



A Greener Process for Gallic Acid Production from Tannic Acid Hydrolysis with Hydrochloric Acid

JIE FU, YINGJIE ZHANG and XIUYANG LU*

Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, Zhejiang Province, P.R. China

*Corresponding author: Tel/Fax: +86 571 87952683, E-mail: luxiyang@zju.edu.cn

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The traditional technology for gallic acid production from tannic acid with sodium hydroxide causes severe pollution to the environment. Focusing on this issue, a greener process for gallic acid production from tannic acid hydrolysis with hydrochloric acid was developed. The catalytic activities of HCl, H₂SO₄ and NaOH for tannic acid hydrolysis were evaluated. The HCl-catalyzed hydrolysis of tannic acid could achieve similar yield of gallic acid as traditional NaOH-catalyzed hydrolysis, although the hydrolysis rate of tannic acid with HCl was not as fast as that with NaOH. Afterwards, the effects of tannic acid initial concentration, reaction temperature, HCl concentration on tannic acid hydrolysis were investigated. The HCl-catalyzed hydrolysis rate of tannic acid increased as temperature rose and the increase of HCl concentration could significantly facilitate the hydrolysis rate of tannic acid. The hydrolysis rate constants at different temperatures and acid concentrations were obtained by first-order equation and the activation energies were obtained by Arrhenius equation. The rate constants of tannic acid hydrolysis (k_1) with HCl are much smaller than decarboxylation rate constants (k_2), indicating that hydrolysis is easier to occur than decarboxylation of gallic acid.

Keywords: Tannic acid, Hydrolysis, Hydrochloric acid, Gallic acid.

INTRODUCTION

Gallic acid (3,4,5-trihydroxybenzoic acid) is an important chemical widely used in organic synthesis, pharmaceutical, food and integrated circuit manufacturing^{1,2}. Gallic acid is incorporated into chemical synthesis to provide not only the trihydroxylated aromatic ring of biologically active molecules such as trimethoprim (antibiotic), gallamine triethiodide (muscle relaxant) and bendiocarb (insecticide)³, but also useful antioxidants in the oil industry⁴.

The annual industrial output of gallic acid is about 1500 tons all over the world, in which more than 85 % gallic acid is produced in China. Traditionally, gallic acid is mainly produced by the hydrolysis of tannic acid with sodium hydroxide^{1,5}. In this process, NaOH cannot be recycled, producing about 13000 tons waste water per year that needs treatment. In China, many factories are built at the upstream of the rivers. A large amount of waste water is not well treated but drained into the rivers, causing severe environmental pollution. Therefore, it is desirable to develop an environment benign preparation of gallic acid.

Enzymatic production of gallic acid from tannic acid is regarded as an environment benign approach^{6,7}, but the high cost of tannase production, deactivation of enzyme and low yield of gallic acid limit the application of enzymatic method

for gallic acid production in industry. For the chemical method, non-catalytic hydrolysis of tannic acid in high temperature water (140-180 °C) was studied, but the hydrolysis rate was slow and required relative high temperature⁸. A catalyst is necessary for the industrial production of tannic acid. Hydrochloric acid is an acid catalyst possible to be recycled by distillation and the reusability of HCl makes the process greener. The process diagram of HCl-catalyzed hydrolysis of tannic acid is shown in Fig. 1. However, serious corrosion for the production equipment can be caused by HCl. Nowadays, due to the technology progress of metal materials^{9,10}, the problem on the corrosion of HCl can be overcome, that offers the possibility for employing HCl to develop a greener process. Yasnitskii *et al.*¹¹ used HCl to catalyze the hydrolysis of tannic acid at 102 °C. Zhang *et al.*¹² studied the stability of gallic acid in the presence of HCl and the results showed that gallic acid was relatively stable in the addition of HCl. On this point, the production of gallic acid from tannic acid with HCl is feasible. Due to the lack of fundamental studies on hydrolysis of tannic acid with HCl such as kinetics and catalysis mechanism, the technology on HCl-catalyzed hydrolysis was not well developed.

