PURIFICATION OF PHENOLIC WASTE WATERS BY CATALYTIC OXIDATION*

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Catalytic oxidation of phenolic substances in industrial waste waters is alternative for pollutants biodegradable with difficulty or toxic for activated sludge. The oxidation of an aqueous phenol solution by oxygen was carried out in the presence of industrial catalyst Cherox 46-11 (30% Cu, Chemopetrol Litvinov) in a stainless steel autoclave at 120 – 160 °C. Compared to the radical reaction, the rate of the catalytic oxidation was two times higher. The reaction order with respect to phenol was close to one. The presence of acids in high concentrations at low oxygen partial pressures speaks for the higher reaction order to oxygen.

Catalytic oxidation of toxic contaminants of waste waters or those biodegradable with difficulty is an alternative way of decontamination of some industrial waste waters as well as waste waters of pharmaceutical and food-stuff processes. These waters are usually toxic for microorganisms of sewage treatment plants, and their combustion would increase tremendously expenses on waste disposal. Catalytic oxidation of contaminants to carbon dioxide or, at least, the decrease of their concentration to the level acceptable for biodegradation is economically and ecologically convenient solution especially for waste waters contaminated with phenolic substances. The biodegradation is the most common method for destruction of soluble organic contaminants of waste waters. However, its application fails for chemicals toxic for microorganisms. The choice of the suitable method should take into account the concentration and type of the waste water contaminants. For waste waters with chemical consumption of oxygen from 15 to 200 kg m^{-3}, the suitable process is their oxidation by oxygen, air or eventually also by other oxidizing agents such as hydrogen peroxide. The waste waters with the higher contaminant concentrations is better to subject to incineration, and those with the lower concentrations – unless they contain hazardous toxic substances – are more advantageously disposed of in sewage treatment plants after their dilution[1].

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The so called wet oxidation of waste waters by air without catalysts takes place at 180 – 330 °C and at the pressures 2 – 25 MPa and is energetically very demanding. The better results but under more drastic conditions are achieved by the supecritical oxidation which is performed above the critical point of water, i.e. at ca 374 °C and 22 MPa. The just mentioned oxidation processes are free radical reactions, and their occurrence as well as the rate of the whole process are favourable affected by e.g. addition of hydrogen peroxide. The advantage of catalytic oxidation lies in reduced energetic and investment expenses due to milder process conditions. For this purpose, usual oxidation catalysts such as Cu, Ag, Mn, Zn, V, and other oxides have been applied, using the following reaction conditions: 1 – 5 MPa, 100 – 200 °C, and pH 5 – 6 (cf. ref.[2]).

Oxidations of organic substances are generally radical, yielding a variety of oxidation products. Phenolic substances are oxidized to polyols, e.g. to hydroquinone and pyrocatechol. Further oxidation then leads to quinones, aldehydes, polycarboxylic acids, the final product being carbon dioxide. The reaction mixture contains usually also products of aldehyde condensations, including resins, which could deactivate the catalyst[3]. If reaction conditions are chosen such that in addition to the oxidation on the active catalyst surface the reaction proceeds also by radical mechanism in homogeneous phase, also concentration of the oxygen dissolved in the reaction mixture volume and within catalyst particles[4] plays an important role.

Stoichiometric equation (*A*) for total phenol oxidation shows the need of seven oxygen molecules per phenol molecule, the reaction is at the same time markedly exothermic, which makes performance of an autothermal process in adiabatic reactor possible. However, the whole reaction system is a set of parallel-consecutive reactions with a great number of intermediates, and the total oxidation rate slows down substantially in the stage of formation of relatively stable carboxylic acids.

$$\mathrm{C_6H_5OH + 7\,O_2 = 6\,CO_2 + 3\,H_2O} \quad (\Delta H^0_{298} = -3\,065\ \mathrm{kJ}) \tag{A}$$

The aim of the present work was examination of applicability of a copper hydrogenation catalyst for liquid phase oxidation of phenol, finding of optimal reaction conditions and determination of parameters of empirical kinetic equation.

