

# Reaction Model Correlation of the 2,3,5-Trimethyl-1,4-Benzoquinone Synthesis Using CuFe<sub>2</sub>O<sub>4</sub> Nano-Powder as the Catalyst

Yenchun Liu, Maochieh Chi, and Chaoming Lin

**Abstract**—Copper ferrite nano-particles were successfully synthesized by microwave-induced combustion process using copper nitrate, iron nitrate and urea. The CuFe<sub>2</sub>O<sub>4</sub> powders were found to be efficient catalysts in oxidizing 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethylhydroquinone (TMHQ) and 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) in acidic reaction conditions. Also, recovery of the catalyst was facilely achieved by simple magnetic decantation. Based on the experimental evidence, a pseudo-steady-state hypothesis (PSSH) was applied to the reaction system. The kinetic behaviors and the characteristics of the reaction were sufficiently described by the pseudo-first-order rate law. This investigation covers the effects on the yield of the product and the apparent rate constants ( $k_{app,2}$ ) that result due to the reaction conditions, including agitation speed, amount of CuFe<sub>2</sub>O<sub>4</sub> powder catalyst, amount of HCl, volume of water, amount of hydrogen peroxide, temperature, and organic solvents.

**Index Terms**—Copper ferrite, combustion process, 2,3,5-trimethyl-1,4-benzoquinone, oxidation, catalyst.

## I. INTRODUCTION

The copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) powder is an effective catalyst in the synthesis of 2,3,5-trimethylbenzoquinone (TMBQ), which is an intermediate in the vitamin E synthesis [1], [2]. Because of its function as an anti-free radical, helping prevent aging, apoplexy, heart disease, cardiovascular vessel disease and anti-cancer, Vitamin E is one of the important vitamins today. At present, the demand has reached several millions pounds every year [3]. The reason for the high cost of Vitamin E is the initial reactant of Vitamin E is difficult to produce on a large scale. Therefore, many scientists are searching for a way to mass produce TMBQ, rapidly, effectively, low cost and at green process [4], [5]. At present, in terms of industrial production and academic research, most researchers use 2,3,6-trimethylphenol (TMP) as the initial reactant for synthesizing TMBQ by metal ions [6]-[13]. Jean-Pierre Aguer *et al.* [14] observed TMP efficiently oxidized in the presence of Fe(III) aqua complexes. The common points of those methods are the metal ions used as catalysts to obtain a high yield. However, those catalysts are

expensive and difficult to prepare. On the other hand, the catalysts and products are separated after reaction when they are dissolved in solution. Molecular collisions are essential for a reaction of two or more molecules to occur. So, the conversion is low from two immiscible reactants to react due to their low mutual solubility and limited contact surface area. The conventional methods to overcome this problem are to carry out the reaction at a higher temperature, with a higher agitation speed or using a solvent or cosolvent which has both lipophilic and hydrophilic properties. However, the improvement in the reaction of the two immiscible reactants is limited because the byproducts are frequently produced from side reactions at higher temperatures. The reactivity of the nucleophilic reagent is decreased for the solvation and hydrogen bonding with the protic solvent. Therefore, the reaction rate is low when the protic solvents are used. The solvation of the aprotic solvent and nucleophilic reagent was minimized, however, the reactions were carried out under anhydrous conditions using an expensive aprotic solvent. Further, the higher boiling point aprotic solvent is difficult to recover. These problems were overcome by introducing phase transfer catalysis [15]. Besides, the combination of oxidizing agent and copper ferrite is industrially important because the oxidation process is environmentally benign and therefore in line with green chemistry.

Spinel CuFe<sub>2</sub>O<sub>4</sub> powder and its properties have been the subject of many recent investigations [16]-[19]. Among bimetallic spinel-type oxides, CuFe<sub>2</sub>O<sub>4</sub> a useful catalyst, the basic properties of microstructure, predominate phase and magnetization were obtained from fine particles [20], [21]. Recently, Liu and Fu reported the entire microwave-induced combustion synthesis process to prepare nano-powder takes only a few minutes to yield nano-powder [2], [22]. The combustion synthesis process dissolves metal nitrate and urea in water, and then heats the solution in a microwave oven. The urea and metal nitrate decompose and produce gasses such as NH<sub>3</sub>, N<sub>2</sub>, and CO<sub>2</sub>, respectively. After the solution reaches the point of spontaneous combustion, it begins burning and becomes solid, and burns at high temperature. The combustion does not finish until all the flammable substances are burned out, which results in a loose substance displaying voids, pores, and high friable formed by the escaping gases during the combustion reaction.