In this study, the catalytic abilities of HCl, H₂SO₄, NaOH were compared. The kinetics of the hydrolysis of tannic acid with HCl were studied. The effects of reactant concentration,

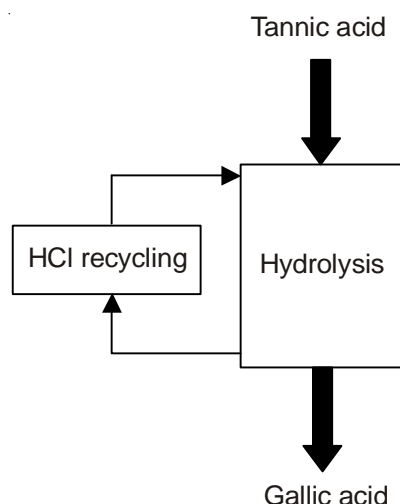


Fig. 1. Process diagram of HCl-catalyzed hydrolysis of tannic acid

reaction temperature and HCl concentration on the HCl-catalyzed hydrolysis of tannic acid were investigated. The hydrolysis rate constants at different temperatures and acid concentrations were obtained by first-order equation and the activation energies were obtained by Arrhenius equation. These results provide insights for the HCl-catalyzed hydrolysis of tannic acid to gallic acid.

EXPERIMENTAL

Gallic acid (> 99 %) was obtained from J&K Scientific, China. Pyrogallol (> 99 %) was obtained from Aladdin Industrial Inc., China. Purpurogallin (≥ 98 %) was obtained from Tokyo Chemical Industry, Japan. Hydrochloric acid (36–38 %), sulphuric acid (98 %) and anhydrous sodium carbonate were obtained from Sinopharm Chemical Reagent Co. Ltd., China. Borax (≥ 99.5 % purity) was obtained from Taicang Meida Reagent Co. Ltd., China. Industrial tannic acid was obtained from Zunyi Forest & Plant Chemical Co. Ltd., China.

A set of 100 mL stainless steel reactors was employed, described by Yang *et al.*¹³. A certain amount of industrial tannic acid was carefully measured and added into the reactor, followed by adding deionized water. The reactor was heated in the water bath until the tannic acid was dissolved. After the solution cooled down, a certain amount of HCl was added into the reactor. Then the reactor was sealed and put in a furnace. The reactor was removed from the furnace at fixed time intervals and put into cool water quickly to quench the reaction. The sample was collected from the cooled reactor and rinsed to a 1000 mL volumetric flask by deionized water. Then 1 mL sample was obtained to 50 mL volumetric flask. The solution was filtered by 0.45 μm filter membrane and analyzed by HPLC.

Analysis method: The samples were quantitatively analyzed by HPLC (Agilent 1100) with UV detector. The HPLC column was Phenomenex-C18 (5 μm, 250 mm × 4.6 mm ID). The mobile phase was 0.5 × 10⁻³ mol/L H₃PO₄ solution: acetonitrile = 90 : 10 (V/V) at a flow rate of 0.6 mL/min. The temperature of column was 25 °C and the wavelength was 215 nm. Peaks were identified by comparison of their retention times with those of standard solutions of pure compounds and quantified by external reference method.

The yield of gallic acid was calculated by the following equation

$$Y = \frac{m_{CA}}{m_{TA} \cdot \omega_{TA}} \times 100 \% \quad (1)$$

Y: yield of gallic acid; m_{GA}: mass of gallic acid. The mass of produced gallic acid was obtained by HPLC; m_{TA}: mass of industrial tannic acid; ω_{TA}: mass percentage of gallic acid to industrial tannic acid after complete hydrolysis. Mass percentage of gallic acid to industrial tannic acid after complete hydrolysis was experimentally obtained as 81.9 %.

RESULTS AND DISCUSSION

Activity of HCl, H₂SO₄ and NaOH on tannic acid hydrolysis: Fig. 2 shows the yields of gallic acid with HCl, H₂SO₄ and NaOH at 393.15 K. The concentration of tannic acid is 16 wt %, the H⁺ concentration of HCl or H₂SO₄ was 1.8 mol/L and the concentration of NaOH was 3.3 mol/L (the standard concentration of NaOH addition amount in industry). At the same temperature, the yield rate of gallic acid with NaOH was the fastest. Within 60 min, the yield of gallic acid had been close to the maximum yield. The yield rate of gallic acid with HCl was faster than that with H₂SO₄. At 120 min, the yield of gallic acid with HCl was close to the maximum yield (that with H₂SO₄ needed 300 min). The maximum yields of gallic acid with these three catalysts were all around 90 %. The acid-catalyzed hydrolysis of tannic acid can achieve similar yield of gallic acid as NaOH-catalyzed hydrolysis.

