

## CATALYTIC EFFECT OF ACTIVE CARBON BLACK CHEZACARB IN WET OXIDATION OF PHENOL

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The catalytic effects of hydrophilic granulated active carbon black Chezacarb have been tested in the oxidation of dilute (5 000 ppm) aqueous solutions of phenol. The research was focused on combined utilization of sorption and chemical (oxygen functional groups) properties of carbon black which support formation of free radicals in oxidation and on the catalytic effects of metals (Fe, Ni and V) present in the sorbent mentioned. The oxidation was carried out in a stainless steel autoclave of 1.25 l capacity. The reaction temperatures and the total pressures varied in the intervals of 120–160 °C and 3–5 MPa, respectively. The reaction mixture was analyzed by means of HPLC with UV detection (254 nm). The experimental data were evaluated by means of the ASPEN PLUS 9.2 program. The model of laboratory autoclave involved the reaction kinetics as well as the phase equilibria and dissolution of oxygen and carbon dioxide in the reaction mixture. Although the active carbon black shows a lower catalytic activity than the usual copper catalyst in the wet oxidation, it has the advantage of avoiding the undesirable releases of heavy metals in waste waters, which escapes accompany the application of copper catalysts.

**Key words:** Catalytic oxidation; Phenol in waste waters; Active carbon black Chezacarb.

Toxic or not readily biodegradable substances are often removed from waste waters by sorption on active charcoal which is then regenerated or combusted. An alternative procedure consists in the so-called wet oxidation of solutions of these substances at enhanced temperatures and pressures giving biologically unobjectionable products or – in the end – even carbon dioxide and water<sup>1</sup>. As the wet oxidation is also adopted as a method for regeneration of sorbents based on charcoal, there arises an idea of application of potential catalytic effects of these materials in oxidation reactions. The active carbon black Chezacarb formed in the production of hydrogen by partial oxidation of crude oil raw materials contains active groups at its surface (–SH, –OH, –OOH, –COOH) which can support free radical reactions and, in addition to that, the presence of iron, nickel, and vanadium oxides<sup>2</sup> in the original crude oil enables catalytic effects.

The purpose of wet oxidation is liquidation of toxic and not readily biodegradable substances in waste waters particularly those from chemical and pharmaceutical industries. The most frequently used typical model compound is phenol<sup>1</sup> although the process itself is designed for chloro-, nitro- (ref.<sup>3</sup>), sulfo-, and other derivatives of phenols and

aromatic hydroxy compounds<sup>4</sup>. The energy requirements of wet oxidation and the overall rate of the process can be improved by using a suitable catalyst. The catalysts most frequently adopted involve the metals: Cu, Fe, Mn, Co, Zn, Ru, and Ce in the form of ions, homogeneous complexes, or coatings on heterogeneous supports<sup>1,3-5</sup>. The procedure is suitable for waste waters with the COD concentration interval of 15–150 kg/m<sup>3</sup>. The problems are concentrated around the considerable energy demands of noncatalytic processes, stability, and activity of potential catalysts, and corrosion of apparatus by atomic oxygen and acid reaction intermediates<sup>4,5</sup>.

The program packet ASPEN PLUS (ref.<sup>6</sup>) represents a sophisticated simulator of technological operations and processes involving unit chemical-engineering operations inclusive of separations, mass transport, and models of basic chemical reactors. However, the basic program is limited to the simulation of steady states of systems, wherefrom follows its limited applicability. The program includes an extensive data base of physico-chemical properties of pure compounds as well as polycomponent mixtures. The involved optimization and regression procedures make it possible, e.g., to identify the parameters of the kinetic equations chosen. The input of starting data is controlled by an expert system.

The aim of the present work was to verify the presumption of catalytic processes of the Chezacarb sorbent in the oxidation of phenol, determine the effects of reaction conditions on the reaction rate, and make use of the simulation program ASPEN PLUS for modelling a laboratory autoclave and identifying the rate constants.

## EXPERIMENTAL

The chemicals used were of p.a. purity grade and were obtained from the following suppliers: phenol and methanol (Penta Prague), distilled water (Prague Institute of Chemical Technology), and oxygen (Technoplyn Prague). The catalyst used was active carbon black Chezacarb XE2 SH (Chemopetrol Group, s.a. Litvinov), brittle granules of 0.5 mm diameter, the surface area of 950 m<sup>2</sup>/g, the bulk weight of 125 g/l. The catalytic effect is enabled by the presence of metals: 0.08% V, 0.25% Ni, and 0.16% Fe. The active carbon black Chemviron Carbon WS4AWD (Germany) extruded (3.8 × 5 mm pieces) and ground to powder of 0.25 mm grain size, specific surface area 1 049 m<sup>2</sup>/g.

