Original article

Formation of Formic Acid from Glucose with Simultaneous Conversion of Ag_2O to Ag under Mild Hydrothermal Conditions

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ABSTRACT

Formation of formic acid from renewable biomass resources is of great interest since formic acid is a widely used platform chemical and has recently been regarded as an important liquid hydrogen carrier. Herein, a novel approach is reported for the conversion of glucose, the constituent carbohydrate from cellulose fraction of biomass, to formic acid under mild hydrothermal conditions with simultaneous reduction of Ag_2O to Ag. Results showed that glucose was selectively converted to formic acid with an optimum yield of 40.7% at a mild reaction temperature of 135 ℃ for 30 min. In addition, Ag_2O was used as a solid oxidant for the glucose oxidation, which avoids the use of traditionally dangerous liquid oxidant H_2O_2. Furthermore, complete conversion of Ag_2O to Ag can be achieved. This study not only developed a new method for value-added chemical production from renewable biomass but also explored an alternative low-carbon and energy-saving route for silver extraction and recovery.

Keywords: Biomass; Glucose oxidation; Formic acid; Solid oxidant; Hydrothermal reaction; Silver recovery

1. Introduction

Formic acid is an important chemical that is widely used in chemical, textile, leather, pharmaceutical, rubber, and other industries [1, 2]. Recent researches have demonstrated that formic acid can be used as a hydrogen storage material in the context of a future hydrogen economy [3-9]. Current methods of formic acid production are mainly based on fossil resources with a negative impact on the environment [3]. Developing alternative routes to directly produce formic acid from sustainable biomass or biomass-derived waste products is desirable from both ecological and economic perspectives [1, 10-12]. Various promising methods were proposed for the rapid conversion of biomass into high-value chemicals [13-20]. Particularly, hydrothermal reaction is often used for biomass conversion since high-temperature water has unique properties as a reaction medium such as low dielectric constant, few and weak hydrogen bonds and high isothermal compressibility [13, 21-29]. However, in reported conversion routes of biomass to formic acid, H_2O_2, or O_2 were generally used as oxidants, and thus led to high energy costs due to the compressing gas or potential insecurity hazards[30]. On the other hand, the poor selectivity of formic acid, high reaction temperature, or expensive and tedious preparation of noble-metal catalyst make these methods inappropriate for the synthesis of formic acid [31]. For example, CuO was used in biomass conversion as a solid oxidant but only acetic acid was acquirable[32].

Recently, the cost of silver production increases rapidly with the decreasing natural silver resources, but silver has a huge demand for photography, radiography, electronics, photonics, catalysis, jewellery, silverware, dental material, medicines, and disinfectants in wastewater treatment [33, 34]. Therefore, the market demand urgently requires the recovery of silver from silver-containing wastes through new cost-effective and environmentally friendly technologies [35]. Many researchers studied the methods to recycle silver by chemical reduction, chemical replacement and ion exchange [36-38]. However, these methods were short of economy and environmental friendliness due to the use of expensive resins or high energy input. Herein, we propose a new method for selective conversion of glucose into formic acid with easy separation by-product glycolic acid using Ag_2O as a solid oxidant and a simultaneous transformation of Ag_2O into Ag under mild hydrothermal conditions. Results shows that glucose was selectively converted to formic acid with an optimum yield of 40.7% and glycolic acid yield of 10% at a mild reaction temperature of 135 ℃ for 30 min. The proposed method is not only a promising way for conversion of biomass into value-added chemicals but also an effective and green route for silver extraction.

2. Material and methods

2.1 Materials

In this research, glucose (99.9%), formic acid (98%), glycolic acid (98%), methanol (99.5%) and xylose (99.9%) were purchased from Sino-pharm Chemical Regent Co., Ltd. Sodium hydroxide (96%), acetic acid (99.5%) and lactic acid (85%) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Gluconic acid (49~53 wt% in water) was purchased from Sun Chemical Technology (Shanghai) Co., Ltd. Sorbitol (98%) was purchased from Innochem (Beijing) Technology Co., Ltd. Glycolaldehyde dimer was offered by Aladdin Reagent Company. Sodium oxalic (99.8%) and Pyruvaldehyde (40% w/w aq. solution) was purchased from Shanghai Titan Scientific Co., Ltd. Glyceraldehyde (85%) was obtained from Bide pharmatech Ltd. 1,3- dihydroxyacetone (98%) was provided by J&K Scientific Ltd. Ag_2O (99.7%, Macklin Biochemical Co., Ltd) was chose as the model compound of Ag(I) in basic solution, because Ag(I) ion could form AgOH and then generate Ag_2O at a high pH condition (pH > 11). The stoichiometric demand for complete oxidation of glucose to formic acid was defined as a 100% Ag_2O supply according to Eq. (1).

