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Study on the catalytic degradation of sodium lignosulfonate to aromatic aldehydes over nano-CuO: Process optimization and reaction kinetics

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ABSTRACT

As one of the few renewable aromatic resources, the research of depolymerization of lignin into high-value chemicals has attracted extensive attention in recent years. Catalytic wet aerobic oxidation (CWAO) is an effective technology to convert lignin like sodium lignosulfonate (SL), a lignin derivative, into aromatic aldehydes such as vanillin and syringaldehyde. However, how to improve the yield of aromatic aldehyde and conversion efficiency is still a challenge, and many operating conditions that significantly affect the yield of these aromatic compounds have rarely been investigated systematically. In this work, we adopted the stirred tank reactor (STR) for the CWAO process with nano-CuO as catalyst to achieve the conversion of SL into vanillin and syringaldehyde. The effect of operating conditions including reaction time, oxygen partial pressure, reaction temperature, SL concentration, rotational speed, catalyst amount, and NaOH concentration on the yield of single phenolic compound was systematically investigated. The results revealed that all these operating conditions exhibit a significant effect on the aromatic aldehyde yield. Therefore, they should be regulated in an optimal value to obtain high yield of these aldehydes. More importantly, the reaction kinetics of the lignin oxidation was explored. This work could provide basic data for the optimization and design of industrial operation of lignin oxidation.

1. Introduction

Since the energy shortage and environmental pollution caused by the excessive use of fossil resources threaten the survival and development of human beings, more and more attention has been paid to the development and utilization of renewable biological resources such as lignin, which is the third plentiful organic substance in nature, accounting for 15%–30% of plant mass [1]. It can directly produce fine aromatic chemicals and is considered as an ideal substitute for fossil resources to produce chemical raw materials [2,3]. The degradation of lignin into high value-added aromatic chemicals can be used as pharmaceutical intermediates [4]. However, most lignin such as SL, an inexpensive and plentiful byproduct from papermaking, mostly discharged into rivers or directly burned out due to lacking economical and efficient technique [5]. Therefore, in order to reduce environmental pollution and realize the high-value utilization of lignin, the efficient conversion of lignin into aromatic aldehydes like vanillin and syringaldehyde has become one of the research hotspots.

To date, many technologies have been reported for the conversion of lignin into aromatic compounds, such as pyrolysis, gasification, hydrogenolysis, chemical oxidation and hydrolysis [6]. In these processes, CWAO using oxygen and homogeneous and heterogeneous catalysts to improve the yield of aldehydes, which has been proved to be a conventional and effective method. Pinto *et al.* [7] used lignin isolated from kraft liquor as the raw material for oxidation, reaching to 28 kg of syringaldehyde and 12 kg of vanillin per ton of lignin, with advantage also for selectivity reported as aldehyde/acid ratio.

According to the presence of the catalyst in the system, the catalyst used for the wet oxidation and degradation of lignin can be divided into homogeneous oxidation catalyst and heterogeneous oxidation catalyst [8,9]. Homogeneous catalysts of nonnoble metals such as Cu, Co, Mn, Fe and so on, have been widely explored in the past [10-12]. However, the main shortcomings are that it is difficult to recycle and reuse, and it is easy to cause secondary pollution. Heterogeneous catalysts have the characteristics of easy separation and reusability, and have become a research hotspot

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today. Sales *et al.* [13] evaluated the oxidation of lignin into aldehydes over Pd/γ-Al_2O_3 prepared in a batch slurry reactor, and indicated that Pd has high catalytic activity in the CWAO of lignin. Nevertheless, the price of noble metals restricts their industrial utilization. Villar *et al.* [14] estimated the catalytic performance of CuO and CoO, and the result showed that higher aldehyde yield can be obtained by CuO. The appearance of nano-catalysts has brought unprecedented opportunities for improving the application of CWAO in lignin degradation due to their excellent catalytic behaviors and relatively easy reuse [15]. Mate *et al.* [16] prepared nano Co_3O_4 catalyst by co-precipitation method, and the result suggested that this efficient catalyst could convert vanillyl alcohol into aldehyde with a selectivity of 81%. The research on the selective oxidation of lignin and its substructure compounds to aromatic aldehydes by nano-catalysts in the presence of alkaline medium is in the exploratory stage.

Study of reaction kinetics is a fundamental work for reaction process optimization and industrialization amplification, which is the core of gas–liquid reaction research. Guan *et al.* [17] prepared TiO_2, SiO_2, Al_2O_3 and Nb_2O_5-Al_2O_3 supported Pt catalysts by urea precipitation method, which were used for the catalytic hydrodeoxygenation of lignin model compounds, and studied their kinetics. Dong *et al.* [18] reported a new multifunctional catalyst Ru/$NbOPO_4$, which achieved the first example of catalytic cleavage of both interunit C—C and C—O bonds in one-pot lignin conversions with yield of 124%–153% of monocyclic hydrocarbons. Fargues *et al.* [19,20] described a kinetic model for kraft lignin oxidation in a temperature range of 383–423 K and pH > 12, $r_c=k_{NC}[O_2]^{1.75}[L]-k_{Cl}[O_2][C]$. Nonetheless, there are few studies on the kinetics of catalytic oxidation of SL [13,21].

At present, the breakthrough of catalytic oxidation of lignin is mainly based on catalysts and catalytic processes. The selection of catalysts is as important as the determination of catalytic process. Therefore, in this experiment, the catalytic degradation of SL to aromatic aldehydes over nano-CuO was studied comprehensively and systematically. It is worth highlighting that the kinetics of lignin oxidation catalyzed by nano-CuO was studied.

2. Materials and Methods

2.1. Characterization of raw materials

For the quantitative analysis of the yield of aromatic aldehydes, the content of lignin Klason in SL was determined in accordance with the TAPPI test method T 222 OM-11 [22].

The alkaline nitrobenzene oxidation of SL could be used to investigate the structural properties of its benzene ring, which was performed in a 500 ml stirred tank reactor. A 13.5 ml of nitrobenzene as an oxidant and 0.9 g of SL were dissolved in 210 ml of 2 mol·L^{-1} NaOH solution [23]. Then, the alkaline nitrobenzene oxidation reaction was carried out at 443 K for 4 h. The reaction mixture was subsequently acidized with 20% (mass) sulfuric acid solution to pH 2−3, followed by extraction with mixed alcohols ($V_{n\text{-butanol}}$:$V_{\text{isopropanol}}$ = 7:3) until the organic phase became colorless. Aromatic products were obtained by evaporation of combined extracts using a rotavapor, and analyzed by high performance liquid chromatography (HPLC) after dilution. HPLC was equipped with a 15 cm C18 column and a 280 nm PDA detector. The separation was conducted at 308 K using an elution gradient composed of three eluents with a flow rate of 0.8 ml·min^{-1} [24].

The yield of aromatic products can be calculated according to the content of Klason lignin in SL. The calculation method is as follows:

$$\omega = \frac{m_{\text{mono}}}{m_{\text{lignin}}} \times 100\%$$

where m_{lignin} and m_{mono} are the mass of lignin added before degradation and aromatic compounds produced, respectively.

The content of phenolic hydroxyl groups and carboxylic acid groups affected the physicochemical properties of lignin and could be quantified by potentiometric titration [25].

