A two-step process for conversion of cellulose to γ-valerolactone over Raney Ni catalyst using H_2O as a hydrogen source

Yalin Guo,[a,b] *Zhuang Ma,*[a] *Binbin Jin,*[a] *Guodong Yao,*[*,c] *Jia Duo*[*,d,,e,f]

[a] Ms. Y.-L. Guo, Dr. Z. Ma, Dr. B.-B. Jin
School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China.
[b] Ms. Y.-L. Guo
Handan Ecology and Environment Bureau, 298 East Congtai Road, Handan, 056002, China.
[c] Dr. G.-D. Yao
State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China.
[d] Dr. J. Duo
Xinjiang Key Laboratory of Environmental Pollution and Bioremediation, Xinjiang Institute of Ecology and Geography, Chinese Academy of Science, Urumqi 830011, China.
[e] Dr. J. Duo
National Engineering Technology Research Center for Desert-Oasis Ecological Construction, Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, 818 South Beijing Road, Urumqi 830011, Xinjiang, China.
[f] Dr. J. Duo
University of Chinese Academy of Sciences, Beijing 100049, China

E-mail: 2012yao@tongji.edu.cn

Keywords: γ-valerolactone, cellulose, hydrothermal conversion, liquid hydrogen source, Raney Ni

Abstract: Valorization of biomass to value-added platform compounds shows great potential to relieve the pressure on fossil energy consumption. Gamma (γ)-valerolactone (GVL) is a sustainable liquid for energy and carbon-based chemicals. Despite the numerous researches of investigation regarding the GVL synthesis from carbohydrate biomass, most of them involve the use of precious metals accompanying with the high-purity and high-pressure hydrogen, facing high cost in large-scale application and safety risk during the transportation and operation process. In this work, the cheap metal Fe was employed as a reductant for splitting water to produce hydrogen, and Raney Ni was used as a catalyst for in situ hydrogenation of obtained levulinic acid (LA) which is a key hydrolysate of cellulose to GVL. Cellulose was initially hydrolyzed to LA and then reduced to GVL without separation of other hydrolyzed intermediates of cellulose in one pot. The effect of reaction parameters on the yield of LA and GVL were studied for obtaining the optimal conditions. A 61.9 % yield of GVL from cellulose was achieved at mild hydrothermal conditions. This study provides an efficient approach for direct conversion of carbohydrate biomass to GVL with safe and abundant water as hydrogen source.

1. Introduction

The excessive exploitation and heavy rely on fossil resources have not only caused energy depletion, but also brought serious environmental issues such as global warming and acid rain. One of the feasible strategies to reduce our dependence on fossil fuels is to utilize biomass, the most abundant renewable resource on Earth, as feedstock for chemicals and fuels production.[1] Cost effective catalytic approaches were investigated for adapting to the molecular structure of highly functionalized biomass molecules to make the quality and price of chemicals competitive with respect to products obtained by traditional processes from fossil fuels.[2] GVL has attracted considerable attention in the last decade as one of the most promising platform chemicals synthesized from renewable carbohydrate biomass because of its distinct physicochemical properties and potential fuel application. GVL is a 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.[3] GVL can be utilized as a food additive, green solvent,[4] and an efficient fuel additive.[5] Furthermore, GVL can be transformed and upgraded to various derivatives such as liquid alkanes,[6] 1,4-pentanediol [7] and valeric biofuels.[8]

Recently, catalytic conversion of carbohydrate biomass such as glucose and fructose, or their derivatives such as levulinic acid (LA) into GVL has widely attracted much attention.[9] Hydrogenation is necessary process for GVL synthesis from carbohydrate biomass. According to the phase state of hydrogen source in reduction reaction, gaseous hydrogen and non-gaseous hydrogen as hydrogenation reagents have been used for the GVL synthesis. The synthesis way with gaseous hydrogen needs high-pressure and highly pure hydrogen pump into the cylinder, facing high risk of hydrogen storage, transportation and operation. Moreover, due to the need for activating the gaseous hydrogen, noble metal catalysts such as Pd,[10] Ag [11] and Ru[12] were commonly employed for promoting the synthesis of GVL. Although some non-noble metals like Cu, [13]Co[14] and Ni[15] have studied for catalyzing conversion of LA to GVL, developing cost effective and activity stable catalysts remains a significant challenge. The non-gaseous hydrogen sources mainly include formic acid[16] and alcohols as hydrogen donors in the previous reports.[17] Compared with formic acid and alcohols, water is more environment-friendly and abundant hydrogen source in the world. Hydrogen can be easily released from water by active metal replacement reaction. More importantly, in situ hydrogen from water dissociation possess higher reactivity in the hydrogenation reaction.[18] Thus, water is expected to act as an ideal hydrogen source in the GVL synthesis.

In our previous study, a novel method for highly efficient hydrogenation of biomass-derived LA to GVL by splitting water with Zn was proposed.[9d] A considerably high GVL yield of 56% can be obtained even without any addition of catalyst. Direct conversion of cellulose, the most abundant component of carbohydrate biomass, to GVL without separation of the hydrolyzed intermediates of cellulose is more significant to practical production. Although there were some reports of direct conversion of cellulose to GVL,[19] gaseous hydrogen and noble metal catalysts were used for hydrogenation. Herein, a two-step process composed by hydrolyzed of cellulose and hydrogenation of LA to GVL was investigated in one pot (Figure 1). The cost- effective Fe powder was employed for splitting water instead of Zn which was used in our previous report, and commercial porous Ni was taken as a catalyst for hydrogenation of LA.

