# SEPARATION PROCESSES IN H₂O₂ PRODUCTION [#]

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[#]This paper is dedicated to Prof. Roman Modic at his 90th Birthday.
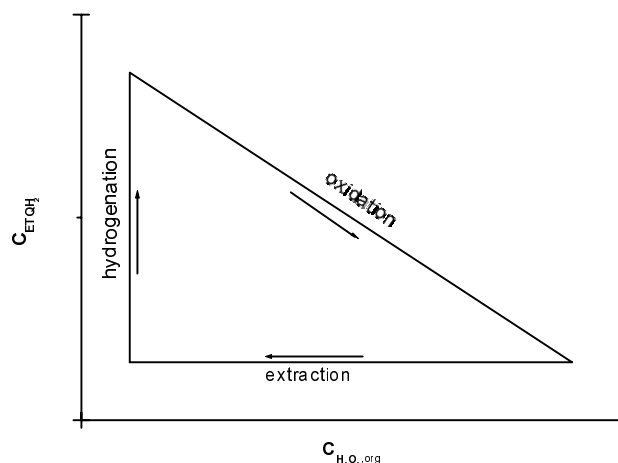
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Abstract

The article presents basic physico-chemical and process parameters, which are important in capacity enhancement design of the hydrogen peroxide production The limiting steps in the greater production, taking into account the existing production plant, are oxidation and extraction. The oxidation is a moderately slow reaction occurring mainly in bulk liquid, whose rate is affected by the mass transfer across the liquid film. Therefore, both interfacial area and liquid hold-up should be maximized in the industrial reactor. In the extraction process, the idea of pseudo equilibrium line is introduced. It was found out that knowing transport coefficients and interfacial area is not enough to predict the process in the extraction column.

Introduction

The production of hydrogen peroxide (H_2O_2) via anthraquinone occurs in three steps (Figure 1), i.e.: (1) hydrogenation of 2-ethyltetrahydroanthraquinone (ETQ); (2) oxidation of the product obtained in a gas-liquid reactor; (3) extraction of hydrogen peroxide with demineralized water. The industrial process is called all-tetra, because the principal active anthraquinone compounds are in tetrahydro forms. A working solution with the active agents consisting of 70% of ETQ and 30% of 2-ethylanthraquinone (EQ) dissolved in a proprietary mixture of organic solvents is used.[1-4] In the hydrogenation step, anthraquinones are reduced to 2-ethyltetrahydroanthraquinol ($ETQH_2$) and 2-ethylanthraquinol (EQH_2). However, the latter readily reacts to give[5]

$$\text{EQH}_2 \quad + \quad \text{ETQ} \quad \rightleftharpoons \quad \text{EQ} \quad + \quad \text{ETQH}_2 \qquad (1)$$
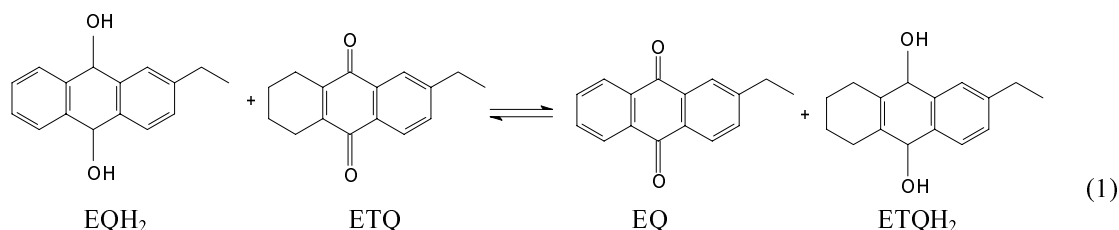
This equilibrium is almost completely shifted to the right. In order to avoid secondary reactions, only 60-70% of the anthraquinone mixture is reduced in the hydrogenation step. Therefore, only $ETQH_2$ is involved in the successive oxidation step.

Figure 1. Schematic representation of H_2O_2 production.

The oxidation step, a gas-liquid reaction, is considered as slow to moderately fast. The absorption rate of oxygen is essential for the overall transfer rate. The oxidation reaction obeys the first-order kinetic law for both oxygen and anthraquinone.[6]

The aim of this work is to define basic physico-chemical and process parameters, which are important in capacity enhancement design of the H_2O_2 production. The limiting steps in the greater production, taking into account the existing production plant, are oxidation and extraction. Therefore, the research was oriented toward (i) the study of oxygen absorption followed by chemical reaction in an oxidizer, (ii) analyzing process parameters which exert an influence on global reaction rate of oxidation, (iii) in the extraction process the determination of equilibrium diagram H_2O_2–water–working solution at 50 ºC, and (iv) the study of effect of process parameters and physico-chemical properties on the efficiency of the column with perforated plates.