$$C_6H_{12}O_6 + 6Ag_2O \rightarrow 6HCOOH + 12Ag \tag{1}$$

2.2 Conversion of Glucose

The conversion of glucose was conducted in a Teflon-lined stainless-steel batch reactor with an inner volume of 25 mL. In a typical procedure, desired amount of glucose, Ag_2O and 6.25 mL NaOH solution were first loaded into the reactor. Then the reactor was sealed and put into an isothermal oven preheated to 135 ℃ for 30 minutes. After the desired reaction time, the reactor was taken out from the oven and cooled to room temperature.

2.3 Analytical Methods

After the reaction, liquid samples were filtered through a 0.22 μm membrane filter and analysed by an Agilent 1200 high-performance liquid chromatography (HPLC), which equipped with two KC-811 columns, a differential refractometer detector and a tunable ultraviolet/visible absorbance detector. A 2 mmol/L $HClO_4$ aqueous solution with a flow rate of 1.0 ml/min was used as the mobile phase of HPLC. Solid samples were washed with deionized water and then dried in a vacuum oven at 40 ℃ for 6 h. X-ray diffraction (XRD) patterns of the solid samples were collected by a Shimadzu 6100 X-ray diffractometer equipped with Cu Kα radiation at a scan rate of 2 °/min and with a 2θ ranging from 10° to 80°.

The conversion X and yield Y of products were defined based on the following equations:

$$\mathrm{X} = \frac{\text{moles of carbons in feedstock consumed}}{\text{moles of carbon in feedstock input}} \times 100\%$$

$$\mathrm{Y} = \frac{\text{moles of carbon in product molecule}}{\text{moles of carbon in feedstock input}} \times 100\%$$

3. Results and discussions

3.1 Characteristics of Ag_2O/Ag with hydrothermal conversion of glucose to formic acid

A series of experiments with glucose and Ag_2O as reactants were carried out under mild hydrothermal conditions to investigate whether glucose could be selectively converted to formic acid. As shown in **Figure 1**, only lactic acid was detected from the liquid sample by HPLC analysis when glucose was reacted without Ag_2O under the basic hydrothermal condition. However, when Ag_2O was added, the product of formic acid was clearly increased and the formation of glycolic acid was also detected. The previous study has revealed that a relatively high yield of lactic acid can be obtained from the hydrothermal conversion of glucose under alkaline conditions [16]. Notably, as show in **Figure 1**, the amount of lactic acid in the presence of Ag_2O was much less than that without Ag_2O, which suggested that glucose was selectively converted into formic acid through reacting with Ag_2O under mild hydrothermal conditions.

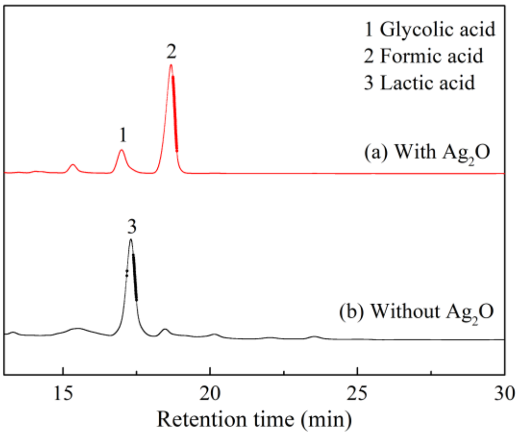


Figure 1. HPLC chromatography of liquid samples after reactions (a) with and (b) without 10 mmol Ag_2O (1 mmol glucose, 1 mol/L NaOH with 6.25 mL, 180 ℃, 2 h).

