Facile conversion of levulinic acid and glucose to *γ*-valerolactone over Raney-Ni catalyst without an external hydrogen donor

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Abstract

Finding sustainable resources has always been a strong research due to the current massive consumption of non-renewable fossil fuels on a global scale. Recently, the transformation of renewable biomass into value-added chemicals has become a crucial alternative to solve this problem. Levulinic acid (LA) and glucose are the most significant biomass-derived compounds and γ-valerolactone (GVL) is considered to be the important intermediate of chemicals and fuels. However, the safety and cost of external hydrogen are the main obstacles for the production of GVL from biomass and its derived chemicals by catalytic transfer hydrogenation process. Herein, we introduce the conversion of LA and glucose-derived LA into GVL without an external hydrogen donor, respectively. One process is the production of GVL from LA in a maximum yield of 99% at relatively mild conditions (150 ^{o}C) for 3 h with hydrogen, which is from the decarboxylation reaction of formic acid (FA) in water with Raney Ni. The other process is conversion of glucose into LA and GVL in two steps. More than 50% yield of LA and 67% yield of GVL could be obtained from glucose with 3% HCl solution and Raney Ni.

Key words: Levulinic acid, γ-Valerolactone, Hydrogenation reaction, Liquid fuels, Raney Ni catalyst

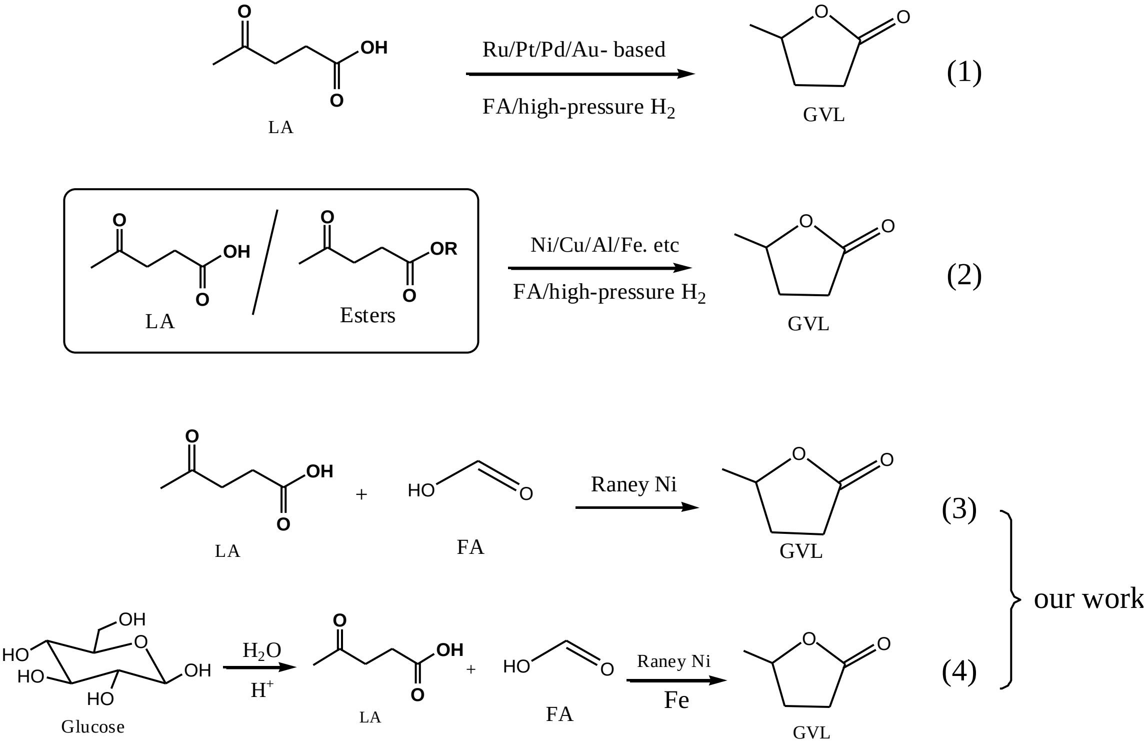
1. Introduction

Nowadays, excessive consumption of fossil fuels due to world population increases, environmental pressure and the bulk of resource needs, has stimulated the effects for the renewable production of chemicals and resources. Lignocellulosic biomass consists of hemicellulose (20-35%), cellulose (35-50%) and lignin (10-25%), is the most abundant, low-cost and renewable carbon materials on the earth[1]. Nature produces over 170 billion metric tons of biomass per year by photosynthesis, 75% of which can be applied to the class of carbohydrates. Surprisingly, only 3-4% used by humans for food and other field purposes[2]. In contrast to other renewable energy, such as solar, hydrogen, tidal, wind energy, biomass is the only renewable resources of fixed carbon of replacing fossil fuels, which is crucial for the production of liquid hydrocarbon fuels and chemicals[3-7]. Meanwhile, It has been predicted that more than 20% of liquid fuels and 25% of chemicals by 2030 will be synthesized from biomass[2, 8-10]. In recent years, conversion of biomass and its derived levulinic acid (LA) into value-added products has been vastly reported, which has attracted worldwide attention. It is well-known that LA has been identified to be a valuable product derived from biomass[11], that can be produced at high yields from cellulose using mineral acids, and can be converted into valuable chemicals and fuels[12-14]. Gamma-valerolactone (GVL), as a sustainable liquid for energy