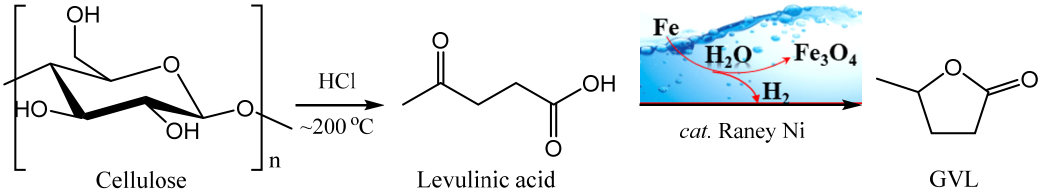


Figure 1. Synthesis of GVL from cellulose by a two-step approach in this study.

2. Results and Discussion

2.1. Conversion of cellulose to GVL by one-step process

Initially, the preliminary experiments were conducted to investigate the feasibility of synthesis of GVL from cellulose in one step, that is, acidic hydrolysis of cellulose synchronized with hydrogenation of hydrolysates. The HPLC analysis (Figure S1a) of liquid sample showed HMF and some organic acids, such as LA and formic acid, were formed in the products. Further GC-MS analysis (Figure S1b) also indicated organic acids formation. HMF was dehydration product of glucose hydrolysed of cellulose and organic acids were further decomposition of HMF.[20] No GVL was detected in the liquid samples. The reason of no GVL formation from cellulose in one step is probably because HCl is favorable to react with Fe instead of cellulose, affecting the cellulose hydrolysis and hydrolysates hydrogenation.

2.2 Conversion of cellulose to GVL by two-step process

2.2.1. Hydrolysis of cellulose to LA

To obtain GVL from cellulose, a two-step method was conducted in the following research. The acidic hydrolysis of cellulose firstly proceeded to obtain LA, and then Ni-catalyzed hydrogenation of LA was carried out with hydrogen produced from water splitting by Fe. Thus, the influence of reaction conditions on the cellulose hydrolysis were investigated initially to obtain high yield of LA. After the first step reaction, the HPLC (Figure S2) and GC-MS (Figure S3) analysis of the collected liquid samples showed LA, HMF, formic acid and other small molecular weight organic acids formed. Further quantitative analysis (Figure 2a) demonstrated the yield of LA increased from 30.8% to 45.0% as the time extended from 60 min to 90 min at 200 ºC. However, the yield of LA decreased to 42.5% when the time prolonged to 120 min. Obviously, excessive reaction time is unfavourable to LA formation. It is probably duo to the decomposition of LA under hydrothermal conditions.[19b, 20] When the reaction temperature increased to 250 ºC, the yields of LA were 44.4% and 48.0% respectively for 60 min and 90 min. Continuous extension of reaction time also is not beneficial to LA production at this temperature. Considering the efficiency and energy saving, the following cellulose hydrolysis were conducted at 200 ºC for 90 min. Further investigation on the influence of HCl concentration was conducted by varying the [H^+] from 0.1 mol/L to 1.0 mol/L. The results showed 0.5 mol/L HCl was suitable for LA formation with 54.0% yield of LA. The reason that higher concentration of HCl is unfavourable to LA production is likely due to the side reactions such as humins formation.[19b]

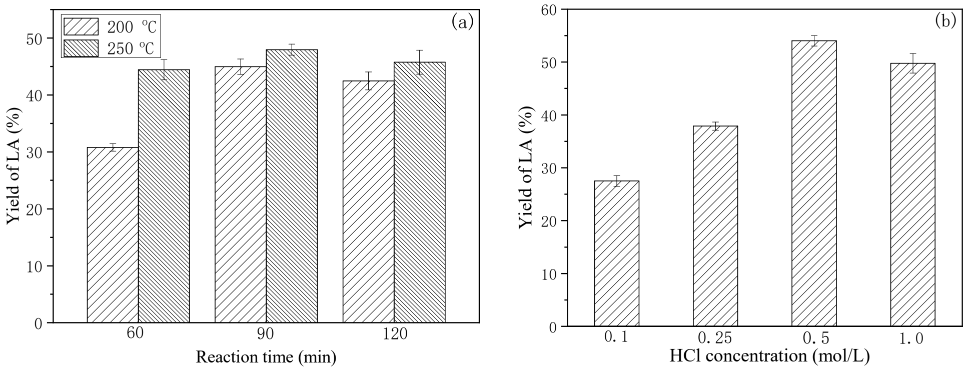


Figure 2. Effect of reaction temperature and time (a), concentration of HCl (b) on the yield of LA ((a) [H^+] 0.5 mol/L; (b) 200 °C, 90 min).