A 10 g·L^{-1} *p*-hydroxybenzoic acid as the internal standard solution was mixed with 1 mol·L^{-1}potassium hydroxide solution. A 5 ml of the prepared solution was kept as a blank test, and another 5 ml was used to dissolve 0.03 g of SL. Then they were titrated using 0.3 mol·L^{-1} hydrochloric acid standard solution.

The content of the phenolic hydroxyl group and carboxylic acid group were calculated according Eq. (1) and Eq. (2), respectively.

$$c_1 = \frac{[(V_2 - V_1) - (V_{02} - V_{01})]c_{\text{HCl}}}{m} \quad (1)$$

$$c_2 = \frac{[(V_3 - V_2) - (V_{03} - V_{02})]c_{\text{HCl}}}{m} \quad (2)$$

where c_1 and c_2 represent the content of phenolic hydroxyl group and carboxylic acid group, respectively, mol·g^{-1}; c_{HCl} is the concentration of hydrochloric acid standard solution, mol·L^{-1}; m is the mass of SL, g; V_{01}, V_{02}, and V_{03} are the titrant volume corresponding to the 3 titration endpoints when the internal standard solution is titrated, and represent the phenolic hydroxyl peak, the carboxylic acid group peak and the potassium hydroxide peak, respectively, L; V_1, V_2, and V_3 are the volume of titrant corresponding to the three titration endpoints of SL titration, L.

The mass percentage of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in lignin was determined by a Vario EL cube Elemental Analyzer. The oxygen content was calculated from the content of the above four elements.

2.2. Experimental

2.2.1. Preparation of catalyst

Nano-CuO was prepared by precipitation method. First, Cu$(NO_3)_2$ solution was prepared by dissolving a certain amount of Cu$(NO_3)_2{\cdot}3H_2O$ into deionized water, which was heated to 373 K under mechanical stirring. Then solid NaOH particles were rapidly added into the boiling Cu$(NO_3)_2$ solution until the pH reached 12.5. After stirring for 1 h, the obtained precipitate was separated by centrifugation, following by the treatment of washing with deionized water and absolute ethanol for 3–5 times, respectively, drying in vacuum at 333 K for 3 h, and calcining in muffle furnace at 623 K for 4 h to obtain nano-CuO powder. Next, the acidified CuO was prepared by immersing in 0.02 mol·L^{-1} dilute sulfuric acid for 24 h, following by centrifugation and washing with deionized water and dried in a vacuum drying oven at 333 K for 3 h.

Fig. 1 shows the TEM image of the prepared nano-CuO. It was indicated that the prepared nano-CuO particles are short rod-shaped particles with a width of 6–13 nm and a length of 17–40 nm.

2.2.2. The catalytic oxidation of sodium lignosulfonate

The catalytic oxidation process of SL to aromatic aldehyde by nano-CuO was carried out in STR. The operating processes are as follows: 1) Add a certain amount of SL and catalyst into 2 mol·L^{-1} NaOH solution, and then put the mixed solution into STR. 2) Air is pumped into the reactor and react with SL at a certain oxygen pressure. 3) Heating the reaction system, then opening the stirring of STR. After these processes, the sample was token and analyzed every 10 min. In this research, the effect of various operating conditions including reaction time, partial pressure of oxygen, reaction temperature, SL concentration, rotational speed, catalyst amount, and NaOH concentration on the yield of single phenolic compound was investigated systematically.

Lignin oxidation reactions were carried out in a 500 ml batch stirred autoclave equipped with a "K" thermocouple and a digital pressure gauge. Nano-CuO catalyst and 300 ml SL alkaline solution were charged into the reactor at 298 K, and then the electric heating-up program started to reach the reaction temperature. Samples were collected at regular time intervals and stored at 277 K, and then the above analysis was performed.

3. Results and Discussion

3.1. Characterization of lignin

The content of Klason lignin in SL was 89%. Lignin is an amorphous polymer polymerized by three propane structural units of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), and their respective oxidation products are *p*-hydroxybenzaldehyde, vanillin and syringaldehyde via the catalytic degradation process [26], as shown in Fig. 2. In addition, the degradation products of lignin also contain vanillic acid, syringic acid, acetovanillone and acetosyringone, and the chemical structure of which are shown in Fig. 3.

The total yield of phenolic products from Klason lignin through alkaline nitrobenzene oxidation is 14.72% which can be calculated from the data in Table 1.

Noteworthy, the formation of vanillin and syringaldehyde relates to the content of the structural unit in the lignin. Therefore, the ratio of the three structural units H, G and S in SL can be deduced according to the molar ratio of aldehydes. The specific proportion of H, G and S monomers correlates to a certain type of lignin. The experiment showed that the ratio of the three structural units H: G: S in SL is 1: 24: 54, revealing that the experimental material is broad-leaved lignin (G-S type) [27]. Per unit mass (g) of SL contained 0.226 mmol G-lignin and 0.495 mmol S-lignin. The content of methoxy group was calculated by the content of G and S units with a value of 1.26 $mmol \cdot g^{-1}$. The content of phenolic hydroxyl group determined by aqueous phase potentiometric titration is 1.13 $mmol \cdot g^{-1}$. The results of element analysis are shown in Table 2.

The content of methoxy, phenolic hydroxyl, and organic elements are used to determine the structure of C_9 of SL formula, and the formula of lignin is determined to be $C_9H_{11.6}O_{5.72}(OHph)_{0.29}(OCH_3)_{0.33}(SO_3H)_{0.38}$.

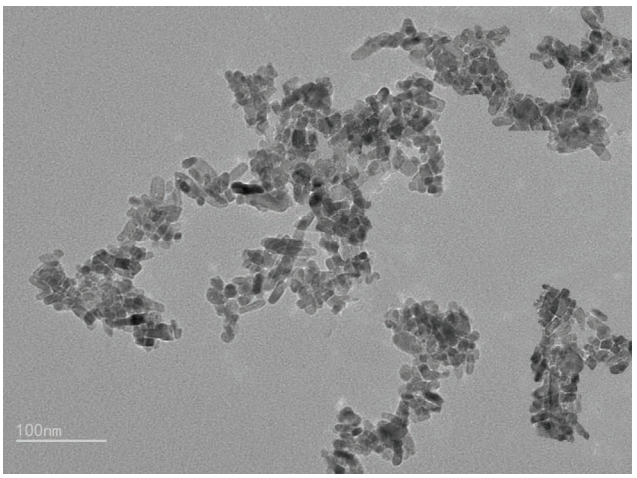

Fig. 1. TEM image of nano-CuO.

3.2. Optimization of lignin oxidation process conditions

3.2.1. Effect of reaction time

As shown in Fig. 4, with the increase of reaction time, the concentration of the major aromatic compound first increased and then decreased. The concentration of syringaldehyde reached the maximum value of 8.24 $mmol \cdot L^{-1}$ in about 30 min, and the concentration of vanillin reached the maximum value of 4.48 $mmol \cdot L^{-1}$ at 50 min. The maximum concentration of syringaldehyde occurred earlier than vanillin, because syringaldehyde has more methoxy groups in benzene ring than vanillin, it is more easily oxidized. The aromatic aldehyde can be further oxidized to aromatic acid, water and carbon dioxide, causing the reduction of aromatic aldehyde concentration. The formation of by-products acetovanillone and acetosyringone proved the mechanism proposed by Tarabanko [28,29], which affects the selectivity of the SL oxidation. These results indicated that, in order to obtain high yield of aromatic aldehyde, it is necessary to control the reaction time to prevent the further oxidation of SL.