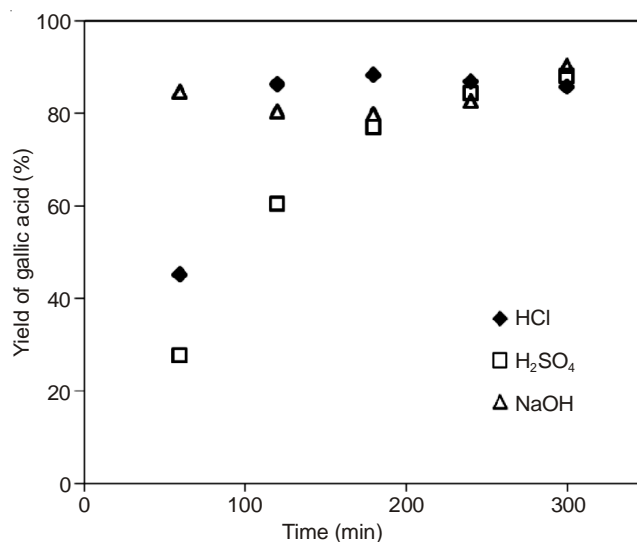


Fig. 2. Yield of gallic acid with HCl, H₂SO₄ and NaOH. Reaction temperature: 393.15 K; initial concentration of tannic acid: 16 wt %; H⁺ concentration of HCl and H₂SO₄: 1.8 mol/L; concentration of NaOH: 3.3 mol/L

Effect of initial concentration on hydrolysis of tannic acid with HCl: Fig. 3 shows the effects of initial concentration of tannic acid on the yield of gallic acid at 393.15 K and a HCl concentration of 1 mol/L. The concentrations of tannic acid are 8, 16, 24 and 32 wt %. The yield of gallic acid slightly decreased with the increase of tannic acid initial concentration, indicating that the increase of tannic acid initial concentration raises the viscosity of tannic acid solution, hindering the mass

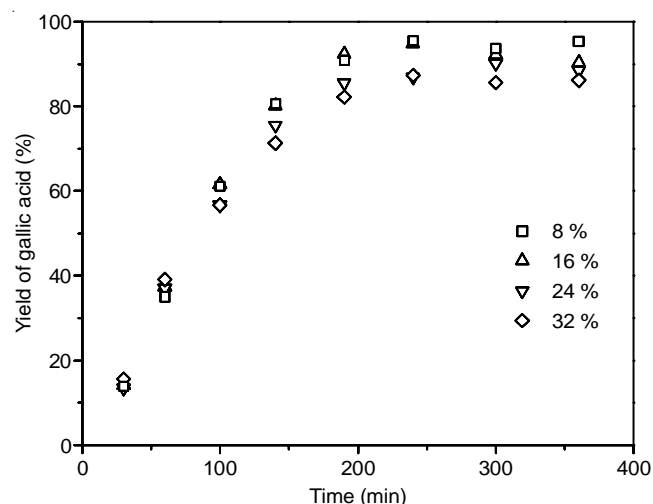


Fig. 3. Effect of initial concentration on the yield of gallic acid with HCl at 393.15 K

transfer. A suitable tannic acid concentration for following experiments was regarded to be 16 wt %.

Effect of temperature on hydrolysis of tannic acid with HCl:

Fig. 4a-d show the effect of temperature on the hydrolysis of tannic acid with HCl concentration of 0.2, 1.0, 1.8, 2.6 mol/L. At all concentrations, the hydrolysis rates were accelerated by temperature rising, but the effects of temperature on hydrolysis at each concentration were different. At the HCl concentration of 0.2 mol/L, the hydrolysis rate increased as the temperature rose and the production rate of gallic acid significantly increased. Within 300 min, the yield of gallic acid did not achieve the maximum value. At the HCl concentration of 1 mol/L, when the temperature was at 383.15 or 393.15 K, the hydrolysis rate speeded up significantly and the yield of gallic acid significant increased. At 403.15 and 413.15 K, the gallic acid yield firstly increased to a maximum value as time elapsed and then slightly decreased. At the HCl concentrations of 1.8 and 2.6 mol/L and 383.15 K, the conversion of tannic acid and the yield of gallic acid significantly increased as time elapsed. The decrease of gallic acid yield indicates that gallic acid is converted to pyrogallac acid and other byproducts.

Effect of HCl concentration on hydrolysis of tannic acid:

The effects of HCl concentration on the hydrolysis of tannic acid are also shown in Fig. 4a-d. At 383.15 K, the yield of gallic acid significantly increased as HCl concentration increased. At 393.15 K, the yield of gallic acid remarkably increased as the time elapsed at the HCl concentrations of 0.2 and 1 mol/L, but first increased then slightly decreased at the HCl concentrations of 1.8 and 2.6 mol/L. At 403.15 and 413.15 K, the yield of gallic acid significantly increased as the time elapsed at the HCl concentrations of 0.2 mol/L, but the yield of gallic acid first increased then slightly decreased at the HCl concentrations of 1.0, 1.8 and 2.6 mol/L. It indicates that gallic acid tends to be converted at high HCl concentration.