Experimental

Oxidation experiments were performed in a batch reactor with a volume of 4.6 L (d = 0.14 m; h = 0.30 m). The mixing equipment consisted of a six-bladed pitch-blade turbine with a diameter of 0.047 m. The reactor was placed in a water-bath thermostat to

maintain a constant reaction temperature and it was fed with a 2.2 L of working solution containing hydrogenated anthraquinone. After reaching a desired reaction temperature (40 and 60 ºC) air was purged at the bottom through a sparger. The flow of air varied between 200 and 500 L/h. Formed H_2O_2 has a greater specific weight as the working solution and tends to deposit at the reactor bottom. To eliminate the separation effect the range of the stirring rate was chosen between 1750 and 2250 min^{-1}. The amount of hydrogen peroxide formed and anthraquinone converted were determined by hydrogen peroxide titration.

Extraction experimental work comprised determination of chemical and physical characteristics of a system working solution – hydrogen peroxide – water at 50 ºC, engineering analysis of extraction process and prediction of industrial experiment. The last phase of the research was realization of an industrial experiment followed by the analysis of the results.

Results and discussion

Oxidation. Oxidation of $ETQH_2$ by oxygen occurs through the following steps: (1) diffusion of oxygen from the gas phase to the gas-liquid interphase, (2) diffusion of oxygen from the liquid interphase into the bulk of the solution and (3) chemical reaction in the solution. It was assumed that the main resistance is at the liquid side. Therefore, the first step can be ignored. The other two steps can occur simultaneously. Therefore, in order to evaluate the extent of the reaction occurring in the liquid film, the enhancing factor or Hatta number, Ha, must be determined.

To define qualitatively the effect of process parameters on chemical reaction and mass transfer the oxidation experiments at different stirring speeds, temperatures and gas flow rates were performed and compared. All experiments were conducted by changing only one parameter at time leaving the other two constant. The effect of mixing is presented at Figure 2. It can be concluded that mass transfer affects the global reaction rate. An interfacial area is higher at higher stirring speed resulting in higher volumetric mass-transfer coefficient, $k_L a$.
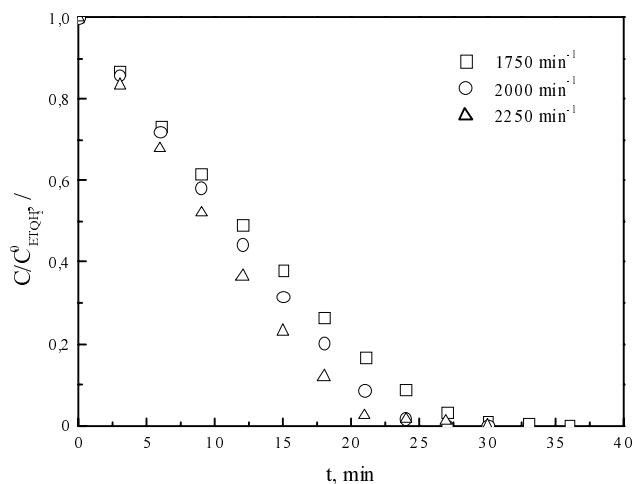
Figure 2. The effect of stirrer speed on the ETQH$_2$ disappearance (T = 60 ºC; ϕ_g = 500 L/h).