and carbon-based chemicals, has been regarded as one of the most promising products as a food additive, fuels, organic solvent, and benign intermediate for the production of more valuable chemicals, such as acetaldehyde, 5-Nonanone and 2-methylglutaric acid [15-16]. Noteworthy, GVL is stable for several weeks at high temperature (150 ^{o}C) and its thermal decomposition only proceed under the presence of appropriate catalysts, and its vapor pressure is remarkably low, even at higher temperatures (3.5 KPa at 80 ^{o}C), making it easy and safe to store and move globally in large quantities[17-18].

Over the past decades, there are extensive studies on production GVL from biomass and LA has been performed, either using heterogeneous or homogeneous catalysts[19-24]. Particularly, noble metal catalysts, such as Ru/C, Ru/grapheme, Pd complex, and Au/ZrO_2, displayed highly activity in LA hydrogenation (Scheme1 (1))[19, 25-27]. Li et al. reported that 99% yield of GVL was received with supported Ru catalysts under optimum reaction conditions (100 ^{o}C, 2.0 MPa H_2, LA= 0.1 g/mL) in water[28]. Manzer et al. screened various noble metal catalyst (Ir, Rh, Ru, Pd, Pt and Re) and pointed out Ru/C exhibited the highest yield of GVL at 97% in dioxane solvent by 5.5 MPa H_2[29]. Although satisfactory results were achieved using noble metal catalysts, the distinct defect of being high cost limited the actual application of these catalysts in large-scale GVL production from biomass. Hence, exploring low-cost, stable, highly active, and easily recycle catalysts is the key process for the present studies.

In recent years, transition metal, such as Ni, Co, Fe, Cu, and Zn, has also been applied in hydrogenation reactions of LA and its esters (Scheme 1(2))[30-35]. In this respect, Zhang et al. developed a series of cheap and magnetic Ni/Cu/Al/Fe catalysts for the selection hydrogenation of LA to GVL, more than 98% GVL yield can be received at 415 K under 2.0 MPa H_2 for 3 h, and the magnetic catalyst could be recycled for more than five cycles without being defeated in its performance[36]. Zhong et al. reported a facile and green method on the production GVL from LA, 98% yield of GVL was obtained over the Fe catalyst at 250 ^{o}C in water by using Zn as reductant and requires neither gaseous hydrogen nor precious metal catalyst[37].

Currently, Formic acid (FA) has considered as an attractive hydrogen carrier because of its relatively high hydrogen content (4.4 wt%), and “hydrogen batteries” have been proposed[38]. In this work, initially, reduction of LA into GVL with FA as H_2 source instead of high-pressure molecular hydrogen, which avoids some problems such as hydrogen storage and transportation (Scheme 1(3)). Later, we studied the conversion of glucose to GVL by two-step process under acid condition over Raney Ni/Fe (Scheme 1(4)). To our delight, more than 95% and 60% yield of GVL was obtained under relatively mild condition from LA and glucose, respectively.