To investigate the reduction of Ag_2O, solid samples were analysed by X-ray diffraction (XRD) and scanning electron microscope (SEM) methods. **Figure 2** shows the XRD patterns of the Ag_2O before the reaction and solid products after the reaction. No Ag peak appeared in the solid sample before reaction (**Figure 2a**). However, four diffraction peaks were observed at 38.20 °, 44.40 °, 64.60 ° and 77.60 °, respectively, which were indexed as the (111), (200), (220) and (311) orientations of cubic Ag (**Figure 2b**). These results indicated that the Ag_2O was converted into Ag after the reaction. Furthermore, the SEM image shows that the obtained Ag particle has a diameter of 0.1 – 0.3 μm (**Figure 3**).

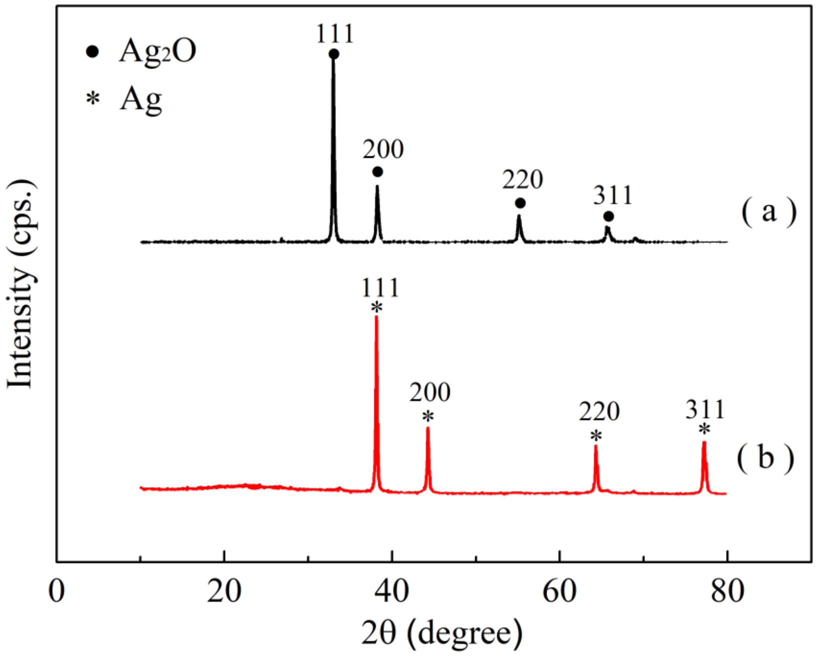


Figure 2. XRD patterns of (a) Ag_2O before the reaction and (b) solid products after the reaction at 180 ℃ for 2 h (1 mmol glucose, 4 mmol Ag_2O, 1 mol/L NaOH)

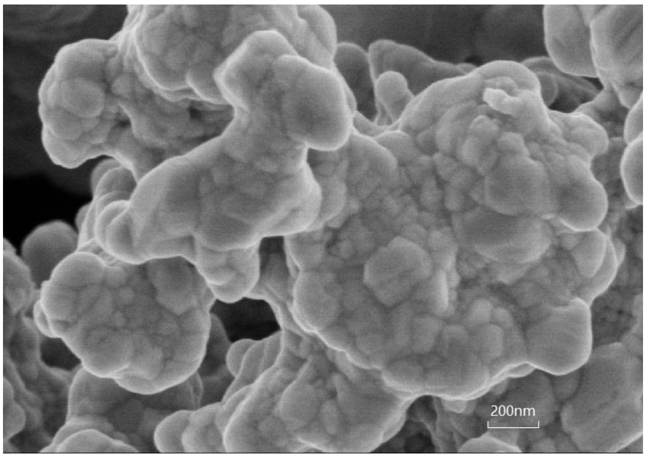


Figure. 3 SEM image of the silver obtained after reaction (4 mmol Ag_2O, 1 mmol glucose, 135℃, 2 h, 1 mol/L NaOH with 6.25 mL)

