to convert the lignin monomers to the fuels and chemicals via hydrogenation.

4.2. Hydrogenation in general

Hydrogenation is one of the depolymerisation strategies of lignin which utilise hydrogen as a reductant to yield aromatic products with lower oxygen content and higher stability than other strategies (c.f. **Figure 6**) [47]. This process operates in mild condition affording high-value fine chemicals. However, it is extremely difficult to selectively yield products towards aromatic such as C=C, linear C=C, C=O, C=C, etc. due to the nature of catalysts and reaction conditions. In this process, the selection of the suitable catalysts is the critical parameter to ensure the desired products can be achieved.

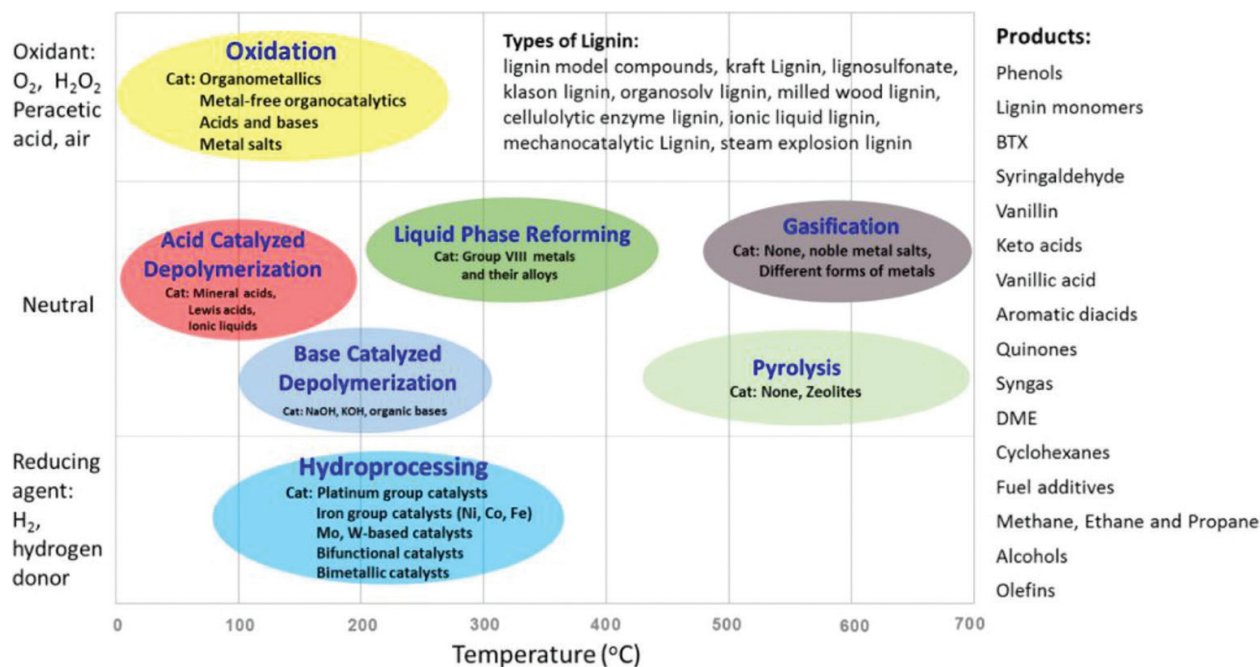


Figure 6. Summary of lignin conversion process (note: the abscissa represents the typical temperature range of the lignin conversion processes). Reprinted with permission Ref. [47]. Copyright (2015) American Chemical Society.

4.3. Examples of lignin hydrogenation

Consumption of fossil fuels would decrease significantly by implementing this approach of hydrogenating lignin to obtain the desirable products. Nevertheless, factors such as product selectivity, cost and the conversion efficiency of using commercially available catalysts are still unsatisfactory [51]. Hence, endless research has been carried out in order to overcome these difficulties.

Yu et al. [52] proposed an in situ catalytic hydrogenation system as relative to conventional method for converting lignin depolymerisation compounds to alcohols. In this work, The Raney Ni has been used for hydrogenation process. They found guaiacol conversion and cyclohexanol selectivity to be 99% and 93.74%, respectively, for 7 h time on stream (TOS). These results were obtained under the optimal conditions of 220°C, initial pressure of 3.0 MPa and mole ratio of H₂O/CH₃OH/feedstock = 20:5:0.8. Thus, this technique offers a new alternative method for hydrogenation of lignin.

The recent work of Shu et al. [53] utilised a highly efficient and selective hydrogenation process for phenolic compounds at a mild condition over step by step precipitated Ni/SiO₂ catalyst. Almost a complete conversion of guaiacol to cyclohexanol was obtained at 120°C, 2.0 MPa for 2 h TOS. The step by step precipitated Ni/SiO₂ preparation method thus significantly improved the conversion of the guaiacol (c.f. **Figure 7**). The structure of catalysts has been significantly modified by increasing the specific surface area and high Ni metal dispersion on the support that translated into high catalytic activity. Furthermore, this method also provides an appropriate acidity of catalyst and, hence, improves the catalytic performance significantly. Interestingly, this method also improves the longevity of the catalyst with an excellent recyclability.