2.2.2. Hydrogenation of LA to GVL without additional catalyst

In the second step, hydrogenation of hydrolysates of cellulose in the absence of additional catalyst was firstly studied. HPLC analysis (Figure S4a) showed the obvious GVL peak except LA and formic acid. The results indicated in situ hydrogen from water splitting by Fe can be used for LA hydrogenation even without any addition of catalyst. To understand Fe transformation after reaction, XRD analysis was conducted. As illustrated in Figure S5, the obvious peaks of Fe and Fe_3O_4 appeared, indicating Fe was partially oxidized under hydrothermal conditions. The influence of Fe amount on GVL production was studied and the results (Figure 3) showed GVL yield increased significantly along with the increase of Fe amount. A 13.6% yield of GVL was achieved with 25 mmol Fe at 200 ºC for 4 h. More Fe facilitated the GVL production could be attributed to the enhancement of hydrogen production by Fe reduction of water.

2.2.3. Hydrogenation of LA to GVL with catalyst

To improve GVL yield, screening of hydrogenation catalysts was conducted subsequently. The metal powder which was commonly used in hydrogenation, such as Cu, Ni, Co, were tested for LA hydrogenation. The solid samples collected after reactions were tested by XRD. As displayed in Figure S6, all additional metals remained element form except Fe. The quantitative analysis (Figure 4) of liquid samples demonstrated all tested metals showed improvement of GVL yield. Ni was the most efficient catalyst for LA hydrogenation during these metals and about 41% improvement was reached compared to the control experiment. Thus, porous Ni which possessed higher surface area was selected as hydrogenation catalyst in the following study.

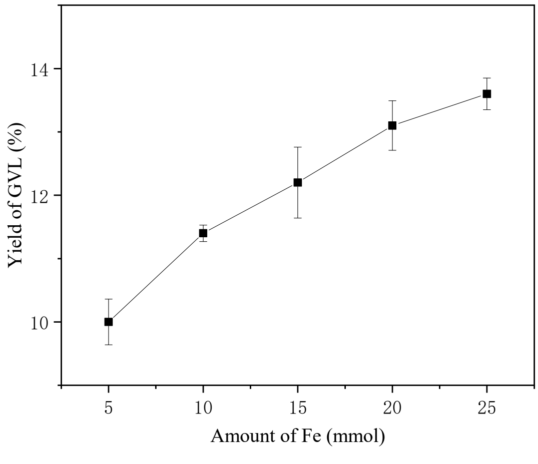


Figure 3. Effect of Fe amount on the yield of GVL (200 ºC, 4 h).

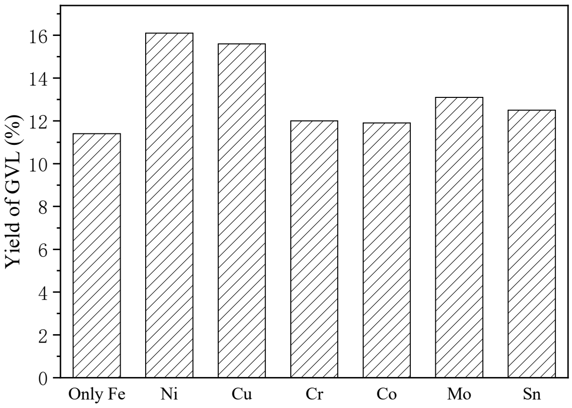


Figure 4. Screening of catalysts for GVL production (Fe 10 mmol, *cat.* 30 mmol, 200 °C, 4 h).

To obtain the optimal conditions of hydrogenation of LA with Raney Ni, the effect of Fe amount on the yield of GVL was firstly studied. As shown in Figure 3&5a, the increase of Fe amount leaded to the remarkable growth of the GVL yield from 13.1% to 55.7% with 3 mmol Raney Ni, indicating the excel catalytic activity of Raney Ni for the improvement of GVL production. The yield of GVL rose slowly with more than 15 mmol Fe and increased 1.4% of GVL with 25 mmol Fe than that with 20 mmol Fe. Thus, 20 mmol Fe was selected in the following investigation. The subsequent study on the influence of Ni amount on GVL yield showed the same growth trend with Fe amount effect. The GVL yield rapidly increased from 30.1% with 1 mmol Ni to 55.7% with 3 mmol Ni, and then grew slightly to 58.0% with 4 mmol Ni. The 3 mmol Raney Ni was suitable due to the cost-effective reason. For the effect of reaction temperature and time, as shown in Figure 5b, the change of GVL yield with the increase of reaction time showed rapid growth followed by slow increase no matter at 200 °C or at 220 °C. The GVL yield at 220 °C was slightly higher than that at 200 °C and a 61.9% yield was reached for 5 h. Interestingly, GVL yields were universally slightly higher than LA, which may be due to the continuous transformation of cellulose hydrolysates (e.g. HMF, see Figure S2) to LA during the hydrogenation process.

Finally, the stability of Raney Ni was examined, as illustrated in Figure S7. Although slight decrease in the yield of GVL was observed in the first two cycles, further decrease was not obvious, indicating Raney Ni could maintain the activity after 3 cycles.