EXPERIMENTAL

All chemicals were of analytical purity grade and of the following provenience: phenol (Reactivul Bucurest), methanol (Penta Prague), distilled water (this Department), and oxygen (Technoplyn Prague). The catalyst tested was powder catalyst Cherox 46-11 (particle size <0.25 mm), containing 30% Cu deposited on mixed SiO_2–MgO–$CaCO_3$ support, calcinated before use at 500 °C.

The reaction conditions were following: pressure 2 – 5 MPa, 110 – 160 °C, initial phenol concentration in water 5 g/l. The experiments were carried out in a stainless steel 1.25 l autoclave equipped with a lift magnetic stirrer containing four horizontal partitions and the stirring frequency 1 s. The reactor was heated by an electric heating jacket with electronic temperature control.

The analysis of samples of reaction mixtures was made by liquid chromatography at 269 nm on Separon SGX C18 7 μm, the flow rate of the eluent (40% aqueous methanol) being 0.6 ml/min. The wavelength used made it possible to detect the presence of dicarboxylic acids (maleic acid and oxalic acid), hydroquinone, benzoquinone, and phenol in the reaction mixture. Figure 1 shows the map of the absorbance of typical sample of the reaction mixture (at phenol conversion 63%) obtained by means of UV detector with the diode array from 210 to 360 nm, in which the region of phenol absorbance (elution time 7.98 min) is much more distinct, compared to dicarboxylic acids and hydroquinone at the start of the record (0.41 and 0.82 min, respectively).

RESULTS AND DISCUSSION

Oxidation of phenol and the intermediates formed is considered to be radical reaction. Notwithstanding, it can proceeds also by another mechanism, as documented by the use of heterogeneous catalysts. Figure 2 presents comparison of the course of the heterogeneous catalyzed oxidation of phenol with the noncatalyzed oxidation. Comparison of the corresponding curves indicate the much faster rate of the catalyzed process (four times higher medium reaction rate), the radical reaction being characterized by an induction period.

A typical reaction course illustrated by the experiments carried out at 153 °C and 4 MPa is shown in Fig. 3 which depicts time concentration profiles of individual identified components of reaction mixture. In contradistinction to the decreasing phenol concentration, the concentration of the intermediates attains maximum. Especially the sum of concentrations of the dicarboxylic acids, i.e. maleic acid and oxalic acid, becomes nearly twice as high as the initial phenol concentration. This fact comports the idea about the stoichiometry of formation of both acids.

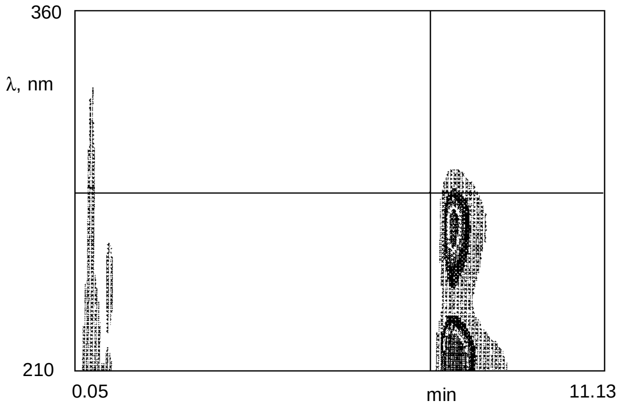

FIG. 1
Chromatogram of the reaction mixture at wavelength λ (nm), and retention time coordinates (min)

The course of acid concentrations is corroborated by the time dependence of pH of the reaction mixture shown in Fig. 4. Minimum pH value achieved in all experiments was 3.5 and was found at the time in which the dicarboxylic acid concentration passed through maximum (Fig. 3). The so high acidity of the reaction mixture can affect negatively the active component of the catalyst (Cu) as well as it can induce corrosion of the reactor material.

The amount and nature of oxidation intermediates in the reaction mixture exert also negative effect on the stability of the catalyst performance, decreasing its activity by adsorption of some intermediates and deposits from simultaneously proceeding condensation reactions.

