Recent progress in conversion of carbohydrate biomass and their derivatives to γ-valerolactone

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Abstract. Biomass, the only renewable resources of fixed carbon, shows great potential to ease the pressure on fossil energy crisis. In recent years, conversion of carbohydrate biomass into value-added products has been vastly reported. Gamma (γ)-valerolactone (GVL), which is one of the platform chemicals, has been extensively used in industrial production. Recent trends proposed an eco-friendly processing using water and biomass-derived materials as hydrogen sources instead of high-pressure and high-purity gaseous hydrogen, avoiding storage, transportation and operation risk in the production. This review summarizes the progress in GVL production from carbohydrate biomass and highlights the novel green approach by using green reductants and non-noble-metal catalysts.

1. Introduction
Conversion of biomass, an abundant renewable resource on earth, into chemicals and fuels is one of the promising solution to relieve the dependence on fossil fuels and reduce the environmental pollution[1]. In contrast to other renewable energy, such as solar, tidal and wind energy, biomass is the only fixed carbon renewable resources which is critical in the production of liquid hydrocarbon fuels and chemicals[2,3]. It is worth mentioning that biofuels and chemicals obtained from biomass not only helps to alleviate the pressure on fuels and chemicals consumption, but also reduce significantly the negative impact on the environment due to non-toxic and biodegradable features of biomass[4].

Gamma(γ)-valerolactone (GVL) has attracted considerable attention in the past decade as one of the most promising platforms synthesized from carbohydrate biomass because of its distinct physicochemical properties. It can be used as fuel additives, advanced fuels, green solvents, and raw materials for some biofuels and chemicals. Herein, the recent progress in the conversion of carbohydrate biomass into GVL was reviewed. Notably, water instead of traditional high-pressure and high-purity hydrogen was employed as hydrogen source in the hydrogenation of biomass or biomass derivatives, avoiding storage, transportation and operation risk in the production.

2. Features and application of GVL
GVL is naturally existing, biodegradable and safe chemical which has low melting (-31 °C), high boiling (207 °C) and open cup flash (96 °C) points, and thus is facile to store and move globally in
large quantities. GVL is non-toxic and miscible with water, organic solvents, resins and waxes, and thus it can be applied in many reactions instead of toxic and harmful solvents. Xue\cite{5} carry out GVL as a solvent to strip the bulk phase g-C3N4, which can form an ultra-stable and thin layer of g-C3N4 nanodispersion at a concentration of 0.8 mg/mL, and the process can be easily scaled up to 200 mL or even more.

GVL also can be used as a biofuel and its additives. Horváth\cite{6} consider GVL to be an important sustainable liquid that has higher energy density and lower saturated vapor pressure compared to gasoline. Besides, it is more efficient and energy-saving to concentrate and purify GVL in aqueous solution than ethanol, because GVL can not form an azeotrope with water. Mellmer\cite{7} studied the performance indicators of GVL and gasoline doping in detail. The study found that the mixture of GVL and gasoline can greatly reduce the index of CO and other substances in automobile exhaust.

GVL has good modification and can improve the properties of GVL through reaction, which can overcome some of the shortcomings of GVL as a biofuel. For example, the product of GVL hydrogenation reaction, 2-methyltetrahydrofuran (2-MHF), is regarded as a biofuel additive with great potential for utilization\cite{8}.

Because of excellent modification, GVL can continue to be converted into high value-added products, like 1, 4-pentanediol, 2-methyltetrahydrofuran, methyl 3-pentenoate, and α-methylene-GVL. Manzer\cite{9} proposed a solid base catalyst, loaded on ruthenium acetate using SiO2, to catalyze the reaction of GVL with formaldehyde to form α-dimethyl-GVL. The conversion of GVL was 60%, and the yield of α-dimethyl-GVL was 25%. Tang\cite{10} obtained a higher yield of methyl 3-pentenoate (3-PTM) from GVL.

Figure 1. Synthesis of high-added chemicals from GVL.

3. Raw material for GVL production

3.1 Production of GVL from levulinic acid and its esters

Over the last two decades, levulinic acid (LA) has been identified to be a valuable product derived from biomass\cite{11}. Excellent studies on production of GVL from LA and its esters has been performed, either using heterogeneous or homogeneous catalysts. Li\cite{12} reported that 99% yield of GVL was achieved from LA under optimum reaction conditions (100 °C, 2.0 MPa H2) in water.

A schematic diagram of the reaction for preparing GVL by hydrogenation of levulinic acid and its esters is shown in Figure 2. (1) The additional H2 attacks the carbon-oxygen double bond on the carbonyl group of the LA (or ester), and the hydrogen atom replaces the oxygen atom to form the γ-hydroxyvaleric acid. γ-Hydroxyvaleric acid will quickly remove one molecule water and carry out internal esterification reaction to produce GVL; (2) Under the high temperature, LA is alcoholized to form angelica lactone, and then the intra-ring double bond in angelic lactone is hydrogenated to obtain GVL\cite{13}.
Figure 2. Reaction routes for conversion of LA and its esters into GVL.

3.2 Production of GVL from cellulose
In order to achieve the industrial production of GVL, the research on the direct production of GVL by using cellulose, hemicellulose and its degradation products caused widespread concern of researchers in recent years. Ding\cite{14} exploited Al-doped niobium phosphate to catalyse cellulose hydrolysis in aqueous solution, and the yield of LA was up to 52%. Moreover, the acidolysis solution can be completely converted into GVL by using catalyst Ru/C. Yang\cite{15} utilized the fructose, sterol and 5-hydroxymethylfurfural (5-HMF) as the substrate to obtain the ethyl levulinate by acid hydrolysis, with R-Ni as the catalyst and isopropanol as the hydrogen donor, and the yield of GVL was 50%, 86% and 66% at room temperature for 9 h, respectively.