The purpose of this work is to synthesize the TMBQ from the reaction of TMP and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) by CuFe<sub>2</sub>O<sub>4</sub> catalysis in an acid /organic solvent two-phase medium. However, when an excessively large amount of H<sub>2</sub>O<sub>2</sub> reagent relative to that of TMP and a large amount of

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Yenchun Liu is with the Graduate School of Opto-Mechatronics and Materials, WuFeng University, Chiayi County, 621 Taiwan (e-mail: blliu@wfu.edu.tw).

Maochieh Chi is with the Department of Fire Science, WuFeng University, Chiayi County, 621 Taiwan (e-mail: jackchi@wfu.edu.tw).

Chaoming Lin is with the Department of Mechanical and Energy Engineering, Chiayi University, Chiayi City, 600 Taiwan (e-mail: cmlin@mail.ncyu.edu.tw).

hydrogenchloric acid (HCl) were used, the oxidation took place in the solution in both cases. The sequential oxidation of *TMP* was examined in detail. The reaction is greatly enhanced both in the presence of HCl and  $\text{CuFe}_2\text{O}_4$  powder. Based on the experimental data, a rational mechanism is proposed to account for the observed reaction. A kinetic model is derived, from which the pseudo-steady-state hypothesis (PSSH) is applied. A simplified pseudo-first order rate equation is derived to describe the experimental data [13], [23]. The reaction conditions including various catalysts, organic solvents, the amount of copper ferrite catalyst, amount of HCl, amount of  $\text{H}_2\text{O}_2$ , volume of dichloromethane, and the volume of water on the yields of *TMBQ* obtained from *TMP* were investigated in detail. A rational reaction mechanism is proposed to satisfactorily explain the experimental results.

## II. EXPERIMENTAL PROGRAM

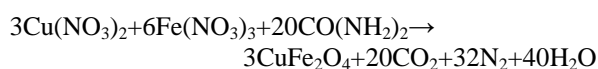
### A. Materials

Copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), Iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Urea ( $\text{CO}(\text{NH}_2)_2$ ), 2,3,6-Trimethylphenol, Copper (II) chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), Hydrochloric acid (HCl), Organic solvents (including dichloroethylene), Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 35 wt% in water) and other reagents are all G.R. grade chemicals for synthesis.

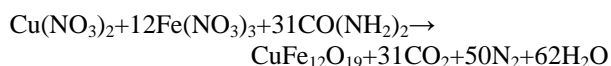
### B. Procedures

#### 1) Copper ferrite synthesis

The synthesis process involved the combustion of redox mixtures, in which metal nitrate acted as oxidizing reactant and urea as reducing agent. The initial composition of the solution containing strontium nitrate, ferric nitrate, and urea was based on the total oxidizing and reducing valences of the oxidizer and the fuel using the concepts of propellant chemistry. Stoichiometric amounts of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), and urea ( $\text{CO}(\text{NH}_2)_2$ ) dissolved in a minimum quantity of water were set in a crucible. The atomic ratio of Fe/Cu was set to be 2. The crucible containing the solution was introduced into an oven (CEM, MDS 81D, 650W). Initially, the solution boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases ( $\text{N}_2$ ,  $\text{NH}_3$ , and  $\text{HNC}$ ). After the solution reaches the point of spontaneous combustion, it began burning and released lots of heat, vaporized all the solution instantly and became a solid burning at the temperature over 1000 °C. The entire combustion process produced copper ferrite powders in an oven taking only 2 hr. A stoichiometric combustion reaction of metal nitrate with urea to form copper ferrite as follows:



and



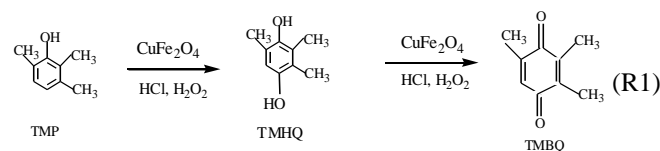
#### 2) Kinetics of synthesizing 2,3,5-trimethylquinone (*TMBQ*)

The reactor is a 125-mL four-necked Pyrex flask able to serve the purposes of agitating the solution, inserting the thermometer, taking samples, and feeding the reactants. A reflux condenser is attached to the port of the reactor to recover the organic solvent. The reactor is submerged into a water bath in which the temperature is controlled to  $\pm 0.1^\circ\text{C}$ . Hereafter are the steps of experiment. First, heat up the reactor to 60 degrees centigrade. Second, weight precisely on *TMP* and internal standard (biphenyl), and add 50 mL of organic solvent (dichloroethane,  $\text{C}_2\text{H}_4\text{Cl}_2$ ) and 20 mL of water, and dissolve them completely. Third, put a proper amount of copper ferrite ( $\text{CuFe}_2\text{O}_4$  or  $\text{CuFe}_{12}\text{O}_{19}$ ) and hydrochloric acid in the reactor for following catalytic reaction. Fourth, 20mL of hydrogen peroxide (oxidant) is added into the above-mentioned solution. The solution is mixed thoroughly. Fifth, a sample was withdrawn at a certain time interval and analyzed by gas chromatograph (GC), and the conversion of *TMP* and the yield of *TMBQ* were measured. During the reaction, sample (0.2 mL) which is diluted to 0.5mL by the same organic solvent. The injection of the dilution sample into gas chromatography was then proceeded for analysis. The conversion of *TMP*, and the yield and the selectivity of *TMBQ* are calculated from the spectrum of gas chromatography and the calibration curve of reactant and product.