3.2 Investigating the influences of reaction conditions on yields of formic acid

Next, the relationship between reaction conditions and yields of formic acid from glucose were further investigated. Above all, the influence of reaction temperature was examined by varying the temperature from 105 to 210 ℃. As shown in **Figure 4a**, formic acid was identified as the major product. When the temperature increased from 105 to 135 ℃, the yield of formic acid increased from 22.9% to 29.1%. However, a further increase of the temperature led to slight decrease in the formic acid yield. For the production of glycolic acid, similar trend was observed. However, when the temperature increased to 210 ℃, lactic acid was detected at the cost of the yields of glycolic acid and formic acid. The change in the product yield and selectivity suggested that the temperature could affect the cleavage patterns of glucose and alter the reaction pathway. Furthermore, there was no glucose detected in the liquid phase after the reaction at all tested temperatures, which showed that glucose was completely decomposed. **Figure 4b** shows the influence of reaction time on yields of different products and conversion of glucose in the hydrothermal oxidation of glucose to formic acid. In the first 30 min, the yield of formic acid dramatically increased to 29.7%, however, a slow decrease in the formic acid yield was observed when the reaction time prolonged to 240 min. Similar trends were observed for the glycolic acid yield. The decrease in the yields of formic acid and glycolic acid with a long reaction time is probably caused by the decomposition of the formed products under hydrothermal conditions.

The influence of the concentration of NaOH on the oxidation of glucose was also investigated. A sharp rise in glucose conversion was noted from 57.4% to 100% when NaOH concentration increased from 0 to 1 M (**Figure 4c**). This is probably because NaOH solution with higher concentration accelerated glucose conversion, which has been studied in detail in previous research [23]. The yield of formic acid was less than 2% in the absence of NaOH. However, formic acid yield ascended simultaneously with increasing NaOH concentration and reached 34% at 0.75 M NaOH. The previous research has demonstrated that a certain amount of alkali could convert the formic acid to formate, which is more stable than formic acid under hydrothermal conditions [39]. Thus, the addition of alkali could prevent the produced formic acid from being decomposed that resulted in the higher yield. However, further increasing the NaOH concentration exceeding 0.75 M got a decrease in the formic acid yield, which is probably because the reaction pathway of glucose conversion was negatively affected by additional NaOH.

The effect of Ag_2O amount was examined (**Figure 4d**). The yield of formic acid first quickly increased from 1.1% to 33.1% when the Ag_2O addition increased from 0 to 116.7% relative to glucose, and then slowly ascended to 40.7% when the Ag_2O supply further increased to 266.7%. In addition, lactic acid with a yield of 44% without any formation of formic acid was observed in the absence of the oxidant. This result was similar with other literatures that glucose was dominantly isomerized into fructose and then cleaved into lactic acid via retro-aldol condensation under alkaline condition [23, 30]. The above results indicated that the Ag_2O oxidant was advantageous for the oxidation of glucose to formic acid, and increasing the amount of Ag_2O had a positive effect on the formic acid yield.