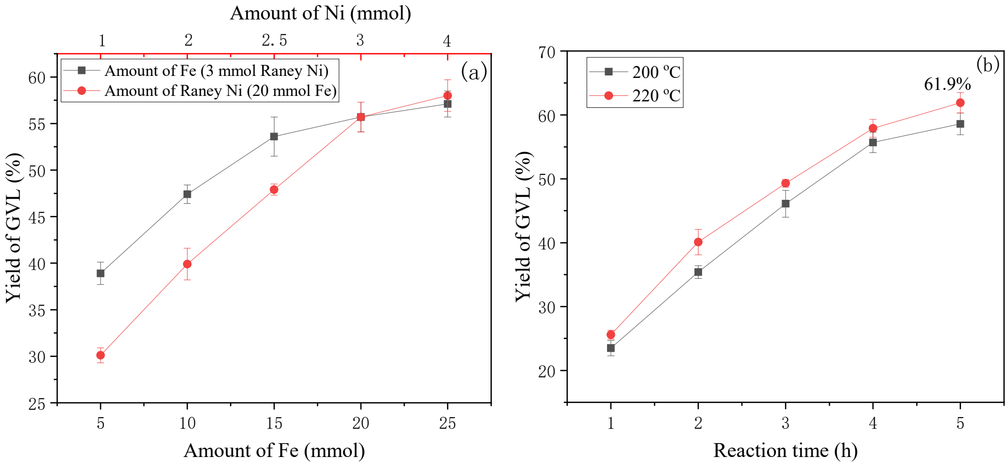


Figure 5. Effect of amounts of Fe and Raney Ni (a), reaction time and temperature (b) on the yields of GVL ((a) 200 °C, 4 h; (b) 3 mmol Raney Ni, 20 mmol Fe).

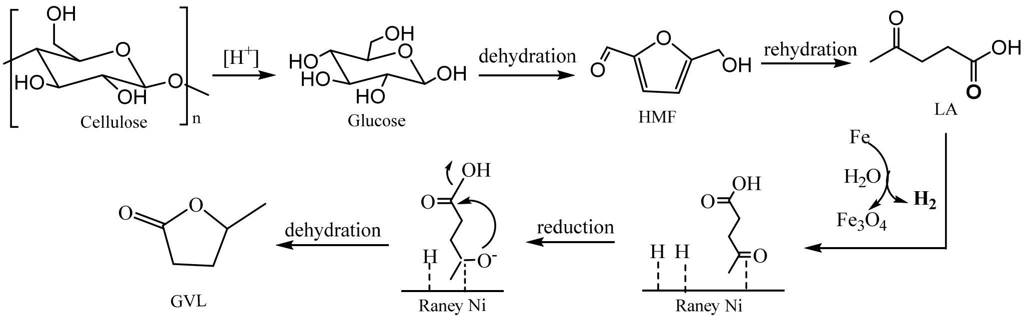


Figure 6. Proposed pathway of GVL synthesis from cellulose using water as hydrogen source.

2.3 Proposed pathway of GVL synthesis from cellulose

Based on the experimental results and the previous study[9d] on the GVL synthesis, a possible pathway of production of GVL from cellulose using hydrogen from water splitting by Fe was proposed as illustrated in Figure 6. First, cellulose was hydrolysed to monosaccharides such as glucose, followed by dehydration to HMF and rehydration to LA under hydrothermal conditions. Subsequently, hydrogen was released by water splitting with Fe. The in situ formed hydrogen was adsorbed and activated on the surface of Raney Ni. Meanwhile, the keto carbonyl group of LA was adsorbed on the Ni surface. Then, the activated hydrogen attacked the carbon of keto carbonyl of LA, leading to the reduction of keto carbonyl group. Finally, the formed O^- in keto carbonyl attacked the carbon in carboxyl with the leaving of hydroxyl and GVL was formed with H_2O.

3. Conclusions

A two-step process for GVL production from cellulose in one pot without separation of intermediate hydrolysates was studied in this paper. The hydrogen was in situ formed by water splitting with Fe and Raney Ni was employed as catalyst for LA hydrogenation to GVL. A 61.9% yield of GVL was achieved at 220 °C for 5 h. This research provides an efficient method for energy valorisation of carbohydrate biomass with safe and abundant water as hydrogen source.

4. Experimental section

4.1. Materials

Formic acid (FA, ≥ 96%, Aladdin), levulinic acid (99.8%, Sigma-Aldrich), HCl (36%-38%, Sino-pharm Chemical Reagent Co., Ltd), α-cellulose (powder, Sigma-Aldrich) and γ-valerolactone (98%, Sino-pharm Chemical Reagent Co., Ltd) were used in the research without further purification. Raney Ni (Aladdin) was ~100-mesh and other metal powder (Fe, Ni, Cu, Cr, Mo, Co, Sn) were 200-mesh and purchased from Sino-pharm Chemical Reagent Co., Ltd.