The mixture was stirred mechanically by a two-blade paddle (5.5 cm) at 800 rpm. During the reaction, an aliquot sample of 0.2 mL was withdrawn from the solution at a chosen time. The sample was immediately introduced into the same organic solvent at  $4^\circ\text{C}$  for dilution to retard the reaction, and then analyzed by gas chromatographic instrument (GC). The product *TMBQ* for identification was synthesized from the reaction of 2, 3, 5-trimethylhydroquinone (*TMHQ*) in a limiting quantity and hydrogen peroxide in an organic solvent without containing catalyst. After completing the reaction, the solution was purified by vacuum evaporation to strip off the organic solvent and hydrogen peroxide. Then, *TMBQ* in solid form was re-dissolved into ethanol for re-crystallization, and a red crystal form of *TMBQ* was obtained at  $4^\circ\text{C}$ . The contents of *TMBQ* and reactants were analyzed by GC instrument.

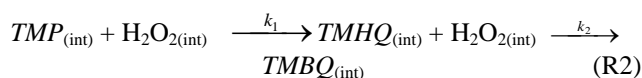
#### C. Reaction Mechanism and Kinetic Model

A detailed description of the copper ferrite and HCl in the two-phase reaction of *TMP* and  $\text{H}_2\text{O}_2$ , and the overall reaction in the two-phase medium is expressed as follows



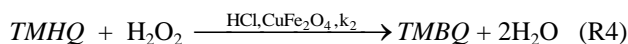
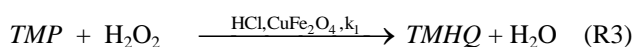
From experimental observation and reference to previous studies, *TMP* dissolves only slightly in pure water. Then,  $\text{H}_2\text{O}_2$  further reacts with reactant *TMP* in the organic phase or on the interface between the two phases to produce the desired *TMBQ* product. Based on the experimental evidence, the mechanism of the reaction of *TMP* and  $\text{H}_2\text{O}_2$  in interface

medium, which can be expressed as



The subscripts “int” represent the species in the interface medium. In the reaction solution, the amount of  $H_2O_2$  is excessive relative to that of  $TMP$ . The  $TMP$  was observed using a limited quantity, and the product of the  $TMBQ$  was only obtained in the solution by oxidation. Further, the reaction of  $TMP$  and  $H_2O_2$  to produce  $TMHQ$  quickly reaches an equilibrium state. In principle, therefore,  $TMP$  first reacts with  $H_2O_2$  in the acid solution to produce the  $TMHQ$ . The  $TMHQ$  further reacts with  $H_2O_2$  in the interface to produce  $TMBQ$ , whereas the aqueous soluble compounds  $H_2O_2$  remain in the aqueous solution.

Clearly, products which are produced in the organic phase are obtained, i.e.,  $TMHQ$  and  $TMBQ$ . From the experimental results, we found that the two products obtained from the organic phase are similar to a type of sequential reactions [23]. Further, the mass transfer rate of the species for  $H_2O_2$  and the aqueous-phase reaction rate are all rapid. In the absence of mass transfer process, the yield of  $TMBQ$  for the first-order kinetic process in which the rate determining step is the surface reaction. Thus, the interface reactions are clearly the rate-controlling step. A simplified kinetic model is thus proposed based on the experimental data, and the above two reactions can be written as,



From reactions (R3) and (R4), we obtain the kinetic rate equations for  $TMP$ ,  $TMHQ$  and  $TMBQ$ , respectively, as follows

$$\frac{d[TMP]_{int}}{dt} = -k_1[TMP]_{int}[H_2O_2]_{int} \quad (1)$$

$$\frac{d[TMHQ]_{int}}{dt} = k_1[TMP]_{int}[H_2O_2]_{int} - k_2[TMHQ]_{int}[H_2O_2]_{int} \quad (2)$$

$$\frac{d[TMBQ]_{int}}{dt} = k_2[TMHQ]_{int}[H_2O_2]_{int} \quad (3)$$

where the subscript “int” denotes the species in the interface and  $k_1$  and  $k_2$  are the rate constants of reactions (R3) and (R4). As stated, an excessive amount of  $HCl$  and  $H_2O_2$  are used during the reaction. Therefore, the concentration of  $H_2O_2$  can be considered a constant. For this, Equations (1) and (2) are reduced,

$$\frac{d[TMP]_{int}}{dt} = -k_{app,1}[TMP]_{int} \quad (4)$$

$$\frac{d[TMHQ]_{int}}{dt} = k_{app,1}[TMP]_{int} - k_{app,2}[TMHQ]_{int} \quad (5)$$

