

Rapid Reduction of Ag₂O into Ag by Wheat Straw and Production of Organic Acids under Mild Hydrothermal Conditions

Teng Ma¹, Fangming Jin^{1,2,3,4*}, Heng Zhong^{2,3}

¹China-UK Low Carbon College, Research Center for Sustainable Technologies and Waste Resource Utilization, Shanghai Jiao Tong University, 3 Yinlian Rd, 201306, Shanghai, China.

²School of Environmental Science and Engineering, State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China.

³Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China.

⁴College of Biological Chemical Science and Engineering, Jiaying University, No.56, South Yuexiu Road, Jiaying 314001, China.

Abstract. Wheat straw is a kind of rich agricultural waste. Resource utilization of wheat straw has received widespread attention. Herein, a novel approach of the rapid reduction of Ag₂O into Ag by wheat straw with the production of organic acids under mild hydrothermal conditions is reported. After parameter optimization, almost all Ag₂O is converted to Ag at a mild reaction temperature of 150 °C and a reaction time of 60 min in sodium hydroxide solution. Meanwhile, wheat straw was converted to organic acid such as formic acid, lactic acid, and acetic acid. This offers a cost-effective approach for Ag recovery and resource utilization of biomass.

1 Introduction

With the rapid growth of population and social development, a large amount of fossil fuel is consumed. This induces environmental pollution, energy crisis, greenhouse effect, etc., and poses a threat to human survival. Developing renewable energy can mitigate these issues. Biomass is the most widely used renewable resources with the advantages of large reserves, carbon neutral, renewable, etc. The utilization of biomass resources is not only conducive to waste disposal, but also to the production of high value-added chemicals and fuels. Wheat straw is a typical cellulose-rich biomass. It is estimated that global wheat straw production in 2008 was 850 million tons.^[1] However, the main processing method of wheat straw is direct combustion, which causes serious pollution to the air.^[2]

Ag is widely used in electronics, batteries, photography, medicine, etc.^[3] With the continuous exploitation, the Ag resources in nature is decreasing and the exploitation cost is increasing. In order to meet the needs of market, environment and economic benefits, the technology of recovering Ag from Ag containing waste has been widely studied. Traditional methods of Ag recovery are very expensive because of electro-winning or chemical reduction processes, etc. Thus, a search for a cost-effective and simple method of Ag recovery is significant.

Hydrothermal reactions have demonstrated many advantages in resource utilization of biomass.^[4,5] Our previous researches have demonstrated that biomass feedstocks, such as glucose, fatty acid, cellulose can be converted into organic acids under hydrothermal

conditions.^[6-8] However, only few studies used practical biomass. Herein, we propose a new method for reduction of Ag₂O into Ag under mild hydrothermal conditions, as well as the formation of organic acids.

2 Experimental sections

2.1 Experimental materials

The wheat straw used in this study was obtained from Jiangsu, China. Grated wheat straw was strained through a 100 mesh sieve. We choose Ag₂O (99.7%) as an oxidant because Ag ion could form AgOH and then generate Ag₂O as precipitate in alkaline environment.^[9] NaOH was obtained from Lingfeng reagent Co., Ltd.

2.2 Experimental procedure

All experiments were conducted in a Teflon reactor with an internal volume of 25 ml. In a typical reaction, desired amount of wheat straw, Ag₂O, NaOH, and deionized water were loaded into the Teflon reactor. Then the reactor was sealed and put into an oven preheated to 150 °C for 1 h. After that, the reactor was taken out and cooled to the room temperature.

2.3 Analytical methods

Solid samples were dried in a vacuum oven at 50 °C for 10 h and then analysed by X-ray diffraction (XRD) equipped with Cu K α radiation at a scan rate of 2 °/min

* Corresponding author: fmjin@sjtu.edu.cn

and with 2θ ranging from 10° to 80° . Liquid samples were filtered through a $0.22\ \mu\text{m}$ filter membrane and analyzed by high-performance liquid chromatography (HPLC).

3 Results and discussion

3.1 Feasibility of green reduction of Ag_2O by wheat straw to produce Ag and organic acids

In order to verify the feasibility of the reaction of wheat straw and Ag_2O to produce Ag and organic acids, the reaction was carried out under the conditions of 0.72 g wheat straw, 0.46 g Ag_2O , 0.75 mol/L NaOH, 135°C of reaction temperature and 2 hours of reaction time. In order to determine the composition of the solid sample after reaction, the dried solid samples were analysed by XRD. The analysis results are shown in Figure. 1. The crystal index of the four diffraction peaks is 111, 200, 220 and 311. No diffraction peak of Ag_2O was detected, indicating that all Ag_2O has been converted into Ag.