4.2. Experimental procedure

All experiments were conducted in a Teflon-lined stainless-steel batch reactor with an inner volume of 28 mL. Cellulose was initially hydrolysed to monosaccharide and further to LA, followed by hydrogenation into GVL without separation of other hydrolysed intermediates. According to our previous study on the conversion of glucose to GVL, HCl is a suitable inorganic acid for acidic hydrolysis of carbohydrate biomass. A typical experimental procedure is as follows. First, a certain amount of cellulose (0.175 g) and HCl were put into the reactor and heated in the oven to set temperature with water (~35% filling rate) for hydrolysis. Second, the reactor was cooled to room temperature naturally and put Fe and Ni into the reactor for the subsequent reaction. Then, the reactor was heated for several hours for hydrogenation. Finally, the reactor was taken out of the oven and cooled naturally again. The liquid products were collected and filtered with a 0.22 μm filter membrane. The collected solid samples were washed with deionized water and absolute ethanol for several times to remove impurities, and dried at 40 °C for 6 h in the vacuum oven. The catalyst reuse experiments were conducted by enclosing catalyst with a SUS316 mesh for separation of Fe. The reaction time was defined as the time that the reactor was placed in the oven. The yield of GVL was defined as the ratio of moles of GVL in the product to moles of glucose (unit of cellulose) in the feedstock input and the mean value of two times experiments (RD < 5%) was adopted.

4.3. Analysis Methods

Liquid samples were analyzed by the high performance liquid chromatography (HPLC, Agilent 1200 LC) equipped with a UV detector and two series Shodex KC-811 columns. The mobile phase is 2 mmol/L $HClO_4$ and the flowing rate is 1 mL/min. The gas chromatography-mass spectroscopy (GC-MS) analysis was conducted on an Aglient 7890A GC system equipped with a 5975C inert MSD. The samples were separated by a HP-INNOWax capillary column with dimensions of 30 m × 250 μm × 0.25 μm and carried by helium gas. Details on the test conditions of HPLC and GC-MS were provided elsewhere. The solid samples were analyzed by X-ray diffraction (XRD, Shimadzu X-ray Diffractometer 6100) using Cu *K*α radiation to determine the solid phase compositions, employing a scanning rate of 2°/min and 2θ angle in the range of 10° to 80°. The accelerating voltage was set at 40 KV with 30 mA flux. Diffraction patterns were compared with reference data in the ICDD PDF-2 database.

Acknowledgements

Authors gratefully acknowledge the financial support from the National Key Research and Development Project (2018YFC1902103), the West Light Foundation of Chinese Academy of Sciences (2018-XBQNXZ-B-014) and the High-level Talents Introduction Project in Xinjiang Uygur Autonomous Region(2018).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

References

[1] a) L. T. Mika, E. Csefalvay, A. Nemeth, *Chem. Rev.* **2018**, *118*, 505-613; b) Y. Yang, H. Zhong, R. He, X. Wang, J. Cheng, G. Tao, F. Jin, *Green Chem.* **2019**, *21*, 1247-1252; c) J. Hu, Y. Xue, H. Guo, M.-T. Gao, J. Li, S. Zhang, Y. F. Tsang, *Bioresour. Technol.* **2017**, *227*, 247-255; d) L. Haghighi Poudeh, I. Berktas, H. Q. Ali, B. Saner Okan, M. Yildiz, *Energy Technol.* **2020**, *8*, 2000714; e) F. Jin, Y. Gao, Y. Jin, Y. Zhang, J. Cao, Z. Wei, R. Smith, *Energy Environ. Sci.* **2011**, *4*, 881-884.

[2] a) X. Xiong, I. K. M. Yu, D. C. W. Tsang, N. S. Bolan, Y. S. Ok, A. D. Igalavithana, M. B. Kirkham, K.-H. Kim, K. Vikrant, *Chem. Eng. J.* **2019**, *375*, 121983; b) Z. Sun, G. Bottari, A. Afanasenko, M. C. A. Stuart, P. J. Deuss, B. Fridrich, K. Barta, *Nature Cat.* **2018**, *1*, 82-92; c) X. Gao, X. Chen, J. Zhang, W. Guo, F. Jin, N. Yan, *ACS Sustain. Chem. Eng.* **2016**, *4*, 3912-3920; d) M. Ma, P. Hou, J. Cao, H. Liu, X. Yan, X. Xu, H. Yu, G. Tian, S. Feng, Green Chem. **2019**, *21*, 5969-5979; e) M. Qi, X. Chen, H. Zhong, J. Wu, F. Jin, *ACS Sustain. Chem. Eng.* **2020**, *8*, 18661-18670.

[3] I. T. Horvath, H. Mehdi, V. Fabos, L. Boda, L. T. Mika, *Green Chem.* **2008**, *10*, 238-242.

[4] a) Q. Ji, X. Yu, L. Chen, A. E. A. Yagoub, C. Zhou, *Energy Technology* **2020**, *8*; b) F. Gao, R. Bai, F. Ferlin, L. Vaccaro, M. Li, Y. Gu, *Green Chem.* **2020**, *22*, 6240-6257.

[5] D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Green Chem.* **2013**, *15*, 584-595.

[6] J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* **2010**, *327*, 1110-1114.

[7] B. M. Stadler, A. Brandt, A. Kux, H. Beck, J. G. de Vries, *ChemSusChem* **2020**, *13*, 556-563.