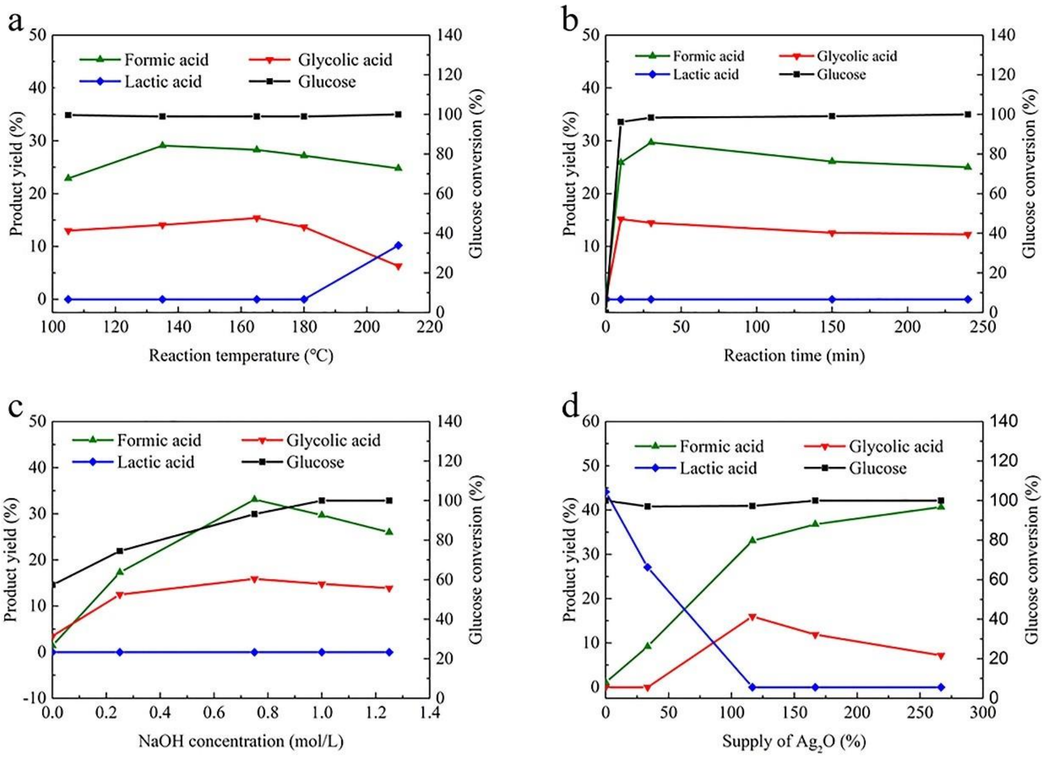


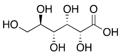
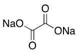
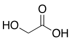
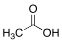
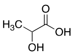
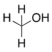
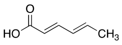
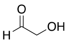
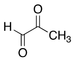
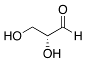
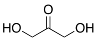
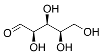
Figure 4. Effect of (a) reaction temperature (7 mmol Ag_2O, 1 mol/L NaOH with 6.25 mL, 120 min), (b) reaction time (7 mmol Ag_2O, 1 mol/L NaOH with 6.25 mL, 135 ℃), (c) NaOH concentration (7mmol Ag_2O, 135 ℃, 30 min, 6.25 mL NaOH solution) and (d) amount of Ag_2O (0.75 mol/L NaOH 6.25 mL, 135 ℃, 30 min) on yields of different products and conversion of glucose in the hydrothermal oxidation of glucose to formic acid (1 mmol glucose was used for all cases).

3.3 Investigating the oxidation pathways of glucose to formic acid

Oxidation pathways of glucose to formic acid were then investigated. Based on the previous research, glucose was probably first oxidized to gluconic acid under basic hydrothermal conditions, which was further converted to formic acid through a series of reactions [23]. Thus, gluconic acid was first chosen as the starting material instead of glucose for the hydrothermal formic acid production. Results revealed that gluconic acid was completely converted and a formic acid yield of 34.4% (**Table 1, Entry 1**), which is close to that obtained from glucose directly. This result indicates that the gluconic acid was a crucial intermediate for formic acid generation. Other organic acids, such as oxalic acid, glycolic acid, acetic acid and lactic acid, could be hardly converted under such hydrothermal condition (**Table 1, Entries 2-5**), which inferred that these organic acids were unlikely the intermediates for formic acid production. Meanwhile, methanol and sorbitol were completely converted but without any production of formic acid (**Table 1, Entries 6 and 7**), which suggested that these alcohols were unlikely the intermediates for formic acid production although they were more reactive than organic acids under hydrothermal condition.

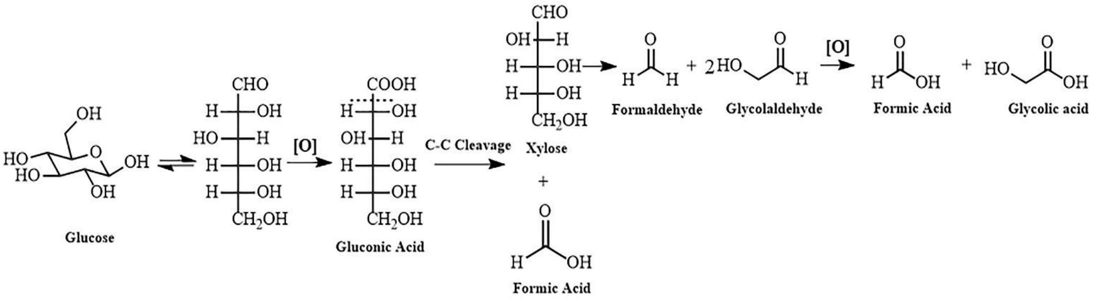
Aldehyde/ketone species such as glycolaldehyde, pyruvaldehyde, glyceraldehyde and 1,3-dihydroxyacetone displayed high reaction activity under hydrothermal conditions and they were all had a 100% conversion (**Table 1, Entries 8-11**). Glycolaldehyde afforded formic acid and glycolic acid as the major products with yields of 24.1% and 16.5%, respectively, which indicated that the glycolaldehyde was likely an intermediate for formic acid generation. Formic acid yields obtained with pyruvaldehyde and glyceraldehyde were 3.2% and 1.1%, respectively. Especially, the major products of pyruvaldehyde were lactic acid and acetic acid with the yields of 53.6% and 21.4%, respectively. Hence, these two aldehydes were unlikely the key intermediates for formic acid production. When 1,3-dihydroxyacetone was engaged as the substrate, glycolic acid was identified as the major product with formic acid, lactic acid and acetic acid as side products. Thus, the 1,3-dihydroxyacetone was unlikely the key intermediates for formic acid production. Furthermore, xylose was tested and displayed high activity to produce formic acid (**Table 1, Entry 12**), which indicated that xylose might be a key intermediate for formic acid production.