Scheme 1. The conversion of LA or biomass into GVL of previous and our work

2. Materials and Methods

2.1 Materials.

Formic acid (≥ 96%, ACS) was purchased from Aladdin, HCl solution (36%~38%, AR) and Glucose were purchased from Sino-pharm Chemical Reagent, Raney Ni (< 150 μm) was also purchased from Aladdin, Fe powder (325 mesh, 97%) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Standard *γ*-valerolactone (GVL, 98%) and levulinic acid (LA, 99%) were purchased from Sino-pharm Chemical Reagent and J&K, respectively, used as standards for the qualitative analysis of the products in the liquid samples.

2.2 Experimental Procedure

All of the experiments were conducted in a Teflon-lined stainless steel batch reactor with an inner volume of 28 mL (the upper limit temperature of the reactors are 250 ^{o}C). The experimental procedure is briefly described as follows: (1) Conversion of LA into GVL: the desired amount of LA, FA and Raney Ni catalysts were loaded into the reactor with filling rate water of 35% (8.4 mL). Then the reactor was sealed and putted into an oven that had been preheated to the desired temperature for 1-4 h. After the reaction, the reactor was taken out from the oven and was cooled to room temperature with electric fan. (2) Direct conversion of glucose to GVL by 2-step method: at the first step, the acidolysis of glucose was performed only with glucose and HCl solution were putter into reactor. Subsequently, desired of Fe and Raney Ni were loaded into reactor desired temperature. The reaction time was defined as the time that the reactor was taken into the oven. The liquid product after reaction was collected and filtered with a 0.22-μm filter membrane. The solid samples were also collected, washed with deionized water and absolute ethanol several times to remove impurities, and dried in vacuum at 40 °C for 6 h. The conversion of LA (X), yield (Y) and selectivity (S) of GVL were defined based on the following equations:

$$X = \frac{mols\ of\ carbon\ in\ feedstock\ consumed}{moles\ of\ carbon\ in\ feedstock\ input} \times 100\% \qquad (1)$$

$$Y = \frac{mols\ of\ carbon\ in\ GVL}{moles\ of\ carbon\ in\ feedstock\ input} \times 100\% \qquad (2)$$

$$S = {}^{Y}\!/_{X} \times 100\% \qquad (3)$$

2.3 Analytic Method.

The liquid samples were analyzed by high performance liquid chromatography (HPLC, Agilent 1200 LC) equipped with two Shodex KC-811 columns and UV detector. The mobile phase is 2 mmol/L $HClO_4$ with flowing rate of 1 mL min^{-1}. The gaseous products were analyzed using a gas chromatograph equipped with thermal conductivity detector (GC-TCD), equipping a carbon molecular sieve (TDX-01) column and detected with TCD in a GC system (HP-5890 Series II). The detail description of the testing method has been reported in our previous study[39].