3.2.2. Effect of oxygen partial pressure

Fig. 5 shows the effect of the oxygen partial pressure on the yield of aromatic compounds. Generally, in order to maintain the liquid phase of the reactants at high temperature, the reaction pressure needs to be controlled within a certain range. Increasing oxygen partial pressure can improve the driving force of oxygen absorption, and increase the oxygen content in the liquid phase, which raised the contact probability between oxygen and CuO. As a consequence, the reaction rate can be improved through accelerating the cycle of $Cu^{2+}/Cu^{\pm}$ [30]. Because the number of methoxy groups on the benzene ring of syringaldehyde is larger, syringaldehyde is more likely to be oxidized, and the increase of oxygen partial pressure has a more significant effect on syringaldehyde. When the oxygen partial pressure is greater than 0.4 MPa, the concentration of aromatic aldehydes decreased, so the oxygen partial pressure should be kept within an appropriate range, 0.4 MPa is reasonable.

3.2.3. Effect of reaction temperature

Fig. 6 shows the yield of aromatic compounds are unambiguously influenced by the reaction temperature. Lignin oxidation belongs to exothermic reaction. When the temperature is below 403 K, the reaction system only contains few activation reactant molecules, giving rise to a low oxidation rate. The concentration of aromatic aldehydes improved quickly as temperature increases from 403 K to 413 K, because higher temperature can induce more activation reactant molecules per time in solution. When the temperature is higher than 423 K, the concentration of the aldehydes decreased due to the formation of the corresponding acid which reduced the selectivity of aromatic aldehyde. Therefore, the yield of aromatic aldehydes can be adjusted by changing the reaction temperature, and the suitable reaction temperature should be approximately 423 K under the experimental conditions.

3.2.4. Effect of SL concentration

Fig. 7 reveals the effect of SL concentration on the content of the aromatic compounds. The results showed that the concentration of aromatic aldehydes increased first and then decreased with the increase of SL concentration. A higher SL concentration can facilitate the conversion of SL into the aldehydes, producing more vanillin and syringaldehyde. However, further increase the SL concentration can improve the viscosity of reactants which suppressed the mass transfer between gas and liquid, and ultimately reduced the reaction rate. The optimal SL concentration is around 50 $g \cdot L^{-1}$ at which the concentration of vanillin and syringaldehyde are 5.48 $mmol \cdot L^{-1}$ (corresponding to 48.5% (mass) of G-lignin) and

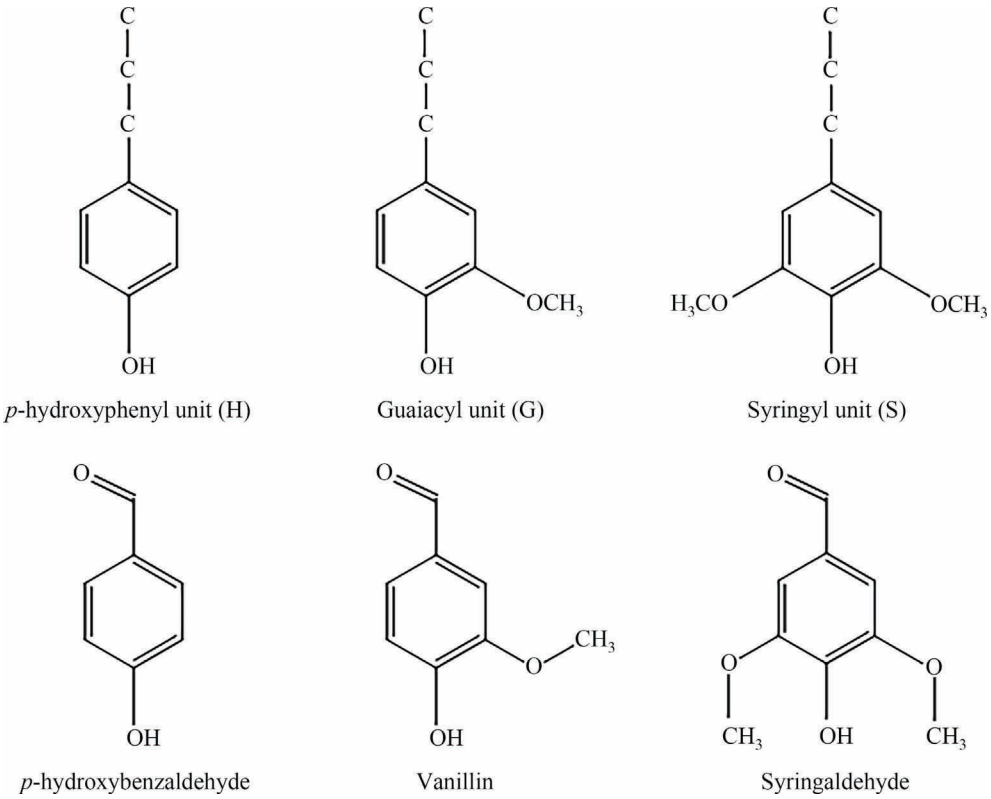

Fig. 2. The chemical structures of the lignin units and their respective oxidation products.

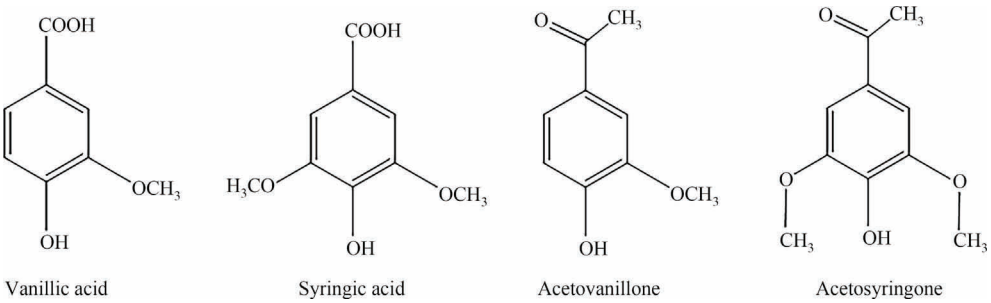

Fig. 3. Chemical structures of other products of lignin oxidation.

Table 1
Percentage of phenolic products

Products	Concentration/mmol·L^{-1}	Yield (Klason lignin)/%
hydroxybenzaldehyde	0.04	0.15
vanillic acid	0.02	0.07
syringic acid	0.25	1.29
vanillin	0.96	3.82
syringaldehyde	1.97	9.39

Table 2
Content of organic elements in SL

Elements	Content/% (mass)
C	43.52
H	5.16
O	46.55
S	4.96
N	0.08

10.90 mmol·L^{-1} (corresponding to 42.2% (mass) of S-lignin), respectively.