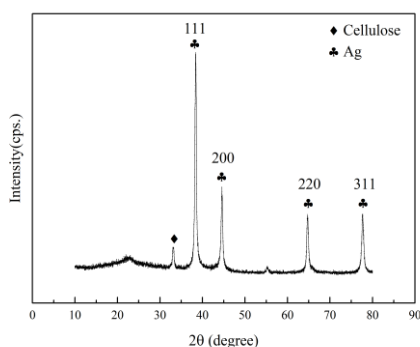


Fig. 1. XRD pattern of solid sample after reaction. (150°C , 2 h, wheat straw: 0.72 g, Ag_2O : 0.46 g, NaOH: 0.75 mol/L).

In order to determine the liquid products after the reaction of wheat straw and Ag_2O , the liquid samples

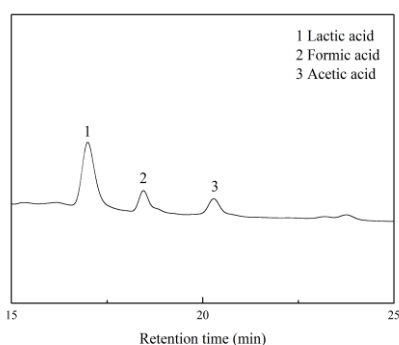


Fig. 2. HPLC of liquid sample after reaction. (150°C , 2 h, wheat straw: 0.72 g, Ag_2O : 0.46 g, NaOH: 0.75 mol/L).

were qualitatively analysed by HPLC. The analysis results are shown in Figure. 2. Which shows that the liquid products of the wheat straw and Ag_2O under mild alkaline hydrothermal conditions are mainly lactic acid, formic acid and acetic acid.

3.2 Effect of reaction conditions on the conversion of Ag_2O to Ag

To obtain the optimum reaction conditions for the conversion of Ag_2O to Ag, we investigated the effect of reaction temperature, reaction time and the concentration of NaOH.

First, reaction temperature was set as 100, 150, 200°C so as to examine the influence of reaction temperature on the yield of Ag. Other reaction conditions were: reaction time 2 h, wheat straw 0.72 g, Ag_2O 0.46 g, NaOH 0.75 mol/L. The analysis results of solid products are show in Figure. 3. When the reaction temperature is 100°C , the yield of Ag is 47.5%. When the temperature is raised to 150°C , the yield of Ag reaches almost 100%, indicating that the complete conversion of Ag_2O can be realized under mild temperature, so 150°C is the best reaction temperature. A better yield of Ag at higher temperature is probably due to the enhancement of the degradation and solubility of wheat straw in high temperature water.^[10]

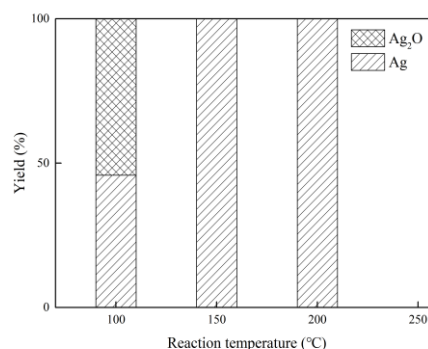


Fig. 3. Effect of reaction temperature on Ag yield. (2 h, wheat straw: 0.72 g, Ag_2O : 0.46 g, NaOH: 0.75 mol/L).

The influence of the reaction time on the yield of Ag was investigated. We set reaction time as 10, 60, 120

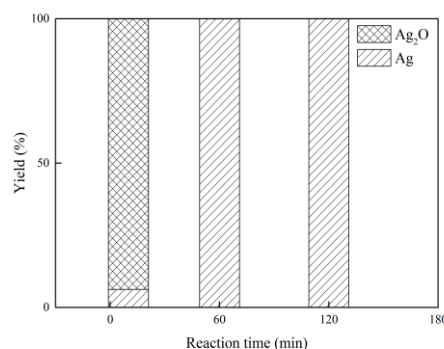


Fig. 4. Effect of reaction time on Ag yield. (150°C , wheat straw: 0.72 g, Ag_2O : 0.46 g, NaOH: 0.75 mol/L).

min, other reaction conditions were: reaction temperature 150°C , wheat straw 0.72 g, Ag_2O 0.46 g, NaOH 0.75 mol/L. The analysis results of solid products are show in Figure. 4. When the reaction time is 10 min, the yield of Ag is 6.3%. When the time is raised to 60 min, the yield of Ag reaches almost 100%, so 60 min is

choose for the best reaction time. The longer reaction time does not affect the yield of Ag, indicating that Ag is very stable under this reaction conditions.

Finally, the effect of NaOH concentration on the yield of Ag was examined by set the NaOH concentration as 0, 0.3, 0.75 mol/L, other reaction conditions were: reaction temperature 150 °C, reaction time 60 min, wheat straw 0.72 g, Ag₂O 0.46 g. The analysis results of solid products are show in Figure. 5. When the NaOH concentration is 0 mol/L, the yield of Ag is 22.5%. Furthermore, when the NaOH concentration is 0.3 mol/L, the yield of Ag is 27.4%. When the NaOH concentration raised to 0.75 mol/L, the yield of Ag reached almost 100%, so 0.75 mol/L is choose for the best NaOH concentration. These showed that NaOH can catalyse the reaction of wheat straw with Ag₂O to produce Ag and 0.75 mol/L NaOH is the best reaction condition.