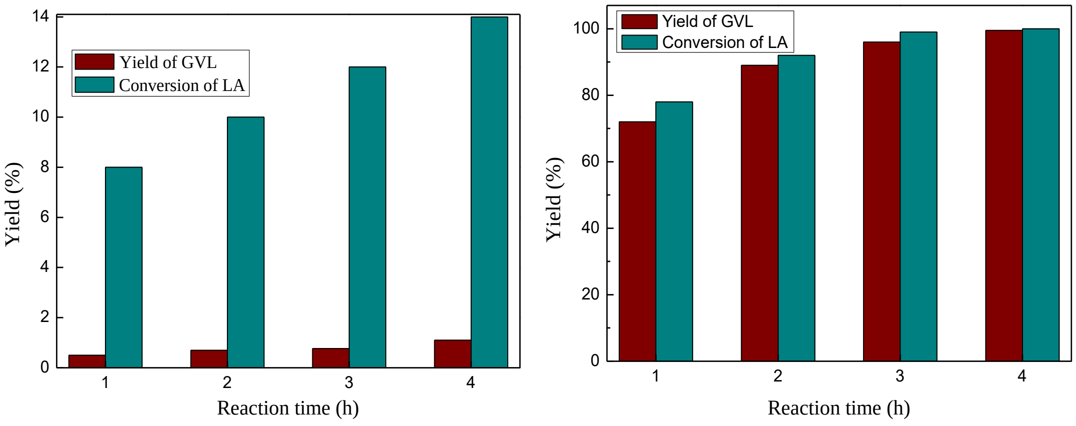
The solid samples were analyzed by X-ray diffraction (XRD, Shimadzu X-ray Diffractometer 6100) to determine the composition and phase purity, employing a scanning rate of 5°/min and 2θ ranges from 10° to 80°. The accelerating voltage was set at 40 KV with a 30-mA flux. Diffraction patterns were compared with reference data in the ICDD PDF-2 database.

3. Results and Discussion

3.1 Conversion of LA into GVL with FA as hydrogen source

Initially, a series of experiments with FA and LA were carried out under high-temperature conditions to investigate the feasibility of hydrogenation of LA into GVL with and without Raney Ni catalyst. Figure 1. shows the effect of Raney Ni on the yield of GVL and conversion of LA with FA as H_2 source. Predictably, the observed phenomenon indicated the reaction of hydrogenation of LA would hardly proceed in absence of Raney Ni at 180 °C. In the same case, however, the yield and selectivity of GVL sharply increased when Raney Ni was added (Figure 1(b)). To explore the reason, the decomposition of FA was conducted at 180 °C for 30-120 min in the presence or absence of Raney Ni (Figure S1). Compared to the reaction without catalyst, the thermal decomposition's rate of FA dramatically increased to 75% with the time increased from

30 min to 120 min by using Raney Ni. Therefore, the results reveal that the production of GVL from LA is feasible with FA as hydrogen source by addition of catalyst.



(a) (b)

Figure 1. Effect of with and without Raney Ni on the GVL yield (a) without Raney Ni, (b) with Raney Ni (LA: 10 g/L, FA: 8 g/L, temperature: 180 °C, Raney Ni: 0.2 g, filling rate of water: 35%)

To investigate the optimum reaction conditions for the conversion of LA into GVL, the effect of reaction temperature and time, molar ratio of LA and FA, the amount of Raney Ni and filling rate were performed. Firstly, the effect of reaction temperature and time on the yield of GVL was examined by changing the time from 1 h to 4 h at 130 °C, 140 °C, 150 °C, 180 °C, respectively. As shown in Figure 2, an increase of in reaction time led to an increase in the yield of GVL at ambient reaction temperatures and more than 90% yield of GVL was easily obtained under relatively mild reaction conditions. With respect to thermodynamics, $\triangle G_{red}$ (the Gibbs free energy for the reduction of oxides) decreases with the reaction temperature increases[40]. Therefore, the improvement in the conversion of LA to GVL at a higher temperature and longer time could be attributed to the decrease of $\triangle G_{red}$. In addition, apart from GVL, other products in liquid samples were also analyzed by HPLC (Figure S2). Noteworthy, other byproducts were not discovered besides added substrate (FA, LA) and targeted production GVL.