3.2.5. Effect of rotational speed

In order to study and optimize the reaction conditions as well as provide guidance for the design of reactor, it is necessary to explore the rate-controlling step of lignin catalytic oxidation over nano-CuO. Fig. 8 demonstrates that the rotational speed significantly impact the yield of aromatic compounds. As exhibited in Fig. 8,

Table 3
Motor power at different rotational speeds in a STR

N/r·min^{-1}	P/W
600	18.85
700	21.99
800	25.13
900	28.27
1000	31.41

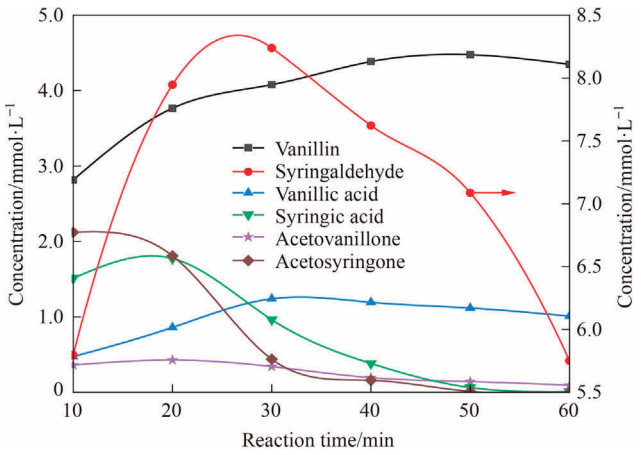

Fig. 4. Effect of reaction time on the concentration of aromatic compounds. (Reaction conditions: P_O = 0.4 MPa, T = 413 K, c_0(SL) = 40 g·L^{-1}, c(cat) = 2.0 g·L^{-1}, c(NaOH) = 2.0 mol·L^{-1}, N = 800 r·min^{-1}).

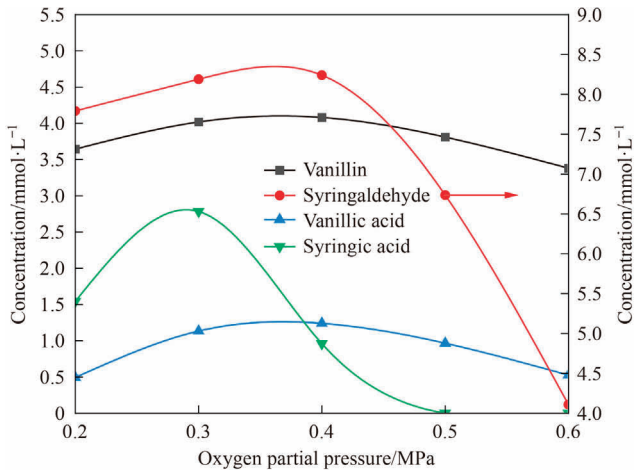

Fig. 5. Effect of oxygen partial pressure on the concentration of aromatic compounds. (Reaction conditions: T = 413 K, c_0(SL) = 40 g·L^{-1}, c(cat) = 2.0 g·L^{-1}, t = 30 min, c(NaOH) = 2.0 mol·L^{-1}, N = 800 r·min^{-1}).

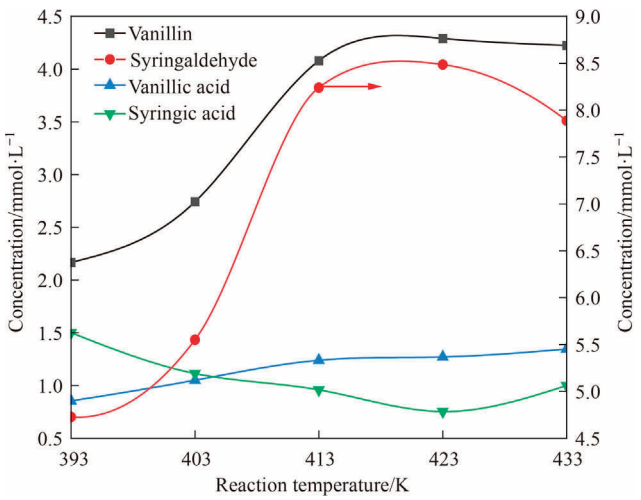

Fig. 6. Effect of reaction temperature on the concentration of aromatic compounds. (Reaction conditions: P_O = 0.4 MPa, c_0(SL) = 40 g·L^{-1}, c(cat) = 2.0 g·L^{-1}, t = 30 min, c(NaOH) = 2.0 mol·L^{-1}, N = 800 r·min^{-1}).

the yield of aromatic aldehydes increased significantly with the increase of rotational speed when the speed is lower than 800 r·min^{-1}. When the rotational speed is greater than 800 r·min^{-1}, as the rotational speed increased, the excessive oxidation of lignin is intensified and the yield of aromatic aldehydes decreased. The oxidation of lignin is an exothermic reaction. At lower speeds, the mixing effect of the batch reactor is unfavorable, the heat generated during the reaction cannot be removed in time, and the reaction solution is prone to local hot spots, which aggravated the occurrence of side reactions. Increasing the rotational speed strengthens the mixing capacity of the reactor and avoids the oxidation of aromatic aldehydes caused by local overheating of the reaction solution. At the same time, strengthen the stirring can enhance the dispersion effect of the nano-catalyst, finally improving the catalytic activity and the selectivity of aromatic aldehydes. Therefore, 800 r·min^{-1} is the optimal speed, and it can be seen from Table 3 that the corresponding motor power is about 25.13 W (Table 3).

3.2.6. Effect of catalyst amount

Generally, the catalyst can lower the activation energy of the reaction, thus promote the reaction rate. Fig. 9 shows that nano-CuO can greatly promote the production of the aromatic aldehydes, and the concentration of the aromatic aldehydes increased with the increase of the catalyst amount. When the amount of catalyst is 2.5 g·L^{-1}, the vanillin concentration is 5.48 mmol·L^{-1}, 1.4 times as much as without catalyst (3.91 mmol·L^{-1}); the concentration of syringaldehyde is 10.90 mmol·L^{-1}, which is 1.8 times of that without catalyst (6.07 mmol·L^{-1}). Therefore, the catalyst amount should be adjusted in an optimal range considering the yield of aromatic aldehyde and the cost of catalyst. Here, 2.5 g·L^{-1} was selected for the optimal catalyst concentration.

3.2.7. Effect of NaOH concentration

Fig. 10 shows that with the increase of NaOH concentration, the concentration of vanillin slightly increased, while the concentration of syringaldehyde considerably increased first and then decreased. It has been reported in the literature that alkali is essential for lignin oxidation. In an alkaline medium, the alcoholic hydroxyl group (–OH) on the α-carbon atom of the side chain of SL are eliminated via dehydration to form a phenolic group anion activated substrate, which enables the subsequent oxidation reactions occurring. Phenolate, generated from ArOH and NaOH, protects ArOH from hydroxylation of the aromatic ring, which is

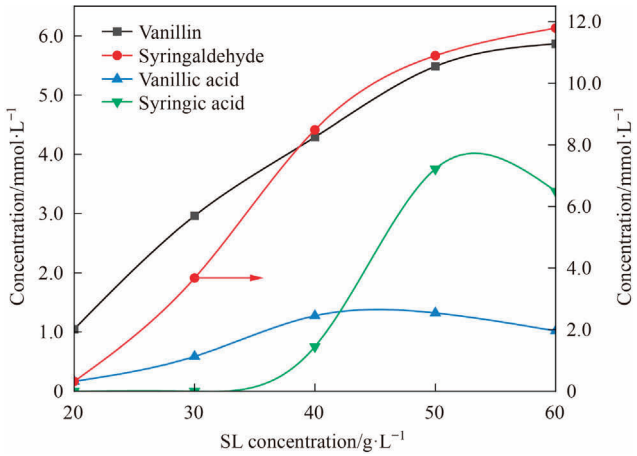

Fig. 7. Effect of SL concentration on the concentration of aromatic compounds. (Reaction conditions: P_O = 0.4 MPa, T = 423 K, c(cat) = 5%, c_0(SL) g·L^{-1}, t = 30 min, c(NaOH) = 2.0 mol·L^{-1}, N = 800 r·min^{-1}).