4. Choice of hydrogen donor
LA and its ester compounds and cellulose can be well converted into GVL in a reactor filled with a certain hydrogen pressure. In the study of the preparation of GVL from carbohydrate and their derivatives, much research has been done on the improvement of hydrogen sources.

4.1 High pressure H₂ as a hydrogen donor
The approach that hydrogenation biomass with molecular hydrogen has been investigate over the past decades. Manzer\cite{9} loaded different metals, Rh, Ir, Pt, Pd, Ru, Re and Ni, on activated carbon (5% loading), and the reaction activity for conversion of LA was: Ru >Ir>Pd> Rh > Pt > Re> Ni, the selectivity of GVL was: Ir> Rh > Pd≈ Ru > Pt ≈ Re > Ni. The results indicated that 5% Ru/C had the best catalytic effect. Furthermore, Manzer found that the conversion of LA was 100% and the selectivity of GVL was more than 97% at 150 °C for 4 h with 35 bar H₂ pressure. Hengn\cite{16} verified GVL still has a high selectivity with water and methanol as reaction solvents respectively. However, gaseous hydrogen needs to be condensed in high-pressure gas cylinder for storage and transportation. The procedure of pumping hydrogen into cylinder is energy intensive process. Moreover, the transportation and operation of hydrogen face safety risk due to explosive and inflammable property of hydrogen.
4.2 Formic acid as a hydrogen donor
Recent research has demonstrated that formic acid (FA) or formate has the potential to serve as an excellent hydrogen storage material since its dehydrogenation can easily proceed under mild conditions over catalysts [17]. Our previous study on biomass and biomass waste resource utilization shows more than 75% yield of FA can be achieved from carbohydrates in some minutes [20]. Therefore, biomass-derived FA could be regarded as a renewable hydrogen source for hydrogenation reactions. Ruppen [18] prepared a Ru/C catalyst by impregnation. The decomposition rate of FA is 48%, and the conversion of LA is 87% and the yield of GVL is 75%. Varkolu [19] used a Ni-based catalyst to carry out hydrogenation of LA under gas phase conditions. Under the conditions of a molar ratio of FA to acetic acid of 1, the conversion of LA was 98.6% and the selectivity of GVL was 86%.

4.3 Alcohols as a hydrogen donor
The cheap and low toxicity alcohol is one choice of hydrogen source because the hydrogenation reaction can proceed through hydrogen transfer reaction. Mu [20] put forward to employ isopropanol as a hydrogen source and Zr-CA as a catalyst for hydrogenation of methyl levulinate, ethyl levulinate, butyl levulinate and LA, respectively. The selectivity of GVL was 97.2%, 97.1%, 86.1% and 96.8%, respectively. Huo [21] used isopropanol as a hydrogen source and Cu/Al2O3/ZnO as a catalyst to synthesize GVL from ethyl levulinate, and the yield of GVL was up to 99%.

4.4 Water as a hydrogen donor
Water is the most abundant and eco-friendly hydrogen source and reaction reagent. Jin [22] proposed water splitting by metal for hydrogen production under mild hydrothermal conditions without additional catalyst. Commercially available nonprecious metals of Fe, Ni, Cu, Cr and Mo exhibited significantly catalytic activities in the hydrogenation of LA into GVL. Over 90% yield of GVL from LA can be obtained at a relatively low temperature of 180 °C, and an excellent 98% yield of GVL was achieved over the Fe catalyst at 250°C. Catalyst Fe is stable and still keeps the high catalytic activity after recycles. This study provides an efficient approach for GVL production from carbohydrate biomass derivatives with water as a hydrogen source.

5. The choice of catalysts
Researchers have successfully designed the synthesis of GVL from LA in both homogeneous and heterogeneous systems. Although homogeneous catalysts display good activity and high selectivity in the reaction [23], they are hard to recycle due to the separation difficulty from products [24]. It is worth noting that heterogeneous noble catalysts, such as Ru/C, Ru/graphene, Au/ZrO2, Pd mixtures, have a significant effect on the hydrogenation of LA to GVL. Upare [25] examined the activity of activated carbon supported Ru, Pd, and Pt catalysts (5% by loading) on the hydrogenation of LA. It was found that Ru/C can exhibit the best catalytic activity, and the GVL yield can reach 98.6%. Li [26] reached 99% yield of GVL under Ru catalyst, 100 °C and 2 MPa H2 by using water as a reaction solvent. However, noble metal catalysts increase the cost of the reaction, and thus hinders the large-scale application. In this regard, inexpensive non-noble-metal catalysts (e.g. Ni, Co, Fe, Cu, Zn) have received considerable attention for the hydrogenation of LA to GVL. Zhang [27] synthesized an inexpensive and magnetic catalyst (Ni/Cu/Al/Fe), which was reached 98% yield of GVL at 2.0 MPa H2 at 415K for 3 hours, and the catalyst remained highly activity after 5 cycles.

6. Conclusions
A variety of methods for efficient synthesis of GVL from carbohydrate biomass and their derivatives have been widely investigated in the past decade. It is necessary to improvement the crafts of production GVL from carbon biomass by using green hydrogen source and cheap catalyst. Water and biomass-derived FA and alcohols are suitable hydrogen sources and some porous non-noble-metals show good catalytic activity in hydrogenation of biomass. In addition, one pot approach for GVL
synthesis from raw biomass feedstocks (e.g. straw, sawdust) without separation of intermediates is needed.

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