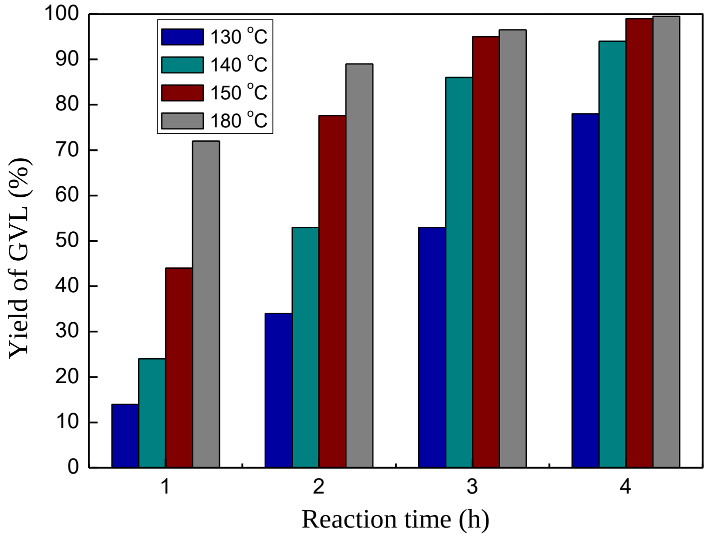


Figure 2. The influence of temperature and time on the yield of GVL (LA: 10 g/L, FA: 8 g/L, Raney Ni: 0.2 g, filling rate of water: 35%)

Subsequently, the influence of hydrogen pressure on the yield and selectivity of GVL was investigated at 150 °C by changing the molar ratio of LA and FA (Figure 3). It is noteworthy that the yield of GVL did not significantly increased with the increased of molar ratio of LA and FA from 1:1 to 1:4, which is most likely the hydrogen pressure isn't a key role for reduction of LA into GVL. Hence, the phenomenon illustrates the synthesis of GVL from LA has a great selectivity and the GVL yield is hardly affected by the molar ratio.

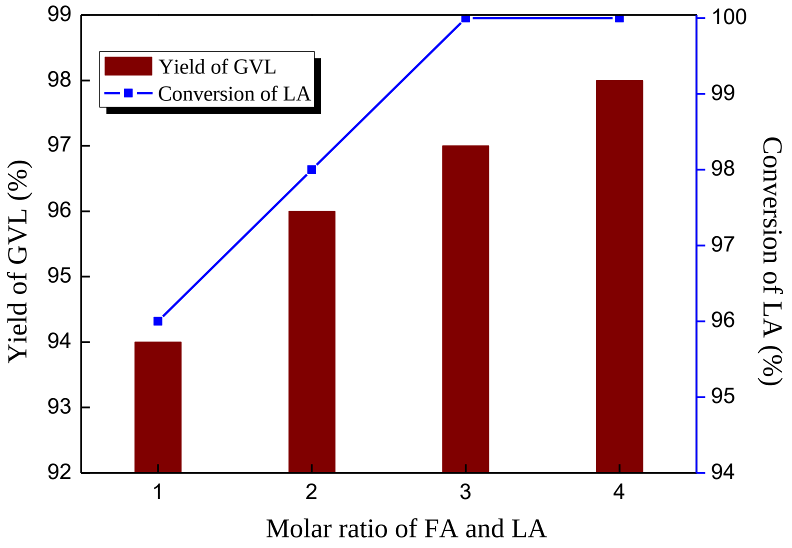


Figure 3. The effect of molar ratio of LA and FA on the yield of GVL and conversion of LA (temperature: 150 ^{o}C, time: 3 h, Raney Ni: 0.2 g, filling rate of water: 35%)

Then, to examined the effect of Raney Ni amount on the yield of GVL and conversion of LA. A series of experiments with different amount of Raney Ni were carried out under relatively mild conditions. As shown in Figure 4, both the yield of GVL and conversion of LA showed an upward trend with the amount of Raney Ni increased from 0.01 g to 0.2 g. It is likely because Raney Ni added not only promotes the thermal decomposition of FA, but also provides more activity site for hydrogenation reaction of LA.