Table 1. Oxidation of different model compounds with Ag_2O under hydrothermal conditions[a]

Entry	Substrate		Conversion %	Formic acid %	Acetic acid %	Lactic acid %	Glycolic acid %
1	Gluconic acid		100	34.4	0	0	2.4
2	Sodium oxalic		0	0	0	0	0
3	Glycolic acid		0	0	0	0	100
4	Acetic acid		0	0	100	0	0
5	Lactic acid		3.3	0	0	96.7	0
6	Methanol		100	0	0	0	0
7	Sorbitol		100	0	0	0	0
8	Glycolaldehyde (dimer)		100	24.1	0	0	16.5
9	Pyruvaldehyde		100	3.2	21.4	53.6	0
10	Glyceraldehyde		100	1.1	0	2.2	2.8
11	1,3-dihydroxyacetone		100	24.7	7.1	14.6	47.4
12	Xylose		100	30.9	0.4	0	7.5

[a]Reaction conditions: 0.5 mmol substrate, 0.75 mol/L NaOH, 100% Ag_2O, 135 ℃, 30 min.

Based on the tested results, **Scheme 1 shows** the proposed reaction pathway for glucose conversion into formic acid with the oxidation of Ag_2O under mild hydrothermal conditions. Glucose first transforms into its open-chain form, and the aldehyde group is oxidized by Ag_2O and then gives the gluconic acid. Subsequently, formic acid and xylose are formed by the breakage of C1-C2 bond of gluconic acid. Finally, xylose transforms into formaldehyde and glycolaldehyde that are further oxidized into formic acid and glycolic acid, respectively.



Scheme 1. Proposed reaction pathway of the oxidation of glucose into formic acid.

4. Conclusions

We developed a new method of one-step conversion of glucose into formic acid with a simultaneous reduction of Ag_2O to Ag under mild hydrothermal conditions. At optimum reaction conditions, a 40.7% yield of formic acid from glucose and a 100% conversion of Ag_2O to Ag were obtained. This study not only developed a new way for value-added chemical production from renewable biomass resource but also proposed an alternative low-carbon and energy-saving route for silver extraction and recovery.

Conflicts of interest

There are no conflicts to declare.

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Uncategorized References

1. Lu, T.; Hou, Y.; Wu, W.; Niu, M.; Wang, Y., Formic acid and acetic acid production from corn cob by catalytic oxidation using O2. *Fuel Process Technol* **2018,** *171*, 133-139.

2. Preuster, P.; Albert, J., Biogenic Formic Acid as a Green Hydrogen Carrier. *Energy Technol. (Weinheim, Ger.)* **2018,** *6* (3), 501-509.

3. Zhang, J.; Sun, M.; Liu, X.; Han, Y., Catalytic oxidative conversion of cellulosic biomass to formic acid and acetic acid with exceptionally high yields. *Catal. Today* **2014,** *233*, 77-82.

4. Zell, T.; Butschke, B.; Ben-David, Y.; Milstein, D., Efficient Hydrogen Liberation from Formic Acid Catalyzed by a Well-Defined Iron Pincer Complex under Mild Conditions. *Chemistry - A European Journal* **2013,** *19* (25), 8068-8072.

5. Wang, Z. L.; Yan, J. M.; Ping, Y.; Wang, H. L.; Zheng, W. T.; Jiang, Q., An efficient CoAuPd/C catalyst for hydrogen generation from formic acid at room temperature. *Angew Chem Int Ed Engl* **2013,** *52* (16), 4406-9.

6. Eppinger, J.; Huang, K.-W., Formic Acid as a Hydrogen Energy Carrier. *ACS Energy Letters* **2016,** *2* (1), 188-195.