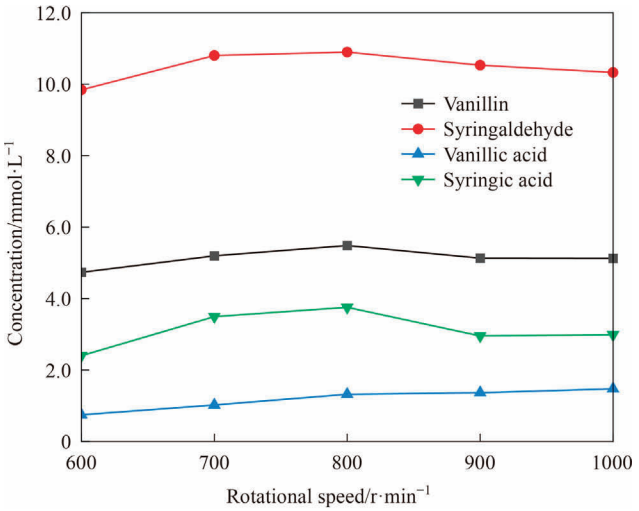

Fig. 8. Effect of rotational speed on the concentration of aromatic compounds. (Reaction conditions: P_O = 0.4 MPa, T = 423 K, c_0(SL) = 50 g·L^{-1}, c(cat) = 2.5 g·L^{-1}, t = 30 min, c(NaOH) = 2.0 mol·L^{-1}).

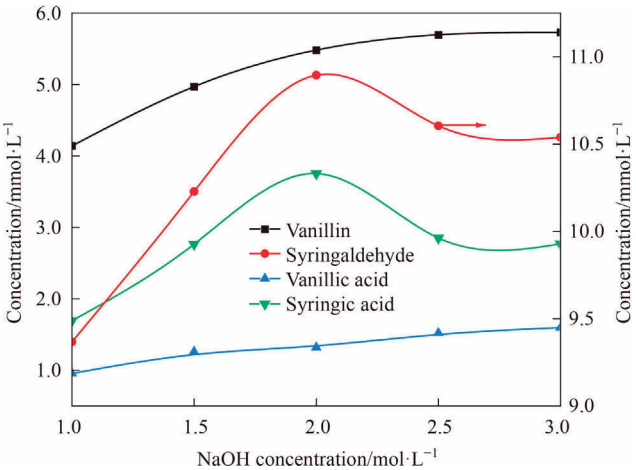

Fig. 10. Effect of NaOH concentration on the concentration of aromatic compounds. (Reaction conditions: P_O = 0.4 MPa, T = 423 K, c_0 (SL) = 50 g·L^{-1}, t = 30 min, c (cat) = 2.5 g·L^{-1}, N = 800 r·min^{-1}).

beneficial to obtain aromatic aldehyde products [31,32]. When the concentration of NaOH solution is greater than 2.0 mol·L^{-1}, syringaldehyde is further oxidized and the concentration decreased. It can be seen that alkali cannot inhibit the deep oxidation of aldehyde. Although the addition of alkali can increase the reaction rate, it derives numerous acid water and inorganic salts, which is not conducive to the separation of oxidation products. Furthermore, in a high alkali solution, the corrosion of the equipment probably occurs. Thus, the optimal concentration of NaOH is 2.0 mol·L^{-1}. When the concentration of NaOH solution is 2.0 mol·L^{-1}, the concentration of vanillin and syringaldehyde are 5.51 mmol·L^{-1} and 10.91 mmol·L^{-1}, respectively.

3.3. Oxidation kinetics of SL catalyzed by nano-CuO

The CWAO of lignin is a complex gas–liquid reaction in which the conversion of the lignin and selectivity of the target products are difficult to reach 100% at the same time. The substrate being incompletely reacted and the generation of by-products of the reaction are common problems in industrial production. At present, many researchers have been carried out a lot of research on the oxidation process of lignin, and speculated the reaction mechanism. However, due to the complex structure and diverse products of lignin, it is not easy to explore the reaction mechanism, and the reaction kinetics is rarely reported. This section focuses on the reaction kinetics of the oxidation of SL catalyzed by nano-CuO. The HPLC was employed to detect the concentration of small molecule phenolic products during the oxidation reaction. The kinetic model of catalytic oxidation was established by the variation of the concentration of phenolic products with time under different conditions.

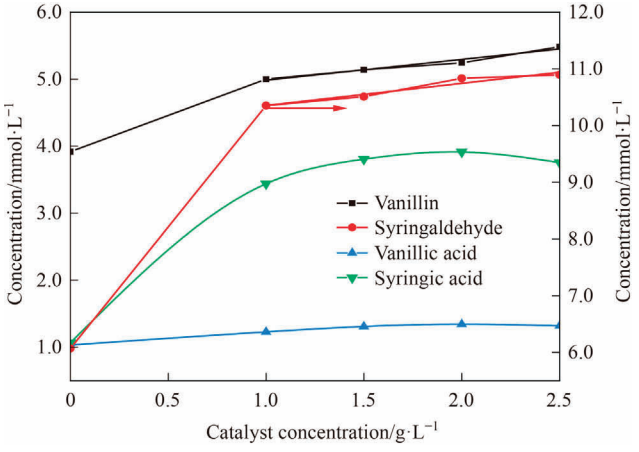

Fig. 9. Effect of catalyst concentration on the concentration of aromatic compounds. (Reaction conditions: P_O = 0.4 MPa, T = 423 K, c_0(SL) = 50 g·L^{-1}, t = 30 min, c (NaOH) = 2.0 mol·L^{-1}, N = 800 r·min^{-1}).

3.3.1. Establishment of kinetic model

It has been reported that the lignin oxidation reaction can be represented by second-order kinetics [12,16,33]. During the SL oxidation process, the SL degrade into small molecular substances which can condense into SL conversely, of which the former reaction rate is much greater than the latter evidenced by the experimental results. The oxidation kinetics of G-lignin and vanillin was studied, and the reaction ignored the generation of acetovanillone and CO_2. The main reaction equations can be simplified as:

$$G + O_2 \xrightarrow{k_1} V$$

$$V + O_2 \xrightarrow{k_2} VA$$

where G is G-lignin; V is vanillin; VA is vanillic acid; k_1 is G-lignin reaction rate constant; k_2 is Vanillin reaction rate constant. The reaction rate expressions can be written as:

$$-\frac{dC_G}{dt} = k_1 C_G P_O \tag{3}$$

$$\frac{dC_V}{dt} = k_1 C_G P_O - k_2 C_V P_O \tag{4}$$

$$\frac{dC_{VA}}{dt} = k_2 C_V P_O \tag{5}$$

where P_O is oxygen partial pressure; C_G, C_V, C_{VA} are the concentrations of G-lignin, Vanillin and Vanillic acid, respectively. Due to the solubility of O_2 in the aqueous solution is very low, the gas–liquid mass transfer is the main resistance in the gas–liquid reaction process, and its mass transfer resistance mainly exists in the liquid membrane. The experimental results indicated the effect of external diffusion can be eliminated as much as possible by increasing the

rotational speed. In addition, the effect of internal diffusion can be eliminated by using small particle size catalyst, and the nano-CuO catalyst used in the experiment with a width of 6–13 nm and a length of 17–40 nm. Therefore, we ignore the effect of internal diffusion on the catalytic reaction. Since the concentration of SL was difficult to determine in the experiment, it was represented by the G-lignin concentration C_G contained in the solution, and given that the oxidation of G-lignin produces only vanillin and vanillin acid. According to the analysis of the alkaline nitrobenzene oxidation products of lignin, the G-lignin content in the SL used in the experiment is 0.226 mmol·g^{-1}.