The global reaction rate also depends on gas flow rate. Higher flow rate results in higher interfacial area and higher amount of oxygen present in the reaction mixture. Therefore, H$_2$O$_2$ production rate is higher. However, there is an upper limit. At flow rate higher then 700 L/h, a contact time between gas and liquid is too short. Consequently, oxidation is not efficient. To eliminate this side effect the experiments were performed at flow rates between 200 and 500 L/h. Figure 3 shows the effect of gas flow rate.
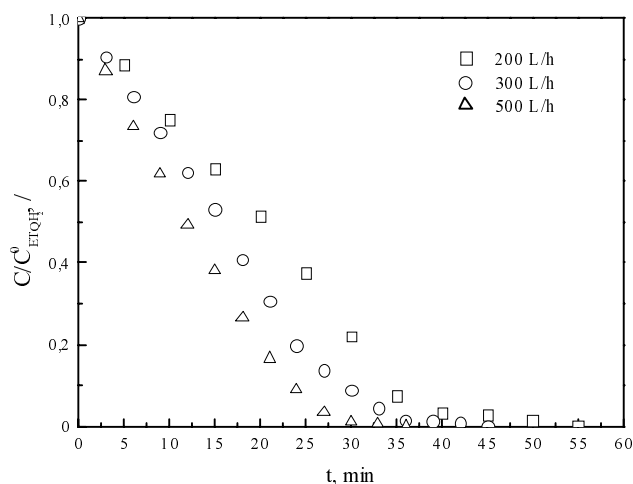
Figure 3. The effect of gas flow rate on the ETQH$_2$ disappearance (T = 60 ºC; N = 2000 min^{-1}).

Temperature dependence of global reaction rate was determined at constant stirrer speed and gas flow rate at two different temperatures (40 and 60 ºC). The effect is presented in Figure 4.
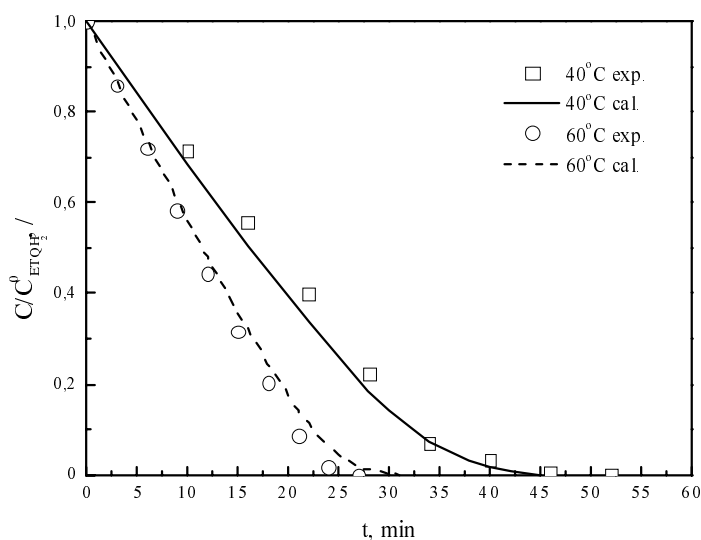
Figure 4. Experimental and calculated concentration profiles (ϕ_g = 500 L/h; N = 2000 min^{-1}).

To quantify the experimental results, it was assumed that the reaction rate obeys a second-order kinetic law.[1] Employing the relation

$$-\frac{dC_B}{dt} = -\frac{dC_A}{dt} = k_L a \cdot (C_B^* - C_B) = k_r \cdot C_A \cdot C_B \tag{2}$$

that is, eliminating C_B the rate of ETQH$_2$ disappearance becomes

$$-\frac{dC_A}{dt} = \frac{C_B^*}{\dfrac{1}{k_r C_A} + \dfrac{1}{k_L a}} \tag{3}$$

where A and B represent ETQH$_2$ and oxygen, respectively. By integrating Eq. 3 the following expression describing consumption of ETQH$_2$ may be written

$$\frac{1}{k_L a} \cdot (C_A^0 - C_A) + \frac{1}{k_r} \cdot \ln \frac{C_A^0}{C_A} = C_B^* \cdot t \tag{4}$$

The values of k$_r$ and Henry constant, He, were used as found in literature[5,6]

$$k_r = (1{,}14 \pm 0{,}08) \cdot 10^{13} \cdot e^{(-(14213 \pm 1036)/RT)} \text{ [cm}^3\text{/mol s]} \tag{5}$$

He (40ºC) = 110 bar L/mol

He (60ºC) = 108 bar L/mol

By fitting experimental data to Eq. 4 the values of k_La may be estimated at different temperatures and gas flow rates. To compare experimentally obtained values of k_La with known correlations the correlation developed by Gaddis[7] was used

$$k_L a = (k_L a)^* /(v / g^2)^{1/3} \tag{6}$$

where is

$$(k_L a)^* = (9.8 \times 10^{-5} (P/V)^{*0.4})/(B^{-0.6} + 0.81 \times 10^{-0.65 \cdot B}) \tag{7}$$

and

$$(P/V)^* = (P/V)/(\rho \cdot (v \cdot g^4)^{1/3}) \tag{8}$$

$$B = (\phi_g / D_r^2) \cdot (v \cdot g)^{-1/4} \tag{9}$$

The comparison of correlated and calculated volumetric mass transfer coefficients is presented in Table 1. The good agreement between calculated results from Eq. 4 and experimental data is presented in Figure 4.