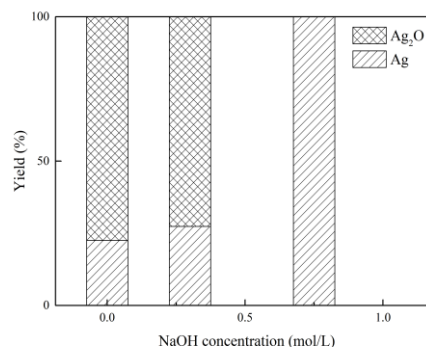


Fig. 5. Effect of NaOH concentration on Ag yield. (150 °C, 60 min, wheat straw: 0.72 g, Ag₂O: 0.46 g).

3.3 Proposed mechanism of reduction of Ag₂O into Ag with wheat straw

Our previous research have proposed mechanism of

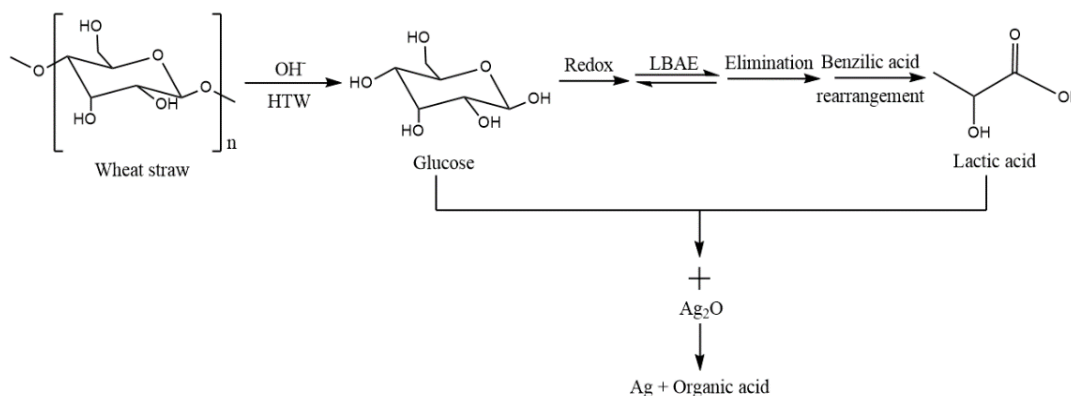


Fig. 6. Proposed mechanism of reduction of Ag₂O into Ag with wheat straw.

reduction of CuO into Cu with wheat straw.^[2] We tentative proposed the mechanism of reduction of Ag₂O in to Ag with wheat straw here based on the experimental results of this paper (Fig. 6). The main components of wheat straw are cellulose, hemicellulose and lignin.^[1] Cellulose and hemicellulose can be hydrolysed into oligosaccharides and monosaccharides such as glucose and xylose in basic solution.^[2] Furthermore, these oligosaccharides and monosaccharides was converted to organic acids via condensation, elimination and rearrangement reactions.^[4] Oligosaccharides and monosaccharides and decomposed products of them that possesses reductive ability conversion of Ag₂O into Ag altogether.

4 Conclusion

In conclusion, a novel method of reduction of Ag₂O into Ag by wheat straw and production of organic acids under mild hydrothermal conditions was developed. The yield of Ag can reached almost 100% under the reaction conditions of 150 °C, 60 min and 0.75 mol/L NaOH. This study provided a promising energy-saving approach for silver recovery by using wheat straw.

Acknowledgement

The authors thank the financial support of the State Key Program of Natural Science Foundation of China (No. 21436007) and the Natural Science Foundation of China (No. 51472159).

References

1. F. Talebnia, D. Karakashev, I. Angelidaki, *Bioresource Technology*, **101**, 4744 (2010)
2. Z. Ma, J. J. Hu, G. D. Yao, J. Duo, B. B. Jin, F. M. Jin, *Process Safety and Environmental Protection*, **115**, 79 (2018)
3. S. Syed, *Waste Management*, **50**, 234 (2016)
4. F. M. Jin, H. Enomoto, *Energy & Environmental Science*, **4**, 382 (2011)
5. P. E. Savage, *The Journal of Supercritical Fluids*, **47**, 407 (2009)

6. F. M. Jin, Z. Y. Zhou, T. Moriya, H. Kishida, H. Higashijima, H. Enomoto, *Environmental Science & Technology*, **39**, 1893 (2005)
7. F. M. Jin, J. Yun, G. M. Li, A. Kishita, K. Tohji, H. Enomoto, *Green Chemistry*, **10**, 612 (2008)
8. J. Duo, Z. S. Zhang, G. D. Yao, Z. B. Huo, F. M. Jin, *Catalysis Today*, **263**, 112 (2016)
9. H. C. Tao, Z. Y. Gao, H. Ding, N. Xu, W. M. Wu, *Bioresource Technology*, **111**, 92, (2012)
10. M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai, *American Chemical Society*, **39**, 2883, (2000)