[8] a) K. G. Martinez Figueredo, D. J. Segobia, N. M. Bertero, *Catal. Commun.* **2020**, *144*; b) D. Wang, B. Wang, Y. Ding, Q. Yuan, H. Wu, Y. Guan, P. Wu, *Chem. Commun.* **2017**, *53*, 10172-10175.

[9] a) W. Luo, M. Sankar, A. M. Beale, Q. He, C. J. Kiely, P. C. A. Bruijnincx, B. M. Weckhuysen, *Nature Commun.* **2015**, *6*; b) H. Li, A. Riisager, S. Saravanamurugan, A. Pandey, R. S. Sangwan, S. Yang, R. Luque, *ACS Cat.* **2018**, *8*, 148-187; c) A. M. R. Galletti, C. Antonetti, V. De Luise, M. Martinelli, *Green Chem.* **2012**, *14*, 688-694; d) H. Zhong, Q. Li, J. Liu, G. Yao, J. Wang, X. Zeng, Z. Huo, F. Jin, *ACS Sustain. Chem. Eng.* **2017**, *5*, 6517-6523.

[10] J. Tan, J. Cuo, Y. Zhu, X. Cui, Y. Shi, W. Yan, Y. Zhao, *ACS Sustain. Chem. Eng.* **2019**, *7*, 10670-10678.

[11] X. Bai, T. Ren, J. Mao, S. Li, J. Yin, J. Zhou, *New J. Chem.* **2020**, *44*, 16526-16536.

[12] a) J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu, Y. Li, *ChemCatChem* **2015**, *7*,

508-512; b) Z. Lin, M. Luo, Y. Zhang, X. Wu, Y. Fu, F. Zhang, W. Zhu, *Appl. Catal., A* **2018**, *563*, 54-63; c) B. Y. Tay, C. Wang, P. H. Phua, L. P. Stubbs, H. V. Huynh, *Dal. Trans.* **2016**, *45*, 3558-3563.

[13] M. Ashokraju, V. Mohan, K. Murali, M. V. Rao, B. D. Raju, K. S. R. Rao, *J. Chem. Sciences* **2018**, *130*.

[14] X. Long, P. Sun, Z. Li, R. Lang, C. Xia, F. Li, *Chinese J. Cat.* **2015**, *36*, 1512-1518.

[15] M. Varkolu, D. R. Burri, S. R. R. Kamaraju, S. B. Jonnalagadda, W. E. van Zyl, *Chem. Eng. Technol.* **2017**, *40*, 719-726.

[16] a) L. Deng, Y. Zhao, J. Li, Y. Fu, B. Liao, Q.-X. Guo, *ChemSusChem* **2010**, *3*, 1172-1175; b) L. Qi, Y. F. Mui, S. W. Lo, M. Y. Lui, G. R. Akien, I. T. Horvath, *ACS Cat.* **2014**, *4*, 1470-1477.

[17] a) L. Ye, Y. Han, J. Feng, X. Lu, *Ind. Crops Products* **2020**, *144*; b) Z. Yu, X. Lu, C. Liu, Y. Han, N. Ji, *Renew. Sustain. Energy Rev.* **2019**, *112*, 140-157.

[18] a) F. Jin, X. Zeng, J. Liu, Y. Jin, L. Wang, H. Zhong, G. Yao, Z. Huo, *Sci. Rep.* **2014**, *4*; b) L. Lyu, X. Zeng, J. Yun, F. Wei, F. Jin, *Environ. Sci. Technol.* **2014**, *48*, 6003-6009; c) R. He, B. Hu, H. Zhong, F. Jin, J. Fan, Y. H. Hu, Z. Jing, *Chem. Commun.* **2019**, *55*, 1056-1059.

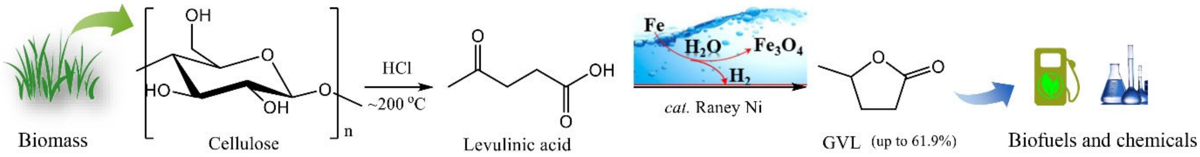
[19] a) H.-F. Ren, D. Zhu, J.-F. Li, C.-L. Liu, R.-Z. Yang, W.-S. Dong, *J. Chem. Technol. Biotechnol.* **2019**, *94*, 2355-2363; b) D. Ding, J. Wang, J. Xi, X. Liu, G. Lu, Y. Wang, *Green Chem.* **2014**, *16*, 3846-3853.

[20] F. M. Jin, H. Enomoto, *Energy Environ. Sci.* **2011**, *4*, 382-397.

A two-step process for conversion of cellulose to γ-valerolactone over Raney Ni catalyst using H_2O as a hydrogen source

Yalin Guo, Zhuang Ma, Binbin Jin, Guodong Yao,* Jia Duo*

Toc title: Energy valorization of biomass: conversion of cellulose to GVL via a two-step process



Energy utilization of biomass, the most abundant carbon-neutral resource on Earth, is crucial to sustainable development of human society. Herein, a two-step process of cellulose to γ-valerolactone (GVL) which can be used as an environmental-benign biofuel was proposed. Water was splitted by Fe to release hydrogen and Raney Ni was used for catalyzing hydrogenation of biomass to GVL.