(1) Effect of SL concentration

On the basis of the experimental results, it is considered that the formation rate of vanillin in the early stage of the oxidation reaction is much faster than those of vanillic acid. Therefore, $-dC_G/dt \approx dC_V/dt$. Combining Eqs. (3) and (4), the following correlation can be obtained:

$$\frac{dC_V}{dt} = k_1 P_O C_G \tag{6}$$

If the formation rate of vanillin is first-order on the initial concentration of G-lignin, then k_1P_O is a constant. Then Eq. (6) can be written as follows:

$$\frac{dC_V}{dt} = k_O C_G$$

(2) Effect of oxygen partial pressure

If lignin oxidation reaction follows a first-order rate law with respect to the initial concentration of G-lignin, the following equation can be obtained from the Eq. (3):

$$\ln\frac{C_{G_0}}{C_G} = k_1 P_O t \tag{7}$$

where t is the reaction time. Setting $k_O = k_1P_O$, k_O should be linearly related to P_O, and the k_O value is constant while P_O is constant.

(3) Effect of reaction temperature

Dividing Eq. (4) by Eq. (3) and rearranging, the following equation can be obtained:

$$-\frac{dC_V}{dC_G} = 1 - \frac{k_2}{k_1}\frac{C_V}{C_G} \tag{8}$$

Setting $C_V = C_G \cdot u$, then it becomes:

$$\frac{dC_V}{dC_G} = u + \frac{du}{dC_G}\cdot C_G \tag{9}$$

Substituting Eq. (9) into Eq. (8), the following equation is obtained:

$$u + \frac{du}{dC_G}\cdot C_G = \frac{k_2}{k_1}\frac{C_V}{C_G} - 1$$

Defining $K = k_2/k_1$, and $C_V/C_G = u$, then the above formula can be transformed to

$$\frac{du}{-1+(K-1)u} = \frac{dC_G}{C_G} \tag{10}$$

Integration of Eq. (10), we can obtain

$$\ln\frac{-1+(K-1)u}{-1+(K-1)u_0} = \ln\left(\frac{C_G}{C_{G_0}}\right)^{(K-1)}$$

The above equation is equivalent to

$$\frac{-1+(K-1)u}{-1+(K-1)u_0} = \left(\frac{C_G}{C_{G_0}}\right)^{(K-1)}$$

In analogy with $u = C_V/C_G$, we define $u_0 = C_{V_0}/C_{G_0}$, obtaining

$$-1+(K-1)\frac{C_V}{C_G} = \left(\frac{C_G}{C_{G_0}}\right)^{(K-1)}\left[-1+(K-1)\frac{C_{V_0}}{C_{G_0}}\right]$$

After rearranging, the final equation can be obtained:

$$\frac{C_V}{C_G} = \frac{1}{1-K}\left[\left(\frac{C_G}{C_{G_0}}\right)^{(K-1)} - 1\right] + \frac{C_{V_0}}{C_{G_0}}\left(\frac{C_G}{C_{G_0}}\right)^{(K-1)}, K\neq 1 \tag{11}$$

The concentration of G-lignin and vanillin at different reaction times in the oxidation reaction process can be obtained by substituting k_1, P_O and K into Eqs. (7) and (11), and the C_G and C_V can be obtained:

$$C_G = \frac{C_{G_0}}{\exp(k_1 P_O t)} \tag{12}$$

$$C_V = C_G \times \left\{\frac{1}{1-K}\left[\left(\frac{C_G}{C_{G_0}}\right)^{(K-1)} - 1\right] + \frac{C_{V_0}}{C_{G_0}}\left(\frac{C_G}{C_{G_0}}\right)^{(K-1)}\right\} \tag{13}$$

3.3.2. Simulation details

(1) SL concentration of simulation details

In this experiment, the initial SL concentrations of 30 g·L^{-1}, 40 g·L^{-1}, 50 g·L^{-1}, and 60 g·L^{-1} were set, and the corresponding initial concentrations of G-lignin were 6.78 mmol·L^{-1}, 9.04 mmol·L^{-1}, 11.30 mmol·L^{-1}, and 13.56 mmol·L^{-1}, respectively. The relationship between the initial vanillin formation rate and the initial concentration of G-lignin is presented in Fig. 11. It clearly shows that the initial vanillin production rate can be described by first-order kinetics with respect to the initial concentration of G-lignin and the correlation coefficient is above 0.95 (95% confidence).

(2) Oxygen partial pressure of simulation details

In this test, the oxygen partial pressures of 0.2 MPa, 0.3 MPa, 0.4 MPa, 0.5 MPa, and 0.6 MPa were selected. The k_O value can be obtained under different oxygen pressures. Plotting k_O *versus* P_O, as shown in Fig. 12, it is evident that the k_O and P_O have a linear relationship with a high goodness of fit of 0.98, indicating that the reaction rate (k_O) is first-order on the oxygen partial pressure (P_O) and lignin oxidation reaction can be described by second-order kinetics.

(3) Temperature of simulation details

In this examination, the reaction temperatures of 403 K, 413 K, and 423 K were selected, and all other conditions kept constant. The $\ln(C_{G_0}\{C_G)$ at different temperatures *versus* reaction time t is

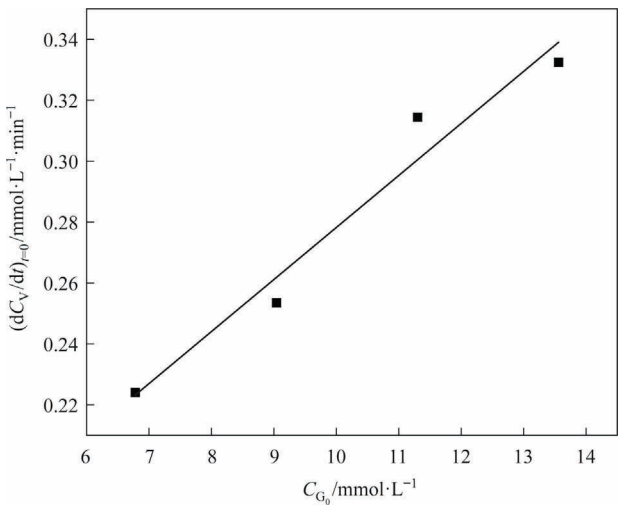

Fig. 11. Initial vanillin formation rate *versus* initial G-lignin concentration. (Reaction conditions: P_O = 0.4 MPa, T = 423 K, c(NaOH) = 2.0 mol·L^{-1}, c(cat) = 5%, c_0(SL) g·L^{-1}, N = 800 r·min^{-1}).