The initial conditions of  $TMP$ ,  $TMHQ$  and  $TMBQ$  are

$$t = 0, [TMP]_{int} = [TMP]_{int,i} \quad (6)$$

$$[TMHQ]_{int} = [TMBQ]_{int} = 0 \quad (7)$$

Equations (3) – (5) are solved to yield,

$$[TMP]_{int} = [TMP]_{int,i} \exp(-k_{app,1}t) \quad (8)$$

$$[TMHQ]_{int} = \frac{k_{app,1}}{k_{app,2} - k_{app,1}} [TMP]_{int,i} \{ \exp(-k_{app,1}t) - \exp(-k_{app,2}t) \} \quad (9)$$

$$[TMBQ]_{int} = \frac{[TMP]_{int,i}}{k_{app,2} - k_{app,1}} \quad (10)$$

$$\{ k_{app,1}[1 - \exp(-k_{app,2}t)] - k_{app,2}[1 - \exp(-k_{app,1}t)] \}$$

A maximum yield of  $[TMHQ]_{int}$  is obtained from the experimental data. Thus, the differentiation of  $[TMHQ]_{int}$  with respect to time is carried out to obtain the time for a maximum yield  $t_{B, max}$ , i.e.,

$$\frac{d[TMHQ]_{int}}{dt} = 0 \quad (11)$$

Therefore, the time which the maximum and concentration of  $TMBQ$  occurs is thus:

$$t_{B, max} = \frac{Ln(\frac{k_{app,2}}{k_{app,1}})}{k_{app,2} - k_{app,1}} \quad (12)$$

$$\frac{[TMHQ]_{int, max}}{[TMP]_{int,i}} = \left( \frac{k_{app,1}}{k_{app,2}} \right)^{k_{app,2} / (k_{app,2} - k_{app,1})} \quad (13)$$

In this work, it is difficult to identify the occurrence of the reaction of  $TMP$  and  $H_2O_2$  on the interface. In fact, the two-phase reaction of  $TMP$  and  $H_2O_2$  may take place on the interface between two phases or in the organic phase because of the water-soluble and organic soluble nature of  $TMP$ . The mass transfer of the  $H_2O_2$ ,  $TMP$ ,  $TMHQ$  and  $TMBQ$  are also rapid, and the reaction of the conformation of  $TMBQ$  is clearly a rate determining step ( $k_1 \gg k_2$ ). Therefore, a simple kinetic rate law is used to model the reaction system in this work. Based on the experimental data, it is noted the concentration of  $TMBQ$  in the organic phase follows a pseudo-first-order rate law. Therefore, we have

$$[TMBQ]_{int} = [TMP]_{int,i} (1 - \exp^{-k_{app,2}t}) \quad (14)$$

where  $k_{app,2}$  is the apparent reaction rate constant of R4, equation (14) is rewritten as

$$-\ln(1 - X) = k_{app,2}t \quad (15)$$

In order to compare the reactivity between the catalysts, the

yield of *TMBQ*(X) is calculated as:

$$X = \frac{[TMBQ]_{int}}{[TMP]_{int,j}} = \frac{\text{quantity of } [TMBQ]_{int}}{\text{theoretical quantity of } [TMBQ]_{int}} \quad (16)$$

By plotting the experimental data  $-\ln(1-X)$  vs.  $t$ , we get a straight line with the slope of the apparent rate constant ( $k_{app,2}$ ).

### III. RESULTS AND DISCUSSION

The mechanism of the catalyzing oxidation reaction of *TMP* by copper catalyst is described as follows: copper ion first reacts with *TMP*, wherein the hydroxyl group (-OH) on the *TMP* is attacked by the copper ion, causing departure of hydrogen ions and the formation of free radicals on -O. Thereafter, the free radicals on the oxygen atom transfer to the carbon atom opposite the oxygen atom on the ring of benzene, and react with oxidant to form *TMBQ*. However, the carbon atom attacked by the copper ion is positioned opposite the hydroxyl group (-OH), resulting in the destruction of the ring of benzene and the formation of a free radical on the carbon atom of the ring of benzene.