Supporting Information

A two-step process for conversion of cellulose to γ-valerolactone over Raney Ni catalyst using H_2O as a hydrogen source

Yalin Guo,[a,b] *Zhuang Ma,*[a] *Binbin Jin,*[a] *Guodong Yao,**[c] *Jia Duo**[d,e,f]

[a] Ms. Y.-L. Guo, Dr. Z. Ma, Dr. B.-B. Jin
School of Environmental Science and Engineering, Shanghai Jiao Tong University,
800 Dongchuan Road, Shanghai 200240, China.
[b] Ms. Y.-L. Guo
Handan Ecology and Environment Bureau, 298 East Congtai Road, Handan, 056002, China.
[c] Dr. G.-D. Yao
State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China.
[d] Dr. J. Duo
Xinjiang Key Laboratory of Environmental Pollution and Bioremediation, Xinjiang Institute of Ecology and Geography, Chinese Academy of Science, Urumqi 830011, China.
[e] Dr. J. Duo
National Engineering Technology Research Center for Desert-Oasis Ecological Construction, Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, 818 South Beijing Road, Urumqi 830011, Xinjiang, China.
[f] Dr. J. Duo
University of Chinese Academy of Sciences, Beijing 100049, China

E-mail: 2012yao@tongji.edu.cn

This supporting information includes 7 figures.

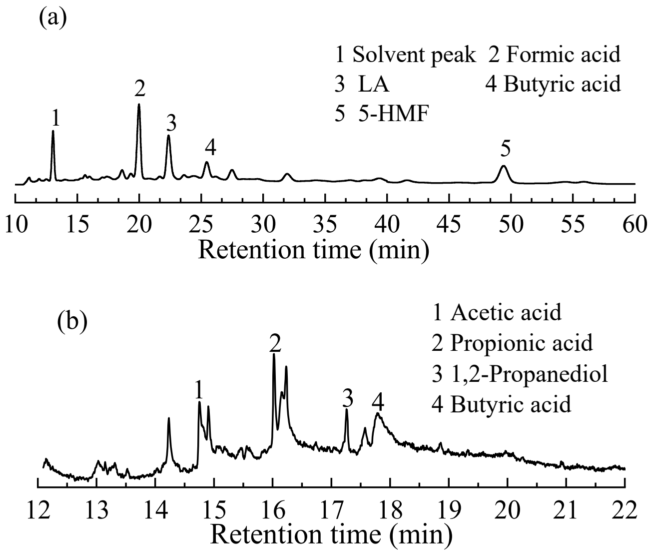


Figure S1 HPLC (a) and GC-MS (b) chromatographs of liquid samples by one-step reaction ([H$^+$]: 0.5 mol/L, Fe: 10 mmol, Raney Ni 3 mmol, 200 ºC, 1 h).

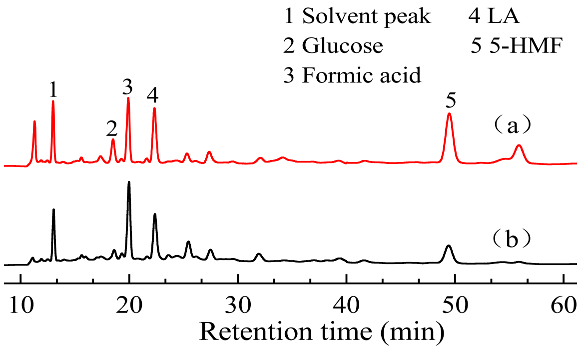


Figure S2 HPLC chromatograph of the liquid samples of cellulose hydrolysis (200 °C, [H$^+$] 0.5 mol/L, (a) 60 min, (b) 90 min).

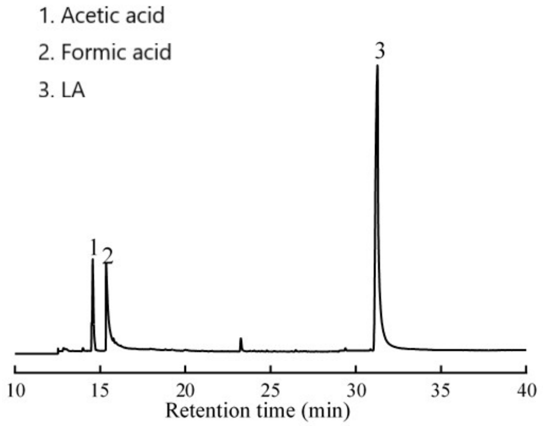


Figure S3 GC-MS chromatograph of the liquid samples of cellulose hydrolysis (200 °C, [H$^+$] 0.5 mol/L, (a) 60 min, (b) 90 min).