7. Liu, X.; Li, S.; Liu, Y.; Cao, Y., Formic acid: A versatile renewable reagent for green and sustainable chemical synthesis. *Chinese J Catal* **2015,** *36* (9), 1461-1475.

8. Valentini, F.; Kozell, V.; Petrucci, C.; Marrocchi, A.; Gu, Y.; Gelman, D.; Vaccaro, L., Formic acid, a biomass-derived source of energy and hydrogen for

biomass upgrading. *Energ Environ Sci* **2019,** *12* (9), 2646-2664.

9. Zhao, B.; Hu, Y.; Gao, J.; Zhao, G.; Ray, M. B.; Xu, C. C., Recent Advances in Hydroliquefaction of Biomass for Bio-oil Production Using In Situ Hydrogen Donors. *Ind Eng Chem Res* **2020**.

10. Vu, H. P.; Nguyen, L. N.; Vu, M. T.; Johir, M. A. H.; McLaughlan, R.; Nghiem, L. D., A comprehensive review on the framework to valorise lignocellulosic biomass as biorefinery feedstocks. *Sci Total Environ* **2020,** *743*, 140630.

11. Morales, G.; Iglesias, J.; Melero, J. A., Sustainable Catalytic Conversion of Biomass for the Production of Biofuels and Bioproducts. *Catalysts* **2020,** *10* (5).

12. Zhang, Z.; Huber, G. W., Catalytic oxidation of carbohydrates into organic acids and furan chemicals. *Chem Soc Rev* **2018,** *47* (4), 1351-1390.

13. Lyu, L.; Zeng, X.; Yun, J.; Wei, F.; Jin, F., No catalyst addition and highly efficient dissociation of H2O for the reduction of CO2 to formic acid with Mn. *Environ Sci Technol* **2014,** *48* (10), 6003-9.

14. Cantero, D. A.; Vaquerizo, L.; Martinez, C.; Bermejo, M. D.; Cocero, M. J., Selective transformation of fructose and high fructose content biomass into lactic acid in supercritical water. *Catal Today* **2015,** *255*, 80-86.

15. Cao, X.; Peng, X.; Sun, S.; Zhong, L.; Chen, W.; Wang, S.; Sun, R.-C., Hydrothermal conversion of xylose, glucose, and cellulose under the catalysis of transition metal sulfates. *Carbohydr. Polym.* **2015,** *118*, 44-51.

16. Choudhary, H.; Nishimura, S.; Ebitani, K., Synthesis of high-value organic acids from sugars promoted by hydrothermally loaded Cu oxide species on magnesia. *Applied Catalysis B: Environmental* **2015,** *162*, 1-10.

17. Hrnčič, M. K.; Kravanja, G.; Knez, Ž., Hydrothermal treatment of biomass for energy and chemicals. *Energy* **2016,** *116*, 1312-1322.

18. Yang, Y.; Zhong, H.; He, R.; Wang, X.; Cheng, J.; Yao, G.; Jin, F., Synergetic conversion of microalgae and CO2 into value-added chemicals under hydrothermal conditions. *Green Chem* **2019,** *21* (6), 1247-1252.

19. Voß, D.; Pickel, H.; Albert, J., Improving the Fractionated Catalytic Oxidation of Lignocellulosic Biomass to Formic Acid and Cellulose by Using Design of Experiments. *Acs Sustain Chem Eng* **2019,** *7* (11), 9754-9762.

20. Huber, G. W.; Lapkin, A.; Yan, N., Introduction to green chemistry and reaction engineering. *Reaction Chemistry & Engineering* **2020,** *5* (12), 2131-2133.

21. Jin, F.; Yun, J.; Li, G.; Kishita, A.; Tohji, K.; Enomoto, H., Hydrothermal conversion of carbohydrate biomass into formic acid at mild temperatures. *Green Chem* **2008,** *10* (6).

22. Savage, P. E., A perspective on catalysis in sub- and supercritical water. *The Journal of Supercritical Fluids* **2009,** *47* (3), 407-414.

23. Jin, F.; Enomoto, H., Rapid and highly selective conversion of biomass into value-added products in hydrothermal conditions: chemistry of acid/base-catalysed and oxidation reactions. *Energy Environ. Sci.* **2011,** *4* (2), 382-397.