#### A. Effect of the Agitation Speed

The effects of the agitation speed on the yield of *TMBQ* were investigated for 1.200 g of *TMP*, 20 mL of  $H_2O_2$ , 5 mL of HCl, 0.402 g of  $CuFe_2O_4$  catalyst at 60°C, with a volume ratio of 50 mL/20 mL of  $C_2H_4Cl_2/H_2O$ . The results are shown in Fig. 1. Clearly, the reaction follows the pseudo first-order rate law. The yield of *TMBQ* is increased with the increase in agitation speed up to 800 rpm. However, there are no significant improvements in the reaction when further increasing the agitation speed from 800 rpm to 1,000 rpm. This result appears to show that the interface reaction of *TMP* and  $H_2O_2$  plays an important role in the entire reaction system. Therefore, to study the reaction phenomena from which the resistance of mass transfer stays at a constant, the agitation speed was set at 1,000 rpm. The agitation speed on the apparent rate constant ( $k_{app,2}$ ) results obtained are given in Table I. It is obvious that the  $k_{app,2}$ -value is increased with increased agitation speed.

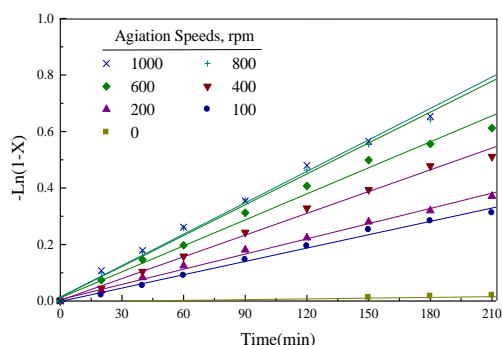


Fig. 1. Effect of the agitation speed on the yield of 2, 3, 5- trimethyl-1, 4 benzoquinone; 2, 3, 6-trimethylphenol: 1.200 g,  $H_2O_2$ =20 mL,  $CuFe_2O_4$ =0.400g, HCl=5 mL,  $C_2H_4Cl_2/H_2O$ =50 mL/20 mL, 60 °C.

#### B. Effect of the Amount of $CuFe_2O_4$ Catalyst

As stated, the reaction is greatly enhanced by adding  $CuFe_2O_4$  catalyst to the yield of *TMBQ*. Fig. 2 illustrates the

influence of the amount of copper ferrite on the yield of 2, 3, 5-trimethyl-1, 4-benzoquinone with hydrogenchloric acid; wherein, the yield of 2,3,5-trimethyl-1,4-benzoquinone is significantly influenced by using copper ferrite as a catalyst for oxidation 2,3,6-trimethylphenol. There is no reaction between *TMP* and  $H_2O_2$  in the absence of the HCl and  $CuFe_2O_4$  agent. The yield of *TMBQ* is still low without the  $CuFe_2O_4$  catalyst, even when HCl is present in the solution, and the reaction is dramatically increased by adding an additional 0.201 g of  $CuFe_2O_4$  catalyst. Clearly,  $CuFe_2O_4$  is an effective catalyst for enhancing the reaction. It possesses more copper active sites, so the oxidation reaction is enhanced, and it can be easily separated from the solution. The magnetic catalyst could be facilely isolated from the reaction mixture by magnetic decantation. Catalysts generally reduce the energy of activation so that the product might be formed at a higher yield of 2,3,5-trimethyl-1,4-benzoquinone. The reaction follows a pseudo-first order rate law with the conversion increasing with increasing amounts of  $CuFe_2O_4$  catalyst up to 0.600 g. The basic  $CuFe_2O_4$  and HCl reacted with *TMP* to produce an active intermediate *TMHQ* which can react with the organic-phase reactant to produce the desired product (*TMBQ*). The value of the amount of  $CuFe_2O_4$  catalyst on the apparent rate constant ( $k_{app,2}$ ) are listed in Table I. Under this situation, the consumption rate of *TMP* is also fast using a larger amount of  $CuFe_2O_4$  catalyst.

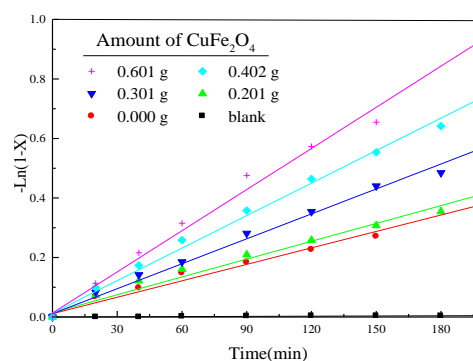


Fig. 2. Effect of  $CuFe_2O_4$  amount on the yield of 2, 3, 5- trimethyl-1, 4 benzoquinone; 2,3,6-trimethylphenol: 1.200 g,  $H_2O_2$ =20 mL, HCl=5 mL,  $C_2H_4Cl_2/H_2O$ =50 mL/20 mL, 1000 rpm, 60 °C (Note: blank denotes no catalyst and HCl participating in the reaction).