The process was studied in a laboratory stainless steel autoclave with a magnetic stirrer with horizontal partitions (Hoffer type) of 1.25 l capacity. The total pressure was maintained in the interval of 3–5 MPa with the accuracy of 5%, the reaction temperature was controlled electronically in the interval of 110–160 °C with the accuracy of 2 °C. The catalyst amounts varied in the interval of 0.1–1 g per 0.8 l reaction mixture. The initial concentration of phenol in water was 5 000 ppm.

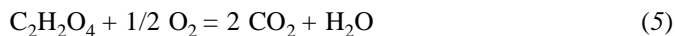
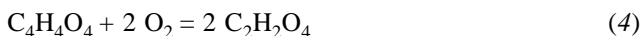
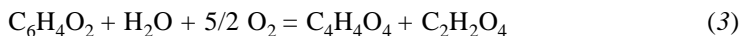
The reaction mixtures were analyzed by means of HPLC with UV detector at 254 nm using Separon SGX C18 7 μm and 40% aqueous methanol as the mobile phase; flow rate 0.6 ml/min. The identified components involved phenol, hydroquinone, benzoquinone, maleic and oxalic acids; at the concentrations above ca 20 mmol/l the acids could not easily be separated and were determined together as dicarboxylic acids.

## CALCULATIONS

For the calculations it was necessary to define the parameters of the laboratory autoclave used, the stoichiometry of reactions and their main components, and assess the form of the rate laws.

For the model of laboratory autoclave we adopted a model of batch reactor enabling the calculation to involve also the phase equilibria between the liquid and vapour phases of water, phenol, and other substances, as well as dissolution of oxygen in the reaction mixture. The reactor parameters were chosen as follows: isothermal batch reactor at 141.5 °C, initial pressure of 5 MPa, and 1 g catalyst.

The complex reaction system involved a great number of parallel consecutive reactions. For the calculation purposes, this number was limited to the reactions that could be monitored analytically. The reaction scheme was simplified to a set of five consecutive steps with the following products: hydroquinone, benzoquinone, maleic acid, oxalic acid, carbon dioxide, water.



The physico-chemical properties (e.g. solubility, volatility, and thermodynamic quantities) of the reaction components were contained in the build-in data base.

For the kinetic description of reactions we chose the power rate laws with unit reaction orders in the substrates and order 1/2 in oxygen.

## RESULTS AND DISCUSSION

The catalytic action of the Chezacarb sorbent in the oxidation of dilute phenol solutions was verified at not much demanding reaction conditions, viz. the temperature about 140 °C

and pressure 5 MPa. If the oxidation reaction did not occur and only sorption took place, neither the reaction intermediates nor even the relatively stable dicarboxylic acids would be observed. Figure 1 shows a typical time course of concentrations of reaction products. The dicarboxylic acids (maleic and oxalic) are presented together since it was difficult to separate them analytically. The concentration of benzoquinone was very low, remaining below 1.3 mmol/l at its maximum.

The effect of temperature on the course of oxidation reactions is depicted in the following figures. Figure 2 shows the dependence of phenol conversion upon the reaction time at various temperatures. From the graph it can be seen that temperature affects very strongly the length of induction period. At a low temperature, 120 °C, the oxidation is very slow; the temperature of 140 °C represents a certain limit above which the oxidation is much faster and probably involves a different oxidation mechanism (not a radical one) since at 160 °C there is no induction period and the form of dependence of phenol conversion corresponds to the zero order of reaction.

Similar conclusions can also be made for the oxidation of the relatively most stable intermediates – dicarboxylic acids, maleic and oxalic – as it can be seen from Fig. 3. The concentration profiles given for two reaction temperatures indicate a strong temperature dependence of oxidation rate of the acids. At the lowest temperature, 120 °C, the acids practically are not formed, their concentration remaining below 1.35 mmol/l; at 140 °C there is an initial pause followed by a steep increase in their concentration; and only at 160 °C the concentrations of acids show the maximum which is followed by their decomposition to carbon dioxide and water.

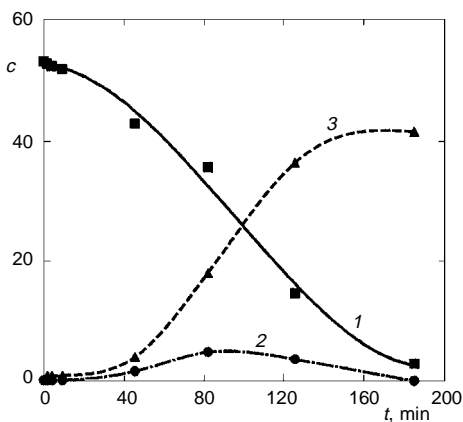


FIG. 1

Concentration profiles ( $c$ , mmol/l) of the reaction components: 1 phenol, 2 hydroquinone, 3 dicarboxylic acids (0.5 g catalyst, 5 MPa, 141.5 °C)