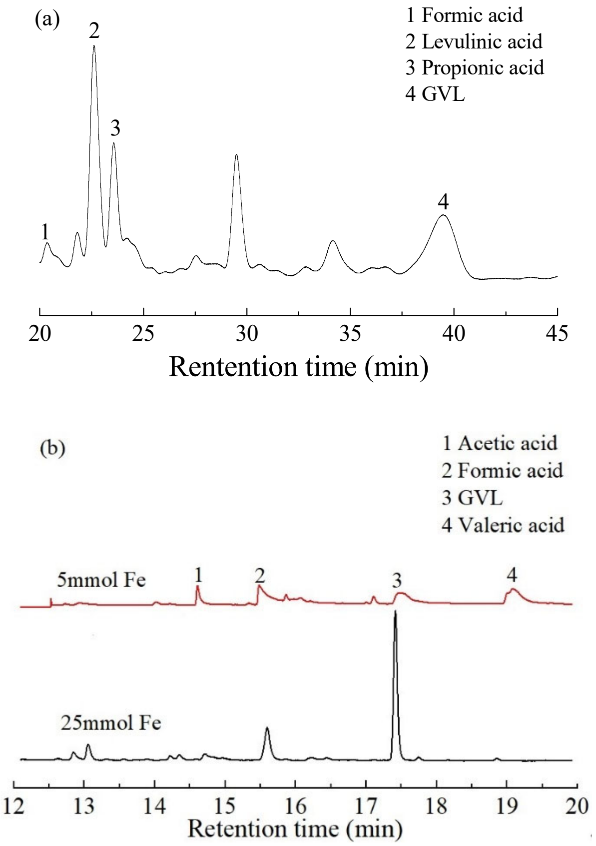


Figure S4 HPLC (a) and GC-MS (b) chromatograph of liquid samples after two-step process (200 ºC, 4 h).

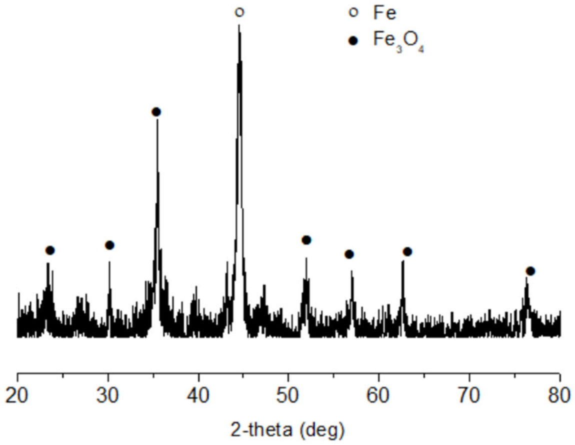


Figure S5 XRD patterns of solid sample (Fe 10 mmol, 200 ºC, 4 h)

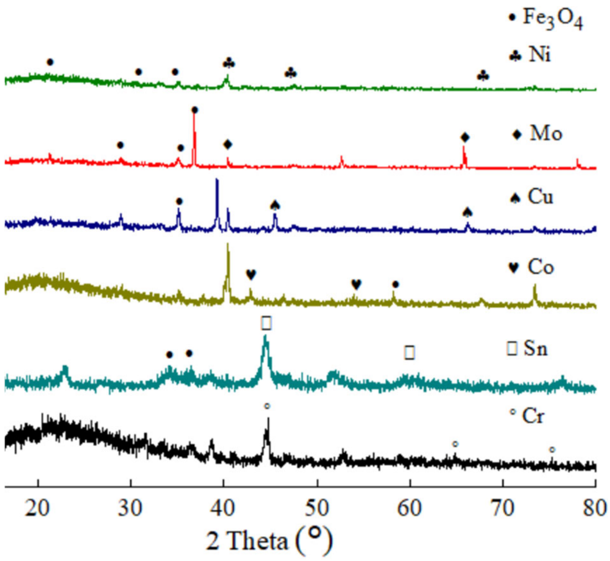


Figure S6 XRD patterns of solid samples (200 ºC, 4 h, Fe 10 mmol, *cat.* 30 mmol).

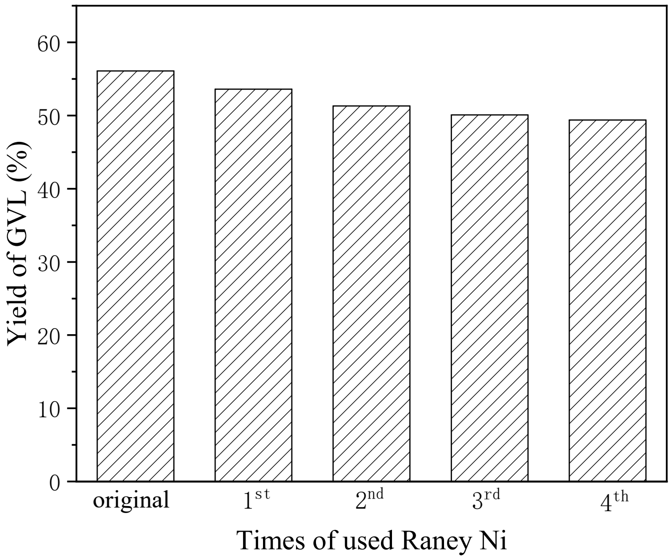


Figure S7 Effect of reused Raney Ni on the yield of GVL (200 ºC, 4 h, 20 mmol Fe, 3 mmol Raney Ni).