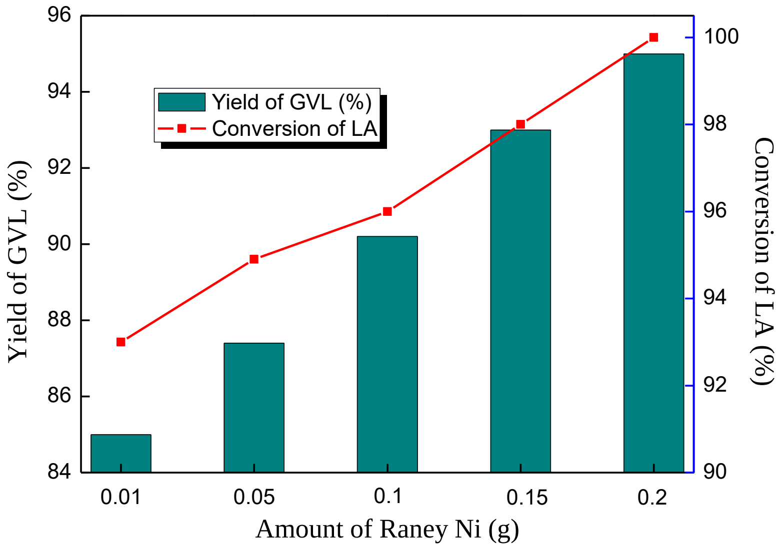


Figure 4. The effect of Raney Ni amount on the yield of GVL and conversion of LA (temperature: 150 ^{o}C, time: 3 h, LA: 10 g/L, FA: 8 g/L, filling rate of water: 35%)

Furthermore, the effect of pressure on the yield of GVL was also investigated by changing the filling rate in the reactor to simplify handling. The yield of GVL and conversion of LA decreased with the filling rate and reached 25% when the filling rate increased to 65% (Figure S3). The increase in water filling would lead to an declined in the concentration of Raney Ni, and thus lead to a weaken of the reaction equilibrium of toward the generation of GVL. This may be one of expositions for the decrease in the yield of GVL with the increase in the filling rate. Meanwhile, this explanation is also consistent with the Le Chatelier's principle[41].

Finally, we investigate the stability and recyclability of Raney Ni catalyst, the Raney Ni after the reaction was recovered and recycled. As shown in Figure 5, the observed phenomenon showed that the yield of GVL decreased from 95% to 69% after being reused for 4 times at 150 °C. The decrease in the yield of GVL with the increase in recycle time is probably because Raney Ni may emerge digestion of metallic ion under high-temperature and acidulous conditions.

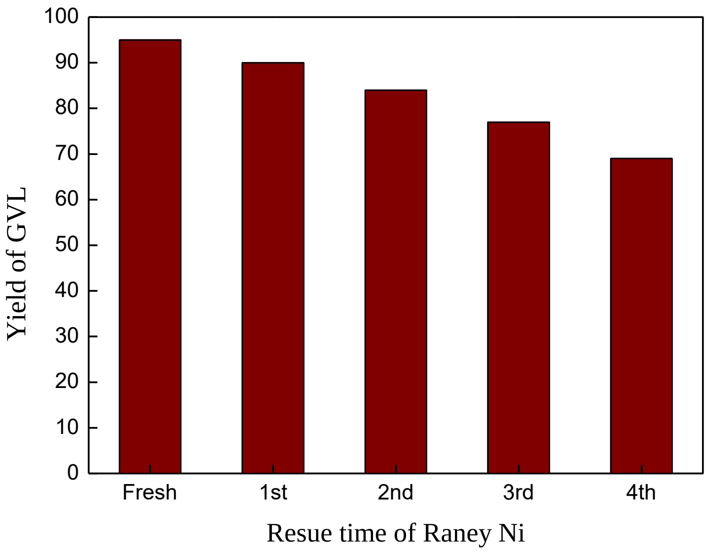


Figure 5. Effect of Raney Ni reuse time on the yield of GVL (temperature: 150 °C, time: 3 h, LA: 10 g/L, FA: 8 g/L, Raney Ni: 0.2 g, filling rate: 35%)

3.2 Conversion of glucose into GVL

As we all know, decomposition of lignocellulosic biomass into FA and LA under acid conditions has been reported[42-44]. Moreover, *in suit* generated FA from biomass would act as hydrogen source to reduction glucose-derived LA without extra hydrogen source.