Kinetics: The reaction pathway of tannic acid decomposition is shown in Fig. 5. Tannic acid was hydrolyzed to gallic acid and glucose (step 1), then sequentially decarboxylated to pyrogallac acid (step 2)⁸. We assumed that each step is pseudo first-order reaction and the kinetics equations can be expressed as follows:

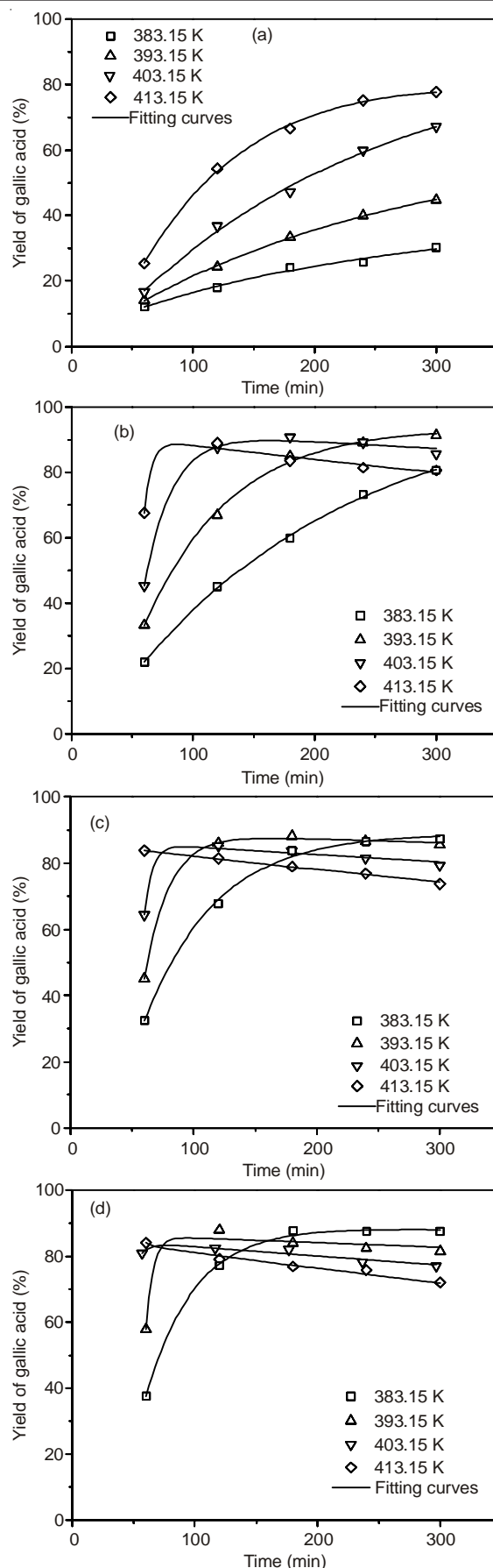


Fig. 4. Yield of gallic acid at different temperatures and HCl concentrations; (a) 0.2 mol/L HCl concentration; (b) 1.0 mol/L HCl concentration; (c) 1.8 mol/L HCl concentration; (d) 2.6 mol/L HCl concentration

$$\ln \frac{1}{1-x} = k_1 t + a \quad (2)$$

$$y = \frac{ak_1}{k_2 - k_1} e^{-k_1 t} + b e^{-k_2 t} \quad (3)$$

$$y = \frac{-a}{k_2 - k_1} e^{-k_1 t} - \frac{b}{k_2} e^{-k_2 t} + c \quad (4)$$

where x is the conversion of tannic acid; y is the yield of gallic acid; k_1 is the rate constant of tannic acid hydrolysis; k_2 is the rate constant of gallic acid decarboxylation; a , b and c are the constants of integration. The decarboxylation rates of gallic acid (k_2) with HCl were obtained in previous research¹², shown in Table-1. With the equations 2-4 and k_2 values in Table-1, the experimental results of tannic acid hydrolysis with HCl were fitted. The hydrolysis rate constants (k_1) with HCl at different H^+ concentrations and temperatures were obtained,

shown in Table-2. The fitting curves are presented in Fig. 4, which indicates good consistence with experimental data. Arrhenius equation was employed to obtain the activation energies of tannic acid hydrolysis with HCl, also shown in Table-2.

The rate constant of tannic acid hydrolysis (k_1) is much larger than the rate constant of gallic acid decarboxylation (k_2), suggesting that tannic acid hydrolysis is easier to occur than gallic acid decarboxylation. High yield of gallic acid is possible to be achieved by controlling the reaction conditions. With the increase of H^+ concentration, the activation energies of tannic acid hydrolysis with HCl first increased and then decreased.