Table 1. Comparison of k_La.

ϕ_g =200 L/h		ϕ_g =300 L/h		ϕ_g =500 L/h	
k_La, s^{-1} cal. (Eq.4)	k_La, s^{-1} (Eq. 6)	k_La, s^{-1} cal. (Eq.4)	k_La, s^{-1} (Eq. 6)	k_La, s^{-1} cal. (Eq.4)	k_La, s^{-1} (Eq. 6)
T = 40°C					
0.0402	0.0358	0.0507	0.0444	0.0542	0.0588
T = 60°C					
0.0471	0.0478	0.0617	0.0594	0.0863	0.0789

To determine the influence of mass transfer on the global reaction rate the Hatta number was introduced. The Hatta number, Ha, compares the maximum chemical conversion in the mass transfer film to the maximum diffusion flux through this liquid film, thus is

$$Ha = \frac{\sqrt{k_r \cdot C_A^0 \cdot D_B}}{k_L} \tag{10}$$

Since the parameter k_L appears independently in the expression of the Hatta number, its value was calculated from the experimentally obtained values of k_La by estimating the value of a from the correlation developed by Calderbank[8]

$$a = 1.44 \times \left[\frac{(P_g/V)^{0.4} \cdot \rho^{0.2}}{\sigma^{0.6}} \right] \cdot \left(\frac{u_g}{u_t} \right)^{0.5} \tag{11}$$

where the terminal velocity, u_t, was taken constant of 0.265 m/s.

Table 2. Hatta numbers.

T, °C	40	60
ϕ_g, L/h	Ha, /	Ha, /
200	0.15	0.24
300	0.16	0.23
500	0.14	0.21

Table 2 presents Ha at different gas flow rates and temperatures. It can be seen that the Hatta number is in the range between 0.14–0.24, that is, an intermediate region , where $0.05 < Ha < 1$, a range to which corresponds an enhancement factor of 1.[9] The conclusion is that oxidation of $ETQH_2$ is a moderately slow reaction occurring mainly in the bulk liquid, whose rate is affected by the mass transfer across the liquid film. Therefore, both interfacial area and liquid hold-up should be maximized in the industrial reactor.

Extraction. A standard method was used to determine the equilibrium concentrations of H_2O_2 in working solution and in water. From the data obtained the equilibrium diagram (Figure 5) was constructed for the system Y [kg H_2O_2/kg H_2O]– C [kg H_2O_2/m^3 WS]. It can be described by linear relation

$$Y = K C \tag{12a}$$

and

$$Y = \frac{y}{1-y} \tag{12b}$$

where the equilibrium constant K at 50 °C was found to be 0.16 m^3 WS/kg H$_2$O at Y < 0.7 (y = 41.2%).
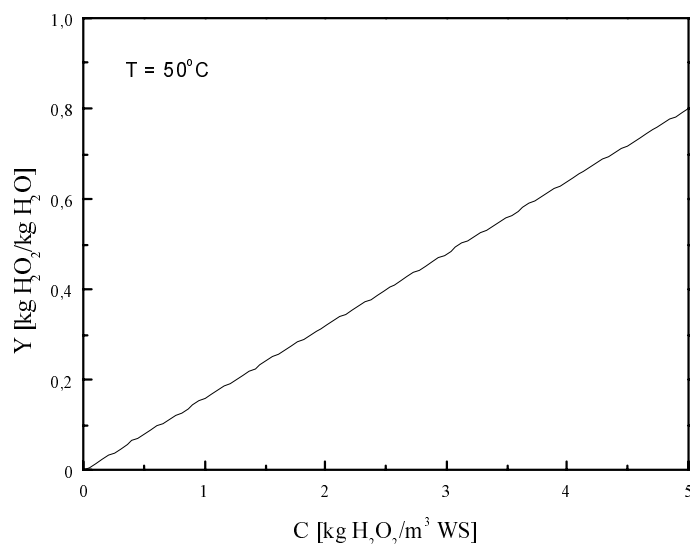
Figure 5. Equilibrium diagram.