Comparison of the total oxidation of organic compounds expressed by the oxygen conversion related to theoretical oxygen consumption with phenol conversion is shown in Fig. 5. While the conversion of phenol is after a certain time essentially complete (100%), the total conversion of organic compounds is around 23%. This is very likely caused by the greater stability of the organic acids under reaction conditions. In spite of this fact, the purpose of the oxidation has been realized, phenol biodegradable only with difficulty being destroyed quantitatively.

Combination of parallel-consecutive reactions and radical mechanisms with surface reaction on the catalyst does not make a simple kinetic description of the reaction rate possible. The oxidation rate depends further on the acidity of the reaction mixture and obviously also on the concentration of intermediates which undergo changes during the

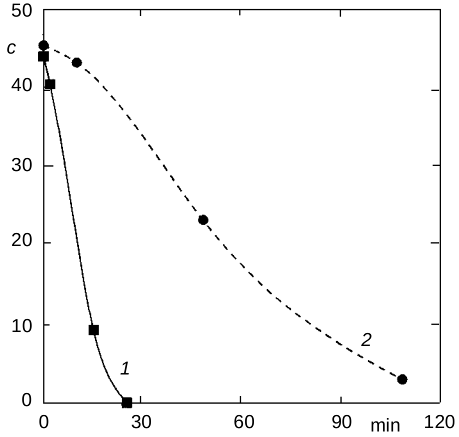

FIG. 2
Comparison of *1* catalytic and *2* noncatalytic oxidation of phenol at 160 °C and 5 MPa (phenol concentration *c* in mmol/l)

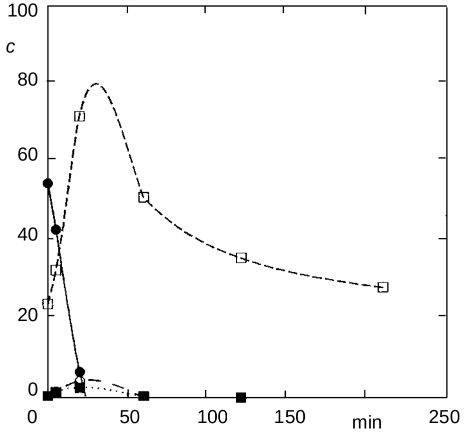

FIG. 3
Concentration profiles (*c*, mmol/l) of reaction components: phenol (●), hydroquinone (■), benzoquinone (❍), dicarboxylic acids (❒) (1.6 g catalyst)

reaction. The empirical dependence of the rate of phenol consumption on its conversion is shown in Fig. 6. Although this dependence speaks for the reaction order in phenol lower than one (which could be caused by parallel radical oxidation), preliminary

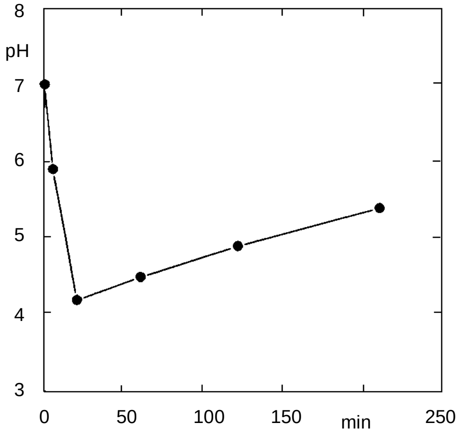

FIG. 4
Time changes of pH of reaction mixture at 153 °C and 4 MPa (1.6 g catalyst)

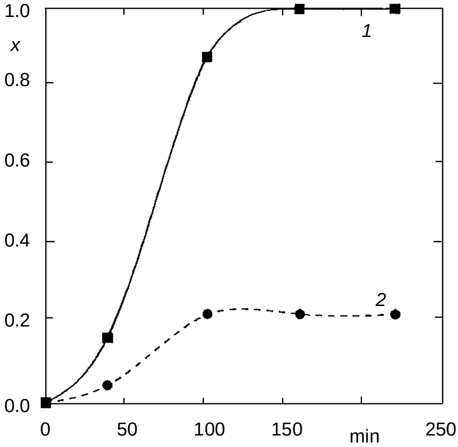

FIG. 5
Conversion x (in mole fraction) of phenol (*1*) and oxygen (*2*) demand at 132 °C and 5 MPa (2 g catalyst)