Firstly, we studied the decomposition of glucose by utilizing different reaction time and different concentration of HCl solution at 250 °C (Figure S4). It is evidently that a reaction time of 30 min and a HCl solution concentration of 3% are the optimum reaction conditions for glucose conversion to LA and FA, the excellent yield of LA and FA achieved were 50% and 14.8% . In addition, with the reaction time extended, the yield of LA and FA further decreased due the formation of humins and other side products[44-45]. Thus, acidolysis of glucose with 3% HCl concentration and 30 min reaction time in one-step process.

Subsequently, the effect of other reaction parameters, such as reaction temperature and time, Raney Ni amount, Fe amount, were examined after acidolysis reaction of glucose. As shown in Figure 6, it is clearly indicated the yield of GVL remarkably increased with the time increased from 1h to 4 h at different temperature. More than 60% yield of GVL can be obtained at 220 °C for 4 h. Meanwhile, due to the amount of FA from glucose obviously less than the amount of LA, thus, besides Raney Ni, we used Fe as reductant to provide hydrogen from water separated. The results were also in line with the Le Chatelier's principle mentioned above.

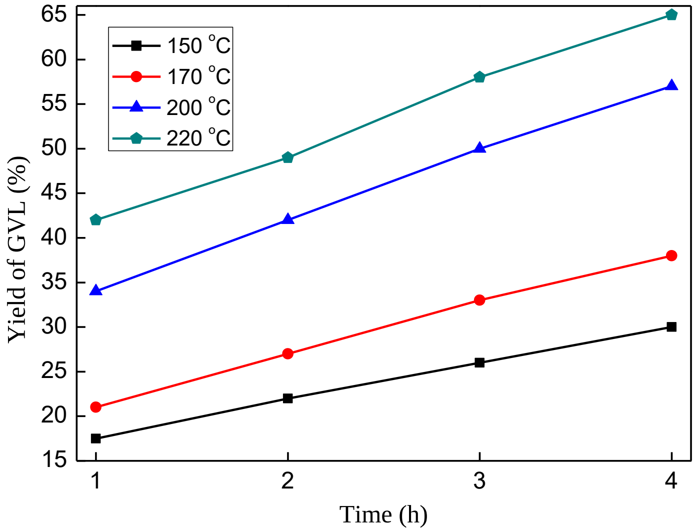


Figure 6. Effect of temperature and time on the yield of GVL from glucose (Raney Ni: 0.2 g, Fe: 10 mmol, glucose: 1 mmol, filling rate: 30%)

Furthermore, from the Figure 7, the yield of GVL slightly increased to 64% and 69% with the Fe amount of increased from 5 to 25 mmol at 200 °C and 220 °C, respectively. Then, the solid samples after reaction were collected and detected by XRD (Figure S5), the results showed the Fe was almost completely oxidized to Fe_3O_4. Moreover, in our previous work, *in suit* Fe_3O_4 would play a co-catalytic role for reduction of $NaHCO_3$ to FA[46]. At the same time, previous studies have also reported that reduction of Fe_3O_4 to Fe can be achieved with biomass-derived glycerol under hydrothermal conditions. Thus, the whole process would be sustainable by integrating the reduction of Fe_3O_4 to Fe with glycerol and the conversion of glucose to GVL with Fe/Raney Ni through a Fe/Fe_3O_4 cycle.