It is known from previous work[10] that the resistance in organic phase is a limiting step in a mass transfer of hydrogen peroxide from organic to water phase, where the mass transfer coefficient may be in the range of 10^{-4} – 10^{-5} m/s depending on hydrodynamics (mass transfer in jet regime volume or dispersion layer). Furthermore, the interfacial area is also dependent on process conditions (~100 m^2/m^3 of dispersion). Due to diversity of both regimes on the tray the study of the $k_L a$ and mass transfer of H$_2$O$_2$ dependence on organic phase flow is very complicated. To define the region and dependence trends an industrial experiment was employed. However, to successfully perform an industrial experiment some key limiting factors of the process should be known, i.e., the coalescence and hydraulic limitations on maximum allowable concentration of organic phase leaving the extraction column which should not be higher than 0.2 g/L.

Hydraulic operation of column can be predicted from semiempirical relationship of dispersion phase height, Δh, and organic phase flow rate. ϕ, (Eq. 13)[11,12] and energetic balance, which can be described as a relation between the height of organic phase below the perforated plate, h_0, and organic flow rate (Eq. 14).[13]

$$\Delta h = K_1 \cdot \phi^3 \left[m^3 / h \right] \tag{13}$$

where are

$$K_1 = t_{sep} \, [s] \left[\frac{1}{3600 \, C \, A_k \, h} \right]^3 = 58.5 \times 10^{-9} \left[\frac{h^3}{m^8} \right],$$

time of the dispersion separation t_{sep} = 36 s with hold-up of the dispersed phase h = 0.5, specific characteristic constant C = 0.15 $(m/s)^{2/3}$, and cross-sectional area of A_k = 3.14 m^2
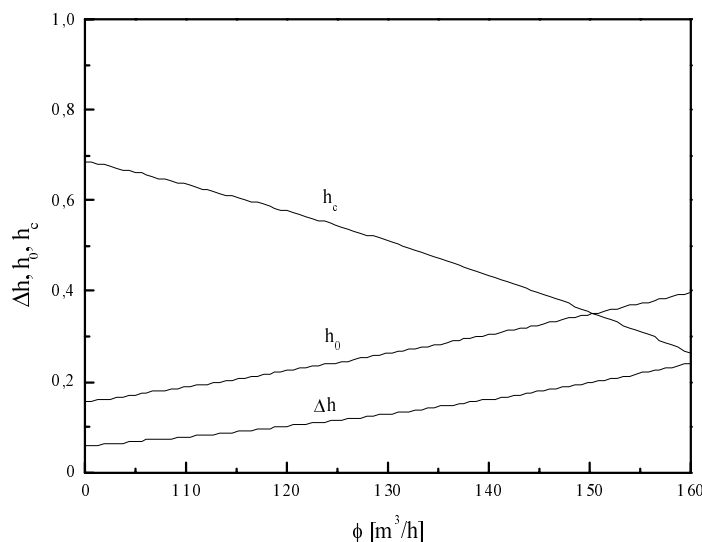
and

$$h_0 \, [m] = K_2 \cdot \phi^2 \left[m^3 / h \right] \tag{14}$$

where is

$$K_2 = \frac{\rho_d}{A_f^2 \, 2 \, \alpha^2 \, g \, \Delta\rho \, 3600^2} = 15.5 \times 10^{-6} \left[\frac{h^2}{m^5} \right]$$

where α = 0.67, ρ_d = 950 kg/m^3, area of perforations A_f = 0.05 m^2, $\Delta\rho$ = 200 kg/m^3 and h_c – water phase layer above the plate, where 0.9 m is the distance between two plates

$$h_c = 0.9 - h_0 - \Delta h \tag{15}$$

**Figure 6.** Heights of layers on a tray at different organic flow rates.

It is reasonable to introduce an idea of pseudo equilibrium line for the extraction columns that are known to operate at efficiency of 0.2–0.25. Pseudo equilibrium line represents actual compositions at tray assuming that the efficiency is equal at all trays. The relation between pseudo equilibrium line and efficiency may be described as

$$f = \frac{Y/K}{C(1-E) + E\,Y/K} \tag{16}$$

where are f×K slope of the pseudo equilibrium line, K slope of the equilibrium line, E efficiency and C,Y compositions in organic and water phase at tray, respectively. For E = 0.23, C = 6.52 kg H_2O_2/m^3, Y = 0.54 kg H_2O_2/kg H_2O and K = 0.16 m^3/kg H_2O f is equal to 0.58 and corresponding slope of pseudo equilibrium line is 0.093 m^3/kg H_2O. A slope of operating line can be calculated from mass balance