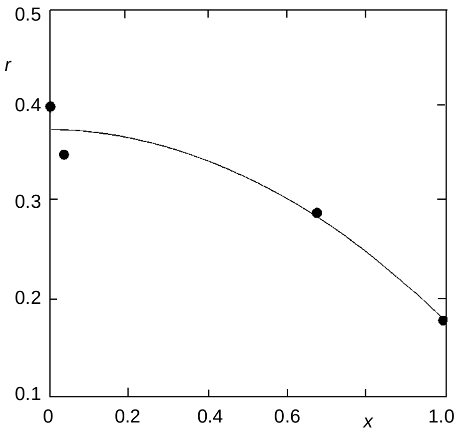

FIG. 6
Rate of phenol oxidation r (mmol/g_{cat} min) at 148 °C and 3 MPa (4 g catalyst, phenol conversion x is given in mole fraction)

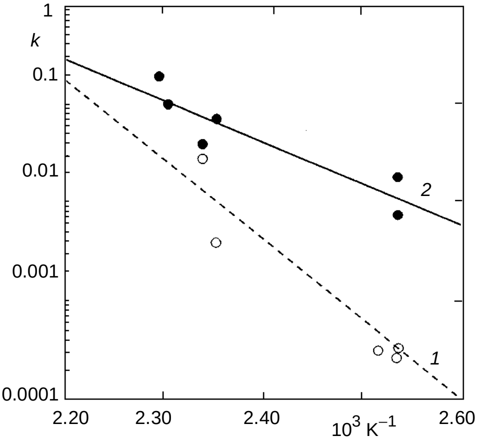

FIG. 7
Arrhenius plot of first-order rate constant of phenol oxidation, k (l/g_{cat} min) at *1* 2 MPa and *2* 5 MPa

evaluation of experimental data was performed with the use of an empirical power-type equation with the first order in phenol. Time dependence of phenol concentration in the reaction mixture in a discontinual reactor is expressed by Eq. (*1*).

$$c_{\mathrm{f}} = c_{\mathrm{f}0} \exp\left(-k\, t\, w/V\right) \quad , \qquad (1)$$

where c_{f} is phenol concentration, $c_{\mathrm{f}0}$ initial phenol concentration (both in mol/l), k is the first-order rate constant (l/g min), t is time (min), V is volume of reaction mixture (l), and w is catalyst weight (g).

The effect of oxygen concentration on the oxidation rate was included into the value of the rate constant. Temperature dependence of estimated first-order rate constants in Arrhenius coordinates is shown in Fig. 7. Comparison of data for two different pressures (2 and 5 MPa) indicates two different slopes, and thus also different activation energies corresponding to 162 and 80 kJ/mol, respectively. Both values agree well with data reported[2] for an analogous catalyst. However, the lower activation energy at the higher total pressure speaks for the existence of diffusion resistance within catalyst particles. With regard to the fine catalyst graining used (<0.25 mm), the effect of internal diffusion can hardly be eliminated.

CONCLUSIONS

The above results document that toxic substances dissolved in water can be transformed to biologically harmless intermediates and carbon dioxide under relatively mild conditions by catalytic oxidation. The higher amount of the catalyst in the reaction mixture promotes formation of the final product, carbon dioxide, when compared to the condensation products formed. Experimental data can be described by a simple power-type kinetic equation of the first order in phenol, and the resulting kinetic parameters agree well with data reported for similar catalysts. The problem is the life time of the catalysts which can be affected unfavourably by parallel polymerization and condensation reactions of the intermediates as well as by the possible dissolution of the active component in the acidic reaction medium.

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