#### C. Effect of the Amount of HCl

Fig. 3 shows the effect of HCl on the yield of *TMBQ* in the presence of 0.400 g of  $CuFe_2O_4$  catalyst. The yield of *TMBQ* is relatively low when no HCl is added, although the expression of the kinetic model shown in the Equation (R3~R4) does not suggest that HCl affects the yield or the reaction rate. However, we believe HCl affects the environment of the reaction. The distribution of the active intermediate (*TMHQ*) in the organic phase is highly influenced by the concentration of HCl. Therefore, the reactivity of the active intermediate (*TMHQ*) is affected by the amount of HCl in the aqueous solution. Fig. 3 shows that both the conversion and the reaction rate increase when increasing the amount of HCl up to 10.0 mL. The effect of the amount of HCl on the apparent rate constant ( $k_{app,2}$ ) is also shown in Table I. The experimental follows a pseudo-first order rate law.

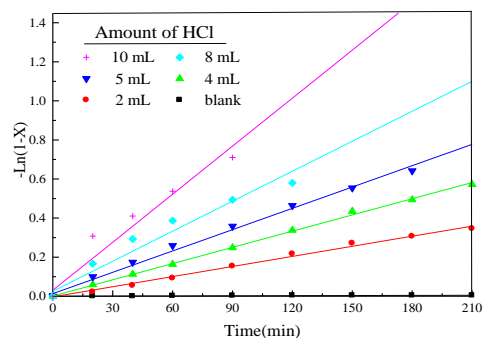


Fig. 3. Effect of the amount of HCl on the yield of 2, 3, 5- trimethyl-1, 4 benzoquinone; 2, 3, 6-trimethylphenol: 1.200 g,  $\text{H}_2\text{O}_2=20$  mL,  $\text{CuFe}_2\text{O}_4=0.400\text{g}$ ,  $\text{C}_2\text{H}_4\text{Cl}_2/\text{H}_2\text{O}=50$  mL/20 mL, 1000 rpm,  $60^\circ\text{C}$ .

#### D. Effect of the Volume of Water

In general, the volume of water directly affects the concentration of HCl in the aqueous phase and the distribution of *TMHQ* between two phases. Therefore, the conversion (or the reaction rate) should be affected by the volume of water. Fig. 4 and Table I represent kinetic curves and first-order plots of the effect of the amount of water on the yield of *TMBQ*. In principle, the yield of *TMBQ* is decreased when the volume of water is increased. The generally accepted reason for this is that the moles or the concentration of *TMHQ* in the organic phase are almost constant when the amount of  $\text{H}_2\text{O}$  is fixed at a certain quantity with an excessive amount of  $\text{H}_2\text{O}_2$ . Therefore, the yield of *TMBQ* is decreased with the increase in the volume of water.

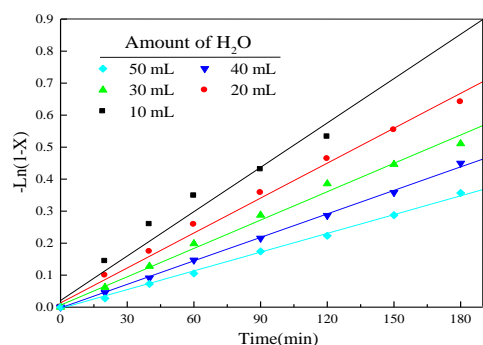


Fig. 4. Effect of the volume of water on the yield of 2, 3, 5- trimethyl-1, 4 benzoquinone; 2, 3, 6-trimethylphenol: 1.200 g,  $\text{H}_2\text{O}_2=20$  mL,  $\text{CuFe}_2\text{O}_4=0.400\text{g}$ ,  $\text{HCl}=5$  mL,  $\text{C}_2\text{H}_4\text{Cl}_2=50$  mL, 1000 rpm,  $60^\circ\text{C}$ .

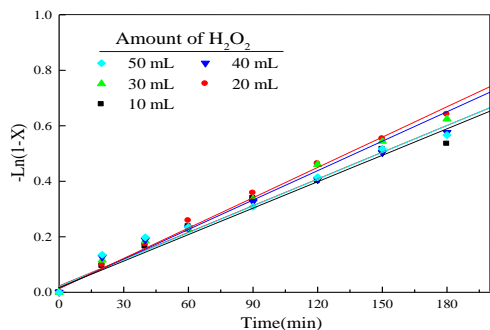


Fig. 5. Effect of the amount of  $\text{H}_2\text{O}_2$  on the yield of 2, 3, 5- trimethyl-1, 4 benzoquinone; 2, 3, 6-trimethylphenol: 1.200 g,  $\text{CuFe}_2\text{O}_4=0.400\text{g}$ ,  $\text{HCl}=5$  mL,  $\text{C}_2\text{H}_4\text{Cl}_2/\text{H}_2\text{O}=50$  mL/20 mL, 1000 rpm,  $60^\circ\text{C}$ .