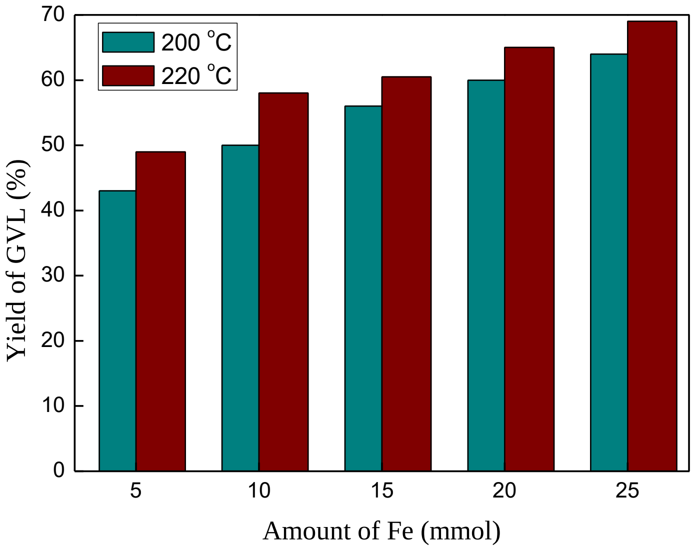
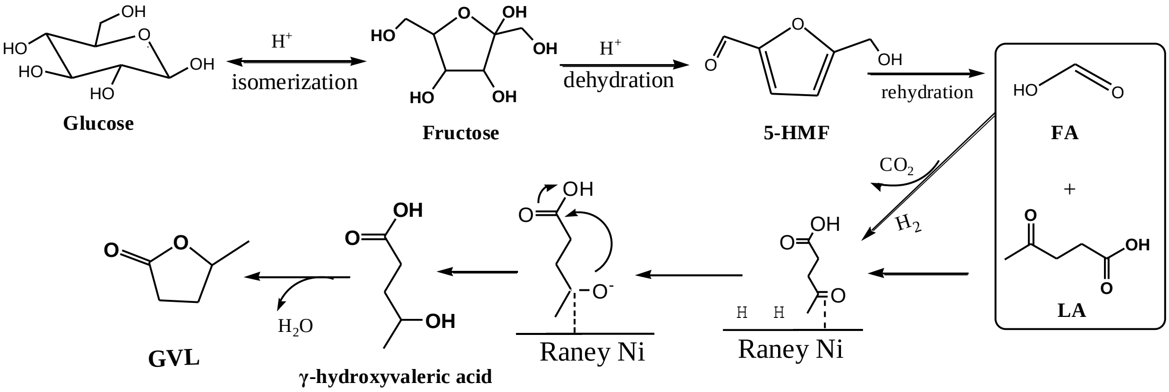


Figure 7. Effect of Fe amount on the yield of GVL (temperature: 200 °C, 220 °C, time: 3 h, Raney Ni: 0.2 g)

3.3 Proposed Reaction Mechanism of Conversion of LA into GVL

On the basis of the obtained results, a possible reaction mechanism of conversion of glucose into GVL was achieved in scheme 2. Generally, glucose would undergo isomerization to fructose, and the decomposed products from fructose similar to those of glucose[47]. Then, Hexose sugars can be degraded to furfural which is formed from pentoses and 5-hydroxymethylfurfural (5-HMF) during thermo chemical reaction (Figure S6). 5-HMF, as a precursor of LA, subsequently decomposes into LA and formic acid under acidic conditions, and the water might play a catalyst role for the decarboxylation reaction [43, 48]. In addition, FA decomposition has been reported to give two reaction pathways: dehydrogenation reaction (1) to form H_2 and CO_2, and dehydration (2) to form H_2O and CO[49]. Thus, the gas samples after decomposition of FA were analyzed by GC-TCD (Table S1), and over 85% (mol/mol) yield of H_2 can be achieved. Finally, generated LA from glucose was converted to GVL via ring-closure reaction. Initially, the in situ formed H_2 from FA or water was adsorbed on the surface of the Raney Ni. Meanwhile, the γ-carbonyl (C=O) of LA was also adsorbed on the surface of catalyst. Then, the activated hydrogen attacks the carbon of the C=O and the double bond was reduced. Finally, the formed O^- attacks the carbon of –COOH with the leaving of hydroxyl and GVL was formed.



Scheme 2. Proposed Mechanism of Synthesis of GVL from LA or glucose with Raney Ni catalyst.

4. Conclusion

In summary, an eco-friendly and facile method was proposed for efficient transformation of LA and glucose into GVL using Raney Ni catalyst in water. A considerably high GVL yield of 99% was obtained with FA as hydrogen source in the absence of extra hydrogen. Also, more than 50% yield of LA and 67% yield of GVL can be achieved from glucose, which is the key to the practical application. These results indicated the meaningful exploration of a simple and effective process for the production of GVL from biomass-derived LA or even directly from biomass.

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Conflicts of interest

There are no conflicts to declare.

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