Conclusion

A greener process for gallic acid production from tannic acid hydrolysis with HCl was developed. The hydrolysis rate

TABLE-1
RATE CONSTANTS (k_2) AND ACTIVATION ENERGIES OF GALLIC ACID DECARBOXYLATION [Ref. 12]

Temperature (K)		H^+ concentration of HCl (mol/L)				
		0	0.2	1.0	1.8	2.6
393.15 K	k_2	0.000658	0.0000970	0.000109	0.000128	0.000171
	R^2	0.9814	0.8590	0.8461	0.9528	0.9734
413.15 K	k_2	0.002362	0.0004195	0.000493	0.000511	0.000614
	R^2	0.9922	0.9987	0.9695	0.9916	0.9928
433.15 K	k_2	0.009255	0.0021945	0.002443	0.002800	0.003347
	R^2	0.9917	0.9964	0.9953	0.9973	0.9970
453.15 K	k_2	0.028472	0.0090170	0.009980	0.012076	0.013880
	R^2	0.9973	0.9954	0.9946	0.9936	0.9929
E_a (kJ/mol)		93.8	112.8	112.2	113.3	110.0
R^2		0.9990	0.9979	0.9989	0.9956	0.9936

TABLE-2
RATE CONSTANTS (k_1) AND ACTIVATION ENERGIES OF TANNIC ACID HYDROLYSIS WITH HCl

Temperature (K)	H^+ concentration of HCl (mol/L)								
	0.2		1.0		1.8		2.6		
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	
383.15	0.00423	0.9725	0.00534	0.9986	0.01692	0.9950	0.02511	0.9972	
393.15	0.00404	0.9992	0.01371	0.9955	0.05108	0.9986	0.17310	0.9653	
403.15	0.00428	0.9922	0.04416	0.9940	0.15796	0.9820	0.13101	0.7614	
413.15	0.00997	0.9970	0.16829	0.9571	0.75544	0.9868	0.21597	0.9286	
E_a (kJ/mol)		60.54	0.7861	151.31	0.9900	164.48	0.9881	96.27	0.9917

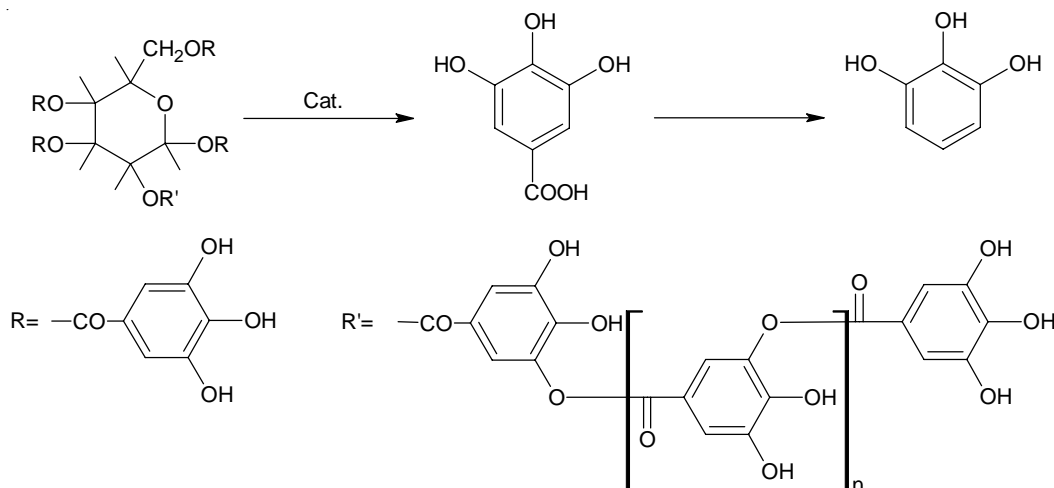


Fig. 5. Reaction pathway of tannic acid decomposition

of tannic acid with HCl was slower than that with NaOH, but faster than that of H₂SO₄. The acid-catalyzed hydrolysis of tannic acid could achieve similar yield of gallic acid as NaOH-catalyzed hydrolysis. The hydrolysis rate of tannic acid with HCl increased as temperature increase. The increase of HCl concentration could significantly facilitate the hydrolysis rate of tannic acid. The rate constants of tannic acid hydrolysis (k_1) with HCl were much smaller than decarboxylation rate constants (k_2), indicating that hydrolysis was easier to occur than decarboxylation.

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