#### E. Effect of the Amount of $\text{H}_2\text{O}_2$

The effect of the amount of  $\text{H}_2\text{O}_2$  on the yield of *TMBQ* is shown in Fig. 5. It can be seen that the conversion of *TMBQ* (or the reaction rate) is not affected by the amount of  $\text{H}_2\text{O}_2$ .

The amount of  $\text{H}_2\text{O}_2$  used is excessive. In this work, TMP, which is an organic soluble compound, is used in a limited quantity relative to the quantity of  $\text{H}_2\text{O}_2$ . The effect of the amount of  $\text{H}_2\text{O}_2$  on the apparent rate constant ( $k_{app,2}$ ) are shown in Table I.

#### F. Effect of Temperature

The effect of temperature on the yield of *TMBQ* for the reaction being carried out in 1, 2-dichloroethane is shown in Fig. 6. The increase in temperature enhances the reaction rate and the yield of *TMBQ*. The reaction also follows the pseudo-first order rate law. The effect of temperature on the apparent rate constant ( $k_{app,2}$ ) are listed in Table I. An Arrhenius plot for  $-\ln(k_{app,2})$  vs.  $1/T$  is shown in Fig. 7. The activation energy is  $73.29$  kJ/mol for  $\text{C}_2\text{H}_4\text{Cl}_2$ .

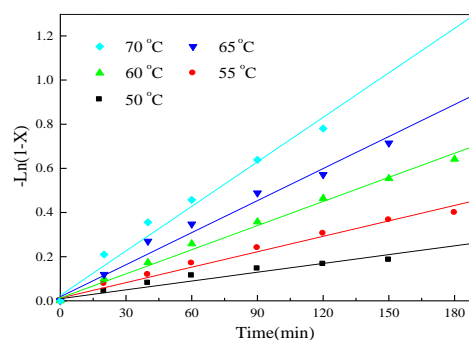


Fig. 6. Effect of temperature on the yield of 2, 3, 5- trimethyl-1, 4 benzoquinone; 2, 3, 6-trimethylphenol: 1.200 g,  $\text{H}_2\text{O}_2=20$  mL,  $\text{CuFe}_2\text{O}_4=0.400\text{g}$ ,  $\text{HCl}=5$  mL,  $\text{C}_2\text{H}_4\text{Cl}_2/\text{H}_2\text{O}=50$  mL/20 mL, 1000 rpm.

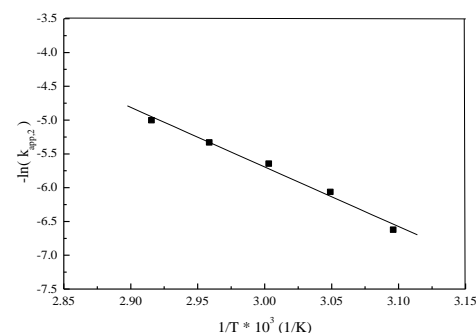


Fig. 7. A Plot of the Arrhenius equation for the reaction in various temperature with the same reaction conditions as given in Fig. 6.

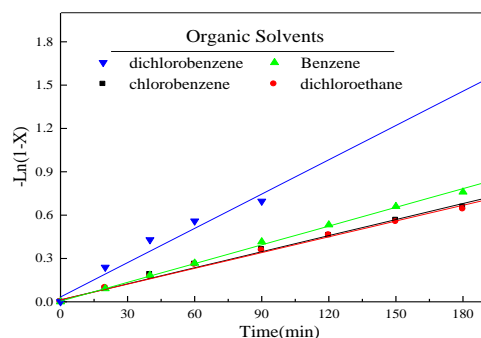


Fig. 8. Effect of the organic solvents on the yield of 2, 3, 5- trimethyl-1, 4 benzoquinone; 2, 3, 6-trimethylphenol: 1.200 g,  $\text{H}_2\text{O}_2=20$  mL,  $\text{CuFe}_2\text{O}_4=0.400\text{g}$ ,  $\text{HCl}=5$  mL, Solvents/ $\text{H}_2\text{O}=50$  mL/20 mL, 1000 rpm,  $60^\circ\text{C}$ .