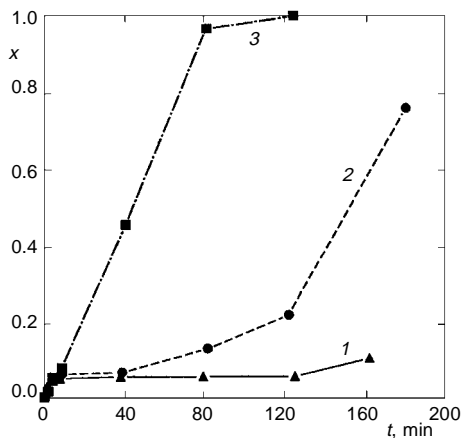


FIG. 2

Profiles of conversion of phenol at various temperatures: 1 121 °C, 2 144 °C, 3 163 °C (0.5 g catalyst, 5 MPa)

The concentration increase of the acids is accompanied by increasing acidity of the reaction mixture which presents considerable corrosion problems in the reactor and apparatus. The corresponding pH profiles are given in Fig. 4. Only for the temperature of 160 °C, the concentration profile of acids in Fig. 3 shows a maximum and the corresponding pH profile in Fig. 4 shows a minimum.

The effect of initial pH value on the oxidation course of the dicarboxylic acids is represented in Fig. 5. The initial pH value was adjusted at 10 (by adding sodium hydroxide) or 2 (by adding sulfuric acid). In the case of alkaline medium we can see a steep initial increase in concentration of the acids, corresponding approximately to the initial amount of phenolate; the curve shows an abrupt break followed by an only small increase in the amount of acids. In contrast to this behaviour, the oxidation course in the acidified solution of phenol is characterized by a slow increase in concentration of the acids. The breaks on the curves and the final course of concentrations of the acids which is the same for both the experiments are probably due to the fact that it was not possible to analytically differentiate the consecutive product of oxidation of maleic acid – oxalic acid – from the maleic acid in the reaction mixture. The steep section of the curves is probably connected with the increase in the maleic acid content, whereas the milder section could be ascribed to the subsequent oxidation of maleic into oxalic acid.

The ASPEN PLUS program made it possible to evaluate the rate constants of the empirical power rate laws of the reactions (1) through (5) using a nonideal pseudohomogeneous model of laboratory autoclave. Table I presents the values of rate constants and activation energies for the individual reactions. The lowest rate constant (and, hence, rate of oxidation) was found – in accordance with the data published<sup>1</sup> – for

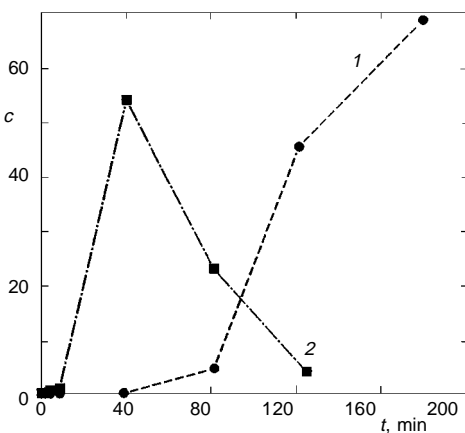


FIG. 3

Concentration profiles of dicarboxylic acids ( $c$ , mmol/l) at various temperatures: 1 144 °C, 2 163 °C (0.5 g catalyst, 5 MPa)

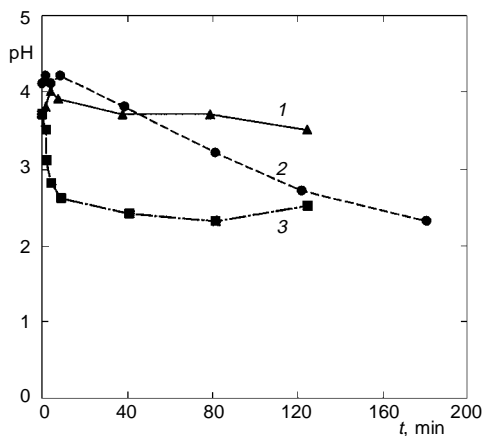


FIG. 4

pH–time profiles of reaction mixtures at various temperatures: 1 121 °C, 2 144 °C, 3 163 °C (0.5 g catalyst, 5 MPa)

maleic acid, whereas benzoquinone was oxidized fastest. The activation energies of the reactions are close to each other except for the oxidation of hydroquinone, which can be ascribed to the well-known equilibrium between hydroquinone and benzoquinone and formation of their complex (which is dependent on the reduction-oxidation potential of the system). This presumption is also supported by the presence of dark brown to black colouration in the reaction solution at the beginning of the oxidation. In spite of the fact that very distinctly limiting presumptions were made, the number of reactions taking place was reduced to 5, and the component reaction orders fixed at 1 and

TABLE I

Kinetic parameters of oxidation reactions (Chezacarb catalyst concentration 0.63 g/l)

Equation	$k(142\text{ }^{\circ}\text{C})^a$ $10^3\text{ mol}^{-0.5}\text{ l}^{0.5}\text{ s}^{-1}$	$E_a^b$ $\text{kJ mol}^{-1}$
1	0.094	28.0
2	0.60	9.9
3	1.4	35.2
4	0.036	33.1
5	0.11	33.6

<sup>a</sup> Rate constant; <sup>b</sup> activation energy.