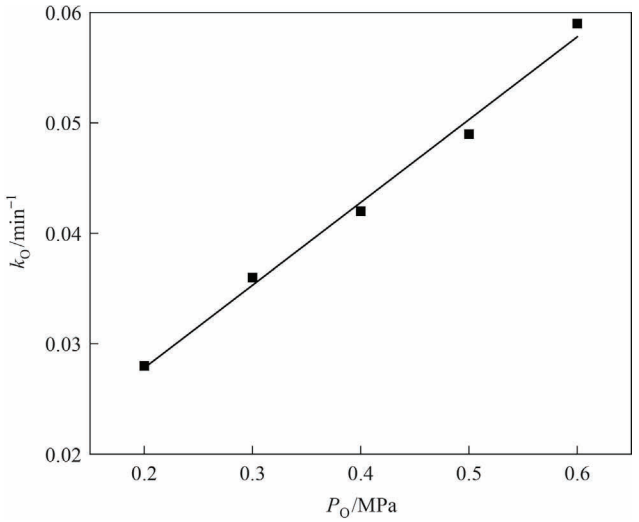

Fig. 12. Relationship between k_o and P_O. (Reaction conditions: T = 413 K, c(NaOH) = 2.0 mol·L^{-1}, c_0(SL) = 40 g·L^{-1}, c(cat) = 2.0 g·L^{-1}, N = 800 r·min^{-1}).

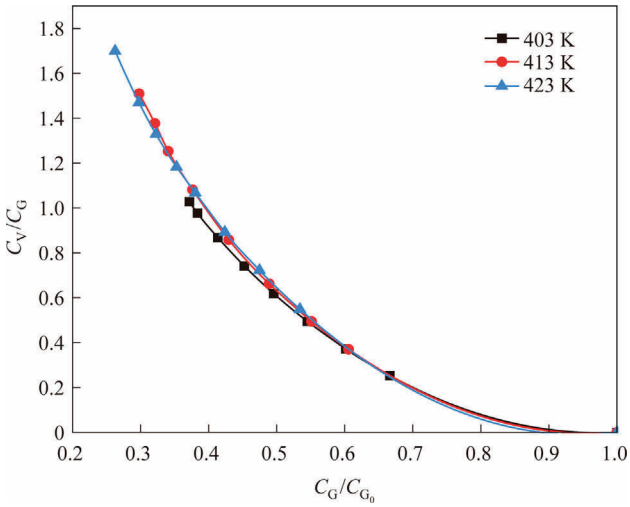

Fig. 14. C_V/C_G *versus* $C_G\{C_{G_0}$ under different reaction temperatures (403 K, 413 K and 423 K). (Reaction conditions: P_O = 0.4 MPa, c(NaOH) = 2.5 mol·L^{-1}, c_0-(SL) = 50 g·L^{-1}, c(cat) = 2.5 g·L^{-1}, N = 800 r·min^{-1}).

demonstrated in Fig. 13, The experimental data ($\ln(C_{G_0}\{C_G\})$, t, P_O) were substituted into Eq. (7) one by one, and after fitting, the reaction rate constant k_1 of G-lignin oxidation at certain temperature can be obtained. The C_V/C_G plotting against $C_G\{C_{G_0}$ is exhibited in Fig. 14. As shown in Fig. 14, the experimental data are substituted into Eq. (11). The ratio K of vanillin oxidation rate constant and G-lignin oxidation rate constant at certain temperature can be obtained by fitting, and k_2 can be determined after calculating. It can be seen from Figs. 13 and 14 that the $\ln(C_{G_0}\{C_G)$ fits well with t and C_V/C_G fits well with $C_G\{C_{G_0}$, both Goodness of Fit are above 0.95. The results of k_1, K, and k_2 are shown in Table 4.

3.3.3. Determination of parameters and equations of kinetics

According to the Arrhenius equation $\ln k = -E_a/RT + \ln A$, $\ln k$ and $1/T$ under different temperatures can be calculated based on the data in Table 4, and the relationship between $\ln k$ and $1/T$ is shown in Fig. 15. The apparent activation energy (E_a) of the two-step reaction can be calculated from the slope of two straight lines, and the pre-exponential factor (A) was calculated from the intercept of straight lines. The results are shown in Table 5, the E_a of

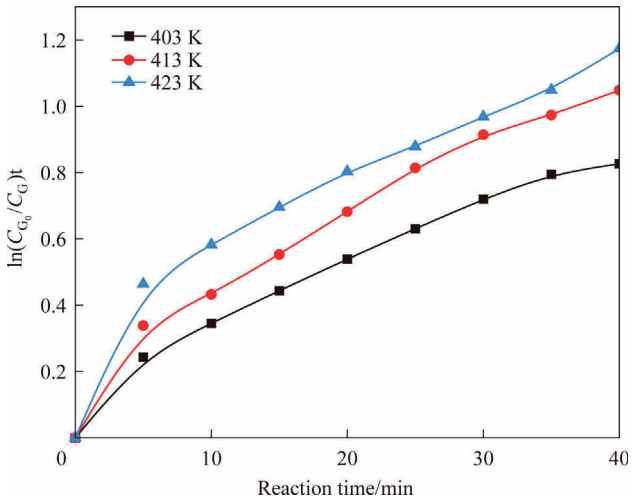

Fig. 13. $\ln(C_{G_0}\{C_G)(C_{G_0}/C_G)$ *versus* reaction time under different reaction temperatures (403 K, 413 K and 423 K). (Reaction conditions: P_O = 0.4 MPa, c(NaOH) = 2.5 mol·L^{-1}, c_0(SL) = 50 g·L^{-1}, c(cat) = 2.5 g·L^{-1}, N = 800 r·min^{-1}).

Table 4
Values of k_1, K and k_2 under different temperatures

T/K	k_1/MPa^{-1}·min^{-1}	K	k_2/MPa^{-1}·min^{-1}
403	0.072	0.397	0.0285
413	0.088	0.359	0.0314
423	0.110	0.341	0.0376

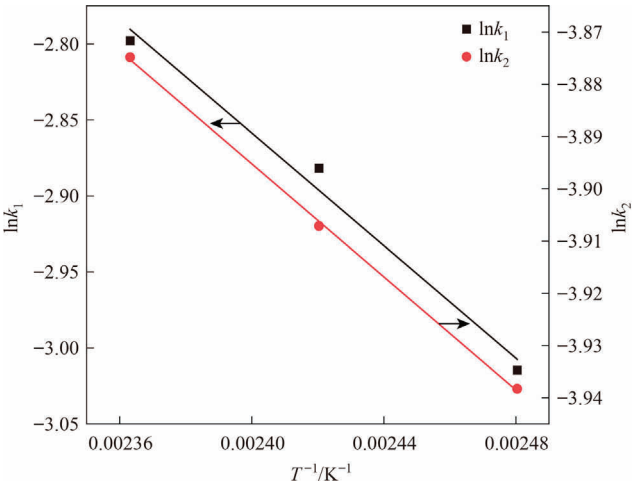

Fig. 15. Relationship between $\ln k$ and $1/T$.

the oxidation of lignin and vanillin are lower (less than 40 kJ·mol^{-1}), which can be considered as a fast reaction [34]. On the basis of these results, it can be concluded that the overall reaction rate is controlled by the rate of oxygen mass transfer, which is consistent with the previous experimental results.