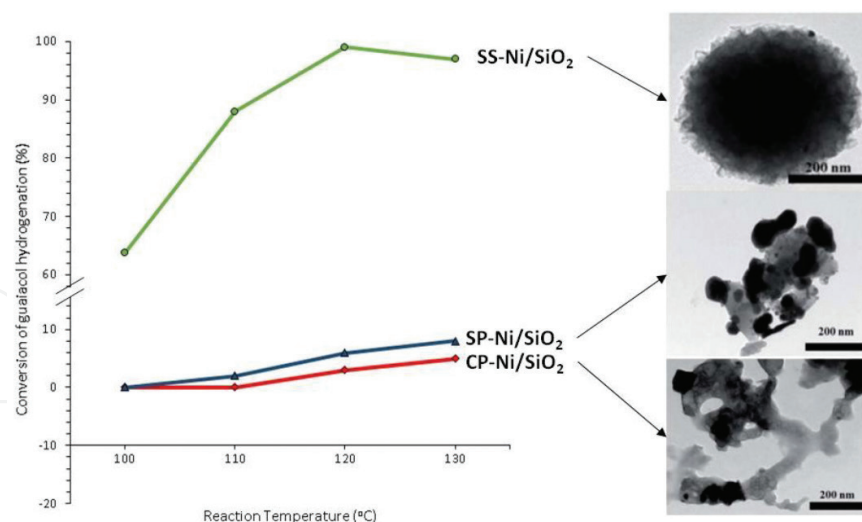


Figure 7. Conversion of guaiacol hydrogenation for different Ni/SiO₂ catalysts under 120°C, 2 MPa H₂ atmosphere for 2 h. Adapted from Ref. [52] with permission of The Royal Society of Chemistry.

Pd also exhibits a good metal to be doped with Al₂O₃ as a catalyst for hydrogenation process using wet impregnation technique. The work of Yi et al. (2016) [54] employed 3 wt.%Pd/Al₂O₃ to convert 4-ethylphenol to cyclohexanols under mild reaction conditions in an aqueous phase. The reaction exhibits 100% conversion at 60°C for 12 h TOS. The catalysts also exhibit water resistance and stability even after recycling four times. This catalyst may provide a new catalyst's formulation to selectively produce cyclohexanol at mild reaction conditions.

Overall, the choice of catalysts is very imperative steps in determining the product selectivity. For example, Raney Ni has been extensively used in hydrogenation of lignin in past decades and regarded as the most common catalysts in hydrogenation process. However, there is not much study in bimetallic catalysts that might be worth to be investigated in order to enhance the product conversion and catalyst's longevity.

5. Future trends

The development of lignin valorisation or degradation remains open for new ideas and approaches. The energy and environmental crises which modern world is experiencing are forcing to re-evaluate the efficient utilisation or finding alternative uses for natural, renewable resources and using clean technologies. In this regard, lignocellulosic biomass holds considerable potential to meet the current energy demand and to overcome the excessive dependence on fossil fuels. Further advanced biotechnologies are crucial for discovery and produce biofuels and bio-chemicals. In current scenario, future trends are being directed to lignocellulosic biotechnology and genetic engineering for improved processes and products [55]. To overcome the current energy problems, it is predicted that lignocellulosic biomass in addition of green biotechnology will be the main focus of the future research [18].

Currently, lignocellulose is processed to product through three steps that include pretreatment, saccharification and fermentation [56]. The chemical pretreatment process has shown it important in the subsequent enzymatic hydrolysis and conversion of cellulosic feedstock to valuable products in the process of fermentation. An analysis of the chemical pretreatment method result shows that the composition of biomass such as hardwood, softwood or grass is the main factor in the selection of pretreatment method [55]. However, any chemical pretreatment that requires lower-cost chemical reagents and conditions and yield more sugar is preferable. The chemical pretreatment process can be divided into six types: acidic pretreatment, alkaline pretreatment, wet oxidation, ionic liquids, oxidative delignification and organosolv [55]. However, it has been reported that chemical pretreatment process adds significantly to the cost of feedstock hydrolysates by consuming energy, expensive catalysts and chemicals while potentially hindering the downstream bioprocess [56, 57], thus requires more research effort, such as the hydrogenolysis of lignin in methanol, however, produced mostly phenols. This clearly shows that the solvent plays an essential role in directing catalytic selectivity and, thus, it must be taken into consideration in the design of catalytic systems for lignin conversion [57].

The necessity of chemical pretreatment of lignin-containing biomass represents a major barrier to downstream fermentation [56] especially involving physical and thermochemical processes that alter the physiochemical recalcitrance of biomass that enhances downstream enzyme digestibility [58–62]. In addition, it has been reported that pretreatment processes modify the polysaccharide matrix reducing overall yield of fermentable sugar or generating by-products that inhibit enzyme hydrolysis and fermentation [63, 64].

Alternatively, it has been reported that microbes with tolerance to the inhibitory compounds produced during pretreatment are of industrial interest as fermenters of sources of saccharolytic enzymes and enhances downstream fermentation capabilities, thus potentially eliminate thermochemical pretreatment steps [18]. Indeed, biological pretreatment processes are an environmental-friendly alternative to thermochemical pretreatments, improving biorefinery economics by reducing pretreatment costs, easing inhibitor formation and increasing downstream fermentation [65–67], as reported that a few fungi suitable for wheat straw biological pretreatment and increased sugar recoveries [67].

6. Conclusion

In a nutshell, the hydrogenation of lignin can potentially become a breakthrough route for production of biofuel if we can unlock the lignin functionality. With the recent findings, it is interesting to observe that the exploitation of lignin valorisation shall make this route become viable and efficient to produce biofuel via hydrogenation of lignin. Further advanced biotechnologies are crucial for discovery such as more efficient biological pretreatment system, bioprospecting and development of stable genetically engineering microorganisms, improved gene cloning and sequencing technologies, characterisation of new enzymes and production in homologous or heterologous systems and ultimately lead

to low-cost conversion of lignocellulose biotechnology for improved processes and productions based on economies of scale more efficient and cost-effective conversions of lignin into value-added products. To overcome the current energy problems, it is envisaged that lignocellulosic biomass in addition of green biotechnology will be the main focus of the future research.

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