$$\frac{L}{V'} = \frac{\Delta Y}{\Delta C} = \frac{0.54 - 0}{6.52 - 0.19} \tag{17}$$

where L and V′ are organic and water phase, respectively, and their ratio is equal to 0.085 m^3/kg H_2O. Lines are presented in Figure 7 where one may find 26 real contact stages. Analysis of the samples of organic and aqueous phase at chosen trays did not correspond to compositions found at pseudo equilibrium line, what does not confirm the assumption of equal efficiency at all trays.
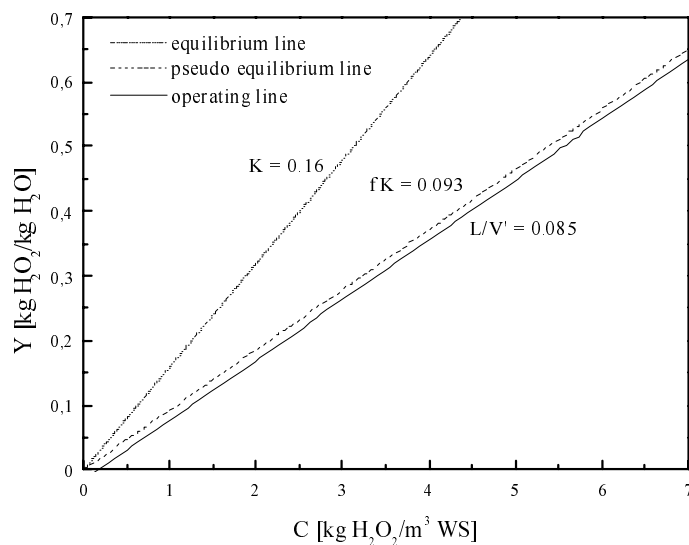
Figure 7. Equilibrium, pseudo equilibrium and operating lines.

The study of the flow rate effect on the H_2O_2 concentration of organic phase in the effluent gave the results in the form of mass transfer presented in Table 3, where is

$$\dot{W}_C = \phi \left(6.52 - C_{org}\right) \left[kg/h\right] \tag{19}$$

Table 3. Mass transfer and relevant process criteria at different flow rates.

ϕ $[m^3/h]$	h_0 [m]	Δh [m]	C_{org}, exp. [mol/L]	$\dot{W}_{C,H_2O_2}$ [kg/h] overall	$\dot{W}_{i,H_2O_2}$ [kg/h] average per tray
130	0.26	0.13	0.18	822	31.6
150	0.35	0.23	0.18	950	36.5
160	0.4	0.2	0.19	1000	38

From the data in Table 3 may be concluded that the column is operating at the upper hydraulic (h_0 = 0.4 m), coalescence (Δh = 0.23 m) and outlet concentration ($C_{org.}$ = 0.19 g/L) conditions.

Conclusions

The value of the Hatta number is often used as a criterion for reactor selection. In the case of fast film reactions a reactor with a high interfacial area should be selected. For a slow bulk reaction the liquid hold-up is to be maximized. For the intermediate region, as the one presented in this article, a reactor with both the interfacial area and liquid hold-up being large should be chosen. In this region, the enhancing effect changes significantly with the Hatta number. Therefore, reactors within this region should not be selected on the basis of Hatta number only.

The raise in the flow of organic phase gives the higher mass transfer arising from one or all the factors in $k_L a \times t_{contact}$ product. Consequently, knowing transport coefficients and interfacial area is not enough to predict the process in the extraction column. It is necessary to know the factors that affect the product $k_L a \times t_{contact}$.

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Povzetek

V članku so prestavljeni osnovni fizikalno-kemijski in procesni parametri, ki so pomembni za povečevanje kapacitete v proizvodnji kapacitete vodikovega peroksida. Limitna procesa sta oksidacija in ekstrakcija. Oksidacija poteka predvsem v glavni masi tekoče faze, njeno hitrost pa omejuje absorpcija kisika v tekočo fazo. Za povečevanje industrijskega reaktorja je zato potrebno zagotoviti čim večjo medfazno površino in sloj tekoče faze. Pri študiju ekstrakcije je bil uveden pojem psevdoravnotežne črte. Ugotovljeno je bilo, da poznavanje transportnih koeficientov in medfazne površine ne zadošča za napoved dogajanja v ekstrakcijski koloni.