It can be known from Table 5 that the reaction rate constants of the two-step reactions are:

$$k_1 = 632.7\exp\left(\frac{-3664}{T}\right) \tag{14}$$

$$k_2 = 9.7\exp\left(\frac{-2354}{T}\right) \tag{15}$$

Table 5
Calculated values of E_a and A

Reaction rate constant	E_a/kJ·mol^{-1}	A/MPa^{-1}·min^{-1}	R^2
k_1	30.5	632.7	0.997
k_2	19.6	9.7	0.968

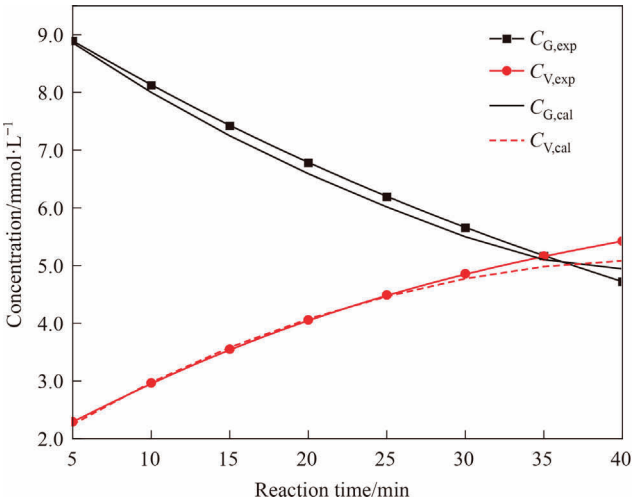

Fig. 16. Comparison of experimental values with calculated values under 403 K.

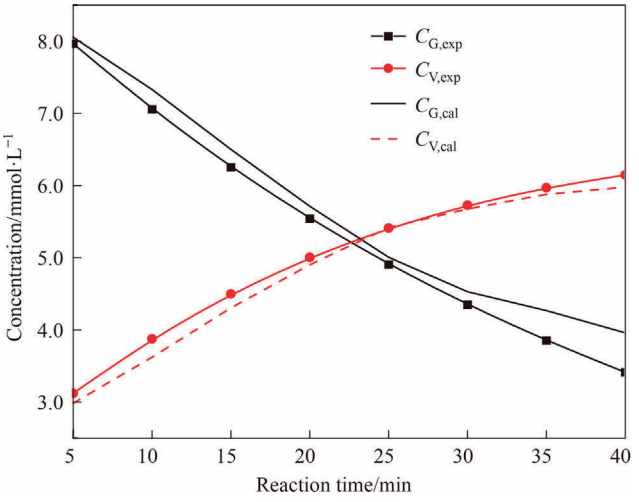

Fig. 17. Comparison of experimental values with calculated values under 413 K.

Therefore, the kinetic equations are as follows:

$$-\frac{dC_G}{dt} = 632.7\exp\left(\frac{-3664}{T}\right)C_G P_O \quad (16)$$

$$\frac{dC_V}{dt} = 632.7\exp\left(\frac{-3664}{T}\right)C_G P_O - 9.7\exp\left(\frac{-2354}{T}\right)C_V P_O \quad (17)$$

3.3.4. Verification of kinetic models

The experimental results under the above reaction temperatures (403 K, 413 K and 423 K) were verified by kinetic equations. Substituting k_1, P_O, and K into Eqs. (12) and (13) to calculate the simulated values of reactant concentrations C_G and C_V at different reaction times. The correlation of experimental values and the calculated values of C_G and C_V is displayed in Figs. 16, 17, and 18. It is revealed that the calculated value of G-lignin concentration is slightly higher than the experimental value, because the generation of acetovanillone and CO_2 was ignored. The calculated values of the G-lignin concentration and vanillin concentration are in good agreement with the experimental values, indicating that the kinetic equation is reliable.

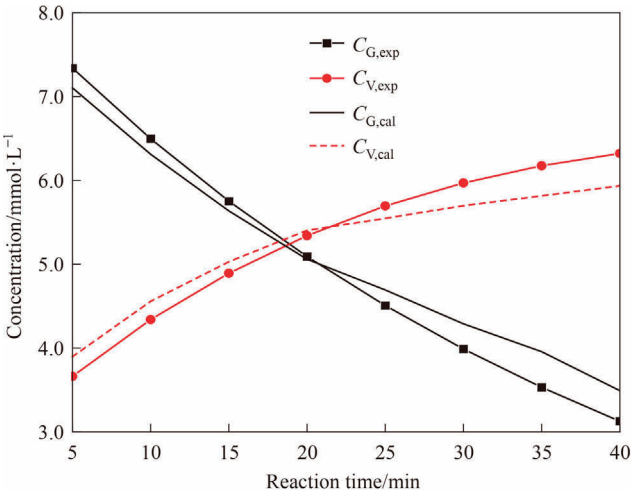

Fig. 18. Comparison of experimental values with calculated values under 423 K.

4. Conclusions

In summary, we systematically investigated the effect of different operating conditions on the oxidation of lignin into vanillin and syringaldehyde in CWAO process by nano-CuO, and the optimal experimental conditions of T = 423 K, N = 800 r·min^{-1}, t = 30 min, P_O = 0.4 MPa, c(NaOH) = 2.0 mol·L^{-1}, c_0(SL) = 50 g·L^{-1}, c(cat) = 2.5 g·L^{-1} were obtained. The yield of syringaldehyde and vanillin can reach 4.46% and 1.88% under the optimal reaction conditions, respectively. The kinetic parameters for lignin oxidation were obtained by fitting experimental data utilizing the Arrhenius equation. The activation energy of the two-step reactions of G-lignin oxidation and vanillin oxidation were 30.5 kJ·mol^{-1} and 19.6 kJ·mol^{-1}, respectively, indicating that these reactions is fast and controlled by oxygen mass transfer. It is difficult to eliminate mass transfer resistance completely, thus strengthening mass transfer is beneficial to increase the reaction rate. Moreover, the kinetic equations of lignin oxidation under experimental conditions was established and the reliability of the model was verified. The kinetic equations of catalytic oxidation of G-lignin were obtained:

$$-\frac{dC_G}{dt} = 632.7\exp\left(\frac{-3664}{T}\right)C_G P_O$$

$$\frac{dC_V}{dt} = 632.7\exp\left(\frac{-3664}{T}\right)C_G P_O - 9.7\exp\left(\frac{-2354}{T}\right)C_V P_O$$

This work pointed out the direction of enhancing lignin degradation by mass transfer enhancement technology, and provided basic data for the industrial application of this lignin catalytic oxidation process.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclatures

A	pre-exponential factor, $MPa^{-1}\cdot min^{-1}$
C_G	the concentration of G-lignin, $mmol\cdot L^{-1}$
C_V	the concentration of vanillin, $mmol\cdot L^{-1}$
C_{VA}	the concentration of vanillic acid, $mmol\cdot L^{-1}$
c(cat)	catalyst amount, $g\cdot L^{-1}$
c(NaOH)	NaOH concentration, $mol\cdot L^{-1}$
c_0(SL)	SL concentration, $g\cdot L^{-1}$
E_a	activation energy, $kJ\cdot mol^{-1}$
k_1	G-lignin reaction rate constant, $MPa^{-1}\cdot min^{-1}$
k_2	vanillin reaction rate constant, $MPa^{-1}\cdot min^{-1}$
m	the mass of SL, g
N	rotational speed, $r\cdot min^{-1}$
P	motor power, W
P_O	oxygen partial pressure, MPa
R	molar gas constant, $J\cdot mol^{-1}\cdot K^{-1}$
R^2	correlation coefficient
T	absolute temperature, K
t	reaction time, min
V	volume, L
ω	the yield of aromatic products, %

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