#### G. Effect of the Organic Solvents

This study examine the influences of four organic solvents, including 1, 2-dichlorobenzene, benzene, chlorobenzene and 1, 2-dichloroethane, on the oxidation of *TMP*, with the results

shown in Fig. 8. The order of reactivity for these four organic solvents is:  $C_6H_4Cl_2$  (9.93) >  $C_6H_6$  (2.27) >  $C_6H_5Cl$  (5.62) >  $C_2H_4Cl_2$  (10.37). The yield of TMBQ is not affected by the dielectric constant of the organic solvent. The effect of the organic solvents on the apparent rate constant ( $k_{app,2}$ ) are listed in Table I.

TABLE I: EFFECTS OF THE REACTION CONDITIONS ON THE APPARENT RATE CONSTANTS  $K_{APP,2}$ ,  $MIN^{-1}$ ; 2, 3, 6-TRIMETHYLPHENOL: 1.200 G,  $H_2O_2=20$  ML,  $HCl=5$  ML,  $C_2H_4Cl_2/H_2O=50$  ML/20 ML, 800 RPM, 60 °C

Stirring speed, rpm	0	100	200	400	600	800	1000
$k_{app,2} \times 10^3$	$8.77 \times 10^{-2}$	1.57	1.79	2.54	3.07	3.64	3.69
CuFe <sub>2</sub> O <sub>4</sub> , g	blank	0	0.201	0.301	0.402	0.601	
$k_{app,2} \times 10^3$	$2.30 \times 10^{-2}$	1.84	2.00	2.79	3.64	4.61	
Amount of HCl, mL	blank	2	4	5	8	10	
$k_{app,2} \times 10^3$	$2.30 \times 10^{-2}$	1.72	2.77	3.64	5.10	8.24	
Volume of H <sub>2</sub> O, mL	10	20	30	40	50		
$k_{app,2} \times 10^3$	4.62	3.64	2.95	2.45	1.95		
Amount of H <sub>2</sub> O <sub>2</sub> , mL	10	20	30	40	50		
$k_{app,2} \times 10^3$	3.31	3.64	3.68	3.62	3.53		
Temperature, °C	50	55	60	65	70		
$k_{app,2} \times 10^3$	1.33	2.33	3.54	4.84	6.72		
Organic solvent	$C_6H_4Cl_2$	$C_6H_6$	$C_6H_5Cl$	$C_2H_4Cl_2$			
$k_{app,2} \times 10^3$	7.91	4.33	3.71	3.64			

#### IV. CONCLUSIONS

This study will perform oxidation reaction of 2, 3, 6-trimethylphenol by hydrogen peroxide in acidic solution. The sequential reaction of oxidations of *TMP* by a  $H_2O_2$  under copper ferrite catalysis was carried out in an acid solution of HCl/organic solvent with a two phase medium. Copper ferrites were employed as the catalysts to promote the reactions. Recovery of the catalyst was facily achieved by simple magnetic decantation in a green chemistry process. This goal was achieved using an excessive amount of  $H_2O_2$  reagent relative to the amount of *TMP* and a high acid concentration of HCl.

The effects of the reaction conditions, including various agitation speeds, the amount of CuFe<sub>2</sub>O<sub>4</sub> powder catalyst, the amount of HCl, the volume of water, the amount of hydrogen peroxide, organic solvents and the temperature, on the yields of *TMBQ* oxidation were examined in detail. A rational reaction mechanism is proposed to satisfactorily explain the experimental results. By plotting the experimental data  $-\ln(1-X)$  vs.  $t$ , we obtain a straight line with the slope of the apparent rate constant ( $k_{app,2}$ ). The kinetic behaviors and the characteristics of the reaction are sufficiently described by the pseudo-first-order rate law, and the apparent rate constant ( $k_{app,2}$ ) is also investigated in detail.

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**Yenchun Liu** received his Ph.D. degree in chemical engineering from the Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan. He is an associate professor of the Graduate School of Opto-Mechatronics and Materials at WuFeng University, Taiwan. His research interests include energy and sustainable development, green technology, lithium ion batteries materials, nanoscience & nanotechnology and chemical

engineer.



**Maochieh Chi** received his Ph.D. and M.D. degrees in civil engineering from the Department of Harbour and River Engineering, National Taiwan Ocean University, Keelung, Taiwan. He is an associate professor of the Department of Fire Science at WuFeng University, Taiwan. He is an active researcher and instructor on topics including physical and mechanical properties, microstructure and durability of concrete, high performance concrete,

environmentalism-conscious design, and green concrete.



**Chaoming Lin** received the M.S. degree and Ph.D. degree from the National Cheng Kung University, Taiwan, in 1993 and 1999, both in mechanical engineering. He has some publications in the areas of electronic packaging and polymer processing. He is currently with the Chiayi University, Taiwan, as an associate professor with research interests in IC packaging, injection molding, electrically conductive adhesive/films, and polymer packaging composites.