24. Jin, F.; Gao, Y.; Jin, Y.; Zhang, Y.; Cao, J.; Wei, Z.; Smith Jr, R. L.,

High-yield reduction of carbon dioxide into formic acid by zero-valent metal/metal oxide redox cycles. *Energ Environ Sci* **2011,** *4* (3).

25. He, R.; Hu, B.; Zhong, H.; Jin, F.; Fan, J.; Hu, Y. H.; Jing, Z., Reduction of CO2 with H2S in a simulated deep-sea hydrothermal vent system. *Chem Commun (Camb)* **2019,** *55* (8), 1056-1059.

26. Zhong, H.; Wang, L.; Yang, Y.; He, R.; Jing, Z.; Jin, F., Ni and Zn/ZnO Synergistically Catalyzed Reduction of Bicarbonate into Formate with Water Splitting. *ACS Appl Mater Interfaces* **2019,** *11* (45), 42149-42155.

27. Müller, N.; Romero, R.; Grandón, H.; Segura, C., Selective Production of Formic Acid by Wet Oxidation of Aqueous-Phase Bio-oil. *Energ Fuel* **2016,** *30* (12), 10417-10424.

28. Koley, S.; Khadase, M. S.; Mathimani, T.; Raheman, H.; Mallick, N., Catalytic and non-catalytic hydrothermal processing of Scenedesmus obliquus biomass for bio-crude production – A sustainable energy perspective. *Energ Convers Manage* **2018,** *163*, 111-121.

29. Ong, H. C.; Chen, W.-H.; Farooq, A.; Gan, Y. Y.; Lee, K. T.; Ashokkumar, V., Catalytic thermochemical conversion of biomass for biofuel production: A comprehensive review. *Renewable and Sustainable Energy Reviews* **2019,** *113*.

30. Jin, F.; Zeng, X.; Jing, Z.; Enomoto, H., A Potentially Useful Technology by Mimicking Nature—Rapid Conversion of Biomass and CO2 into Chemicals and Fuels under Hydrothermal Conditions. *Ind Eng Chem Res* **2012,** *51* (30), 9921-9937.

31. Syed, S., Silver recovery aqueous techniques from diverse sources: Hydrometallurgy in recycling. *Waste Manage* **2016,** *50*, 234-256.

32. Yin, G.; Huo, Z.; Zeng, X.; Yao, G.; Jing, Z.; Jin, F., Reduction of CuO into Cu with Guaiacol as a Model Compound of Lignin with a Homogeneous Catalyst of NaOH. *Ind Eng Chem Res* **2014,** *53* (19), 7856-7865.

33. Gromov, O. G.; Kuz'min, A. P.; Kunshina, G. B.; Lokshin, E. P.; Kalinnikov, V. T., Electrochemical Recovery of Silver from Secondary Raw Materials. *Russ J Appl Chem+* **2004,** *77* (1), 62-66.

34. Anu Iswarya, J.; Rajeshkumar, S.; Ezhilarasan, D., Applications Of Silver Nanoparticles In Dentistry. *International Journal of Research in Pharmaceutical Sciences* **2020,** *11* (SPL3), 1126-1131.

35. Tao, H.-C.; Gao, Z.-Y.; Ding, H.; Xu, N.; Wu, W.-M., Recovery of silver from silver(I)-containing solutions in bioelectrochemical reactors. *Bioresource Technol* **2012,** *111*, 92-97.

36. Zhang, Y.; Zhan, L.; Xu, Z., Recycling Ag, As, Ga of waste light-emitting diodes via subcritical water treatment. *J Hazard Mater* **2020**, 124409.

37. Mohd Suah, F. B.; Teh, B. P.; Mansor, N.; Hamzah, H. H.; Mohamed, N., A closed-loop electrogenerative recycling process for recovery of silver from a diluted cyanide solution. *Rsc Adv* **2019,** *9* (54), 31753-31757.

38. Wang, Z.; Halli, P.; Hannula, P.; Liu, F.; Wilson, B. P.; Yliniemi, K.; Lundström, M., Recovery of Silver from Dilute Effluents via Electrodeposition and

Redox Replacement. *J Electrochem Soc* **2019,** *166* (8), E266-E274.

39. Yan, L.; Qi, X., Degradation of Cellulose to Organic Acids in its Homogeneous Alkaline Aqueous Solution. *ACS Sustainable Chem. Eng.* **2014,** *2* (4), 897-901.