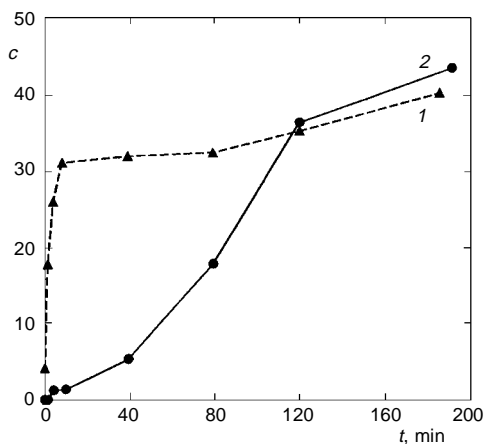


FIG. 5

Concentration profiles of dicarboxylic acids ( $c$ , mmol/l) for various initial pH values: 1 pH 10, 2 pH 2 (0.5 g catalyst, 5 MPa)

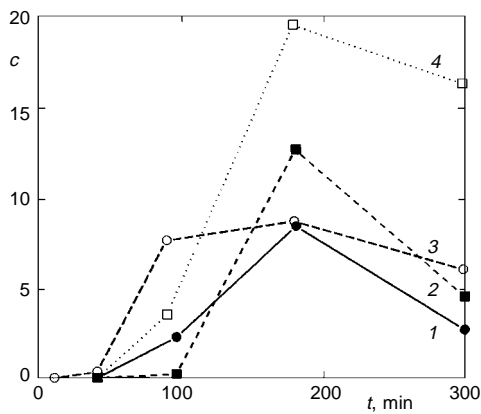


FIG. 6

Concentration profiles of dicarboxylic acids ( $c$ , mmol/l) for Chezacarb carbon black; acids: 1 maleic, 2 oxalic and those for standard Chemviron charcoal; acids: 3 maleic, 4 oxalic (0.5 g catalyst, 5 MPa, 143 °C)

1/2 in phenol and oxygen, respectively, the values of calculated concentrations agreed very well with the experimental data.

The catalytic effect of traces of V, Ni, and Fe in Chezacarb carbon black was proved by comparison with an experiment using a standard Chemviron charcoal. Whereas the two catalysts do not much differ in the oxidation of the starting phenol (where predominance of free radical mechanism is anticipated), the traces of metal oxides make themselves felt in the oxidation of dicarboxylic acids. Figure 6 presents a comparison of concentration profiles of maleic and oxalic acids in the oxidation with active carbon black Chezacarb with those in an experiment with the Chemviron charcoal. The concentrations of both acids are always lower with the application of Chezacarb (approximately half in the case of oxalic acid) showing a typical profile of intermediate with a maximum. With application of charcoal, the profile of maleic acid shows an almost time-independent plateau. The said comparison supports the presumptions<sup>1,3</sup> of metal oxides acting as oxygen carriers in the oxidations of acids.

## CONCLUSIONS

The catalytic action of Chezacarb sorbent in oxidations of diluted phenol solutions has been verified at not much demanding reaction conditions, temperatures above 140 °C and pressure of 5 MPa.

Temperature affects strongly the length of induction period. At low temperatures (120 °C) the oxidation is very slow due to the induction period; at 160 °C no induction period is present and the oxidation is much faster due probably to the effects of active functional groups of Chezacarb. An independent experiment with the Chezacarb alone, however, confirmed that the carbon black does not undergo oxidation in the temperature and pressure regions studied, i.e. the functional groups present do not make themselves felt.

The initial pH values affect the initial phase of the oxidation reaction. In the alkaline solution, the concentrations of acids steeply increase at the beginning, whereas in an acidified solution of phenol the concentrations of acids increase slowly.

The ASPEN PLUS program makes it possible to model laboratory-scale nonideal reactors and determine the parameters of these models inclusive of the parameters of rate equations.

The comparison experiments using a standard charcoal Chemviron supported the presumptions of different oxidation mechanisms of phenol and dicarboxylic acids (free radical and reduction-oxidation, respectively) and those about the catalytic effects of the metal oxides present in Chezacarb particularly upon the oxidation of the acids.

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