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Hydrogenation of 4-*tert*-butylphenol in a three-phase cocurrent upflow reactor

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Abstract

Hydrogenation of 4-*tert*-butylphenol (4-TBP) hydrogenation in isopropanol at 433 K and 1–2 MPa of hydrogen pressure was performed in an upflow three-phase reactor. Overall conversion was ca. 90–97% with 4-*tert*-butylcyclohexanol as the predominant product. The *cis*/*trans* ratio in 4-*tert*-butylcyclohexanol was close to the thermodynamic one (1:2). The data were evaluated with a model, which assumes that at low conversion of organic compound the rate of the process is determined by the hydrogen mass transfer in the liquid film, while at high conversions the transfer of the organic compound to the catalyst surface is the limiting factor.

Keywords: Hydrogenation; 4-*tert*-Butylphenol; Upflow reactor

1. Introduction

Stereoselective hydrogenation of aromatic compounds is a subject of considerable industrial and academic interest. Liquid-phase hydrogenation of 4-*tert*-butylphenol (4-TBP) attracted particular attention, as the hydrogenation product *cis*-4-*tert*-butylcyclohexanol finds application in the perfumery industry (Fig. 1).

Preferentially rhodium catalysts operating in slurry reactors are applied [1]. It is claimed that very high (up to 100%) stereoselectivity could be achieved over Rh catalysts if an acidic co-catalyst is used [2].

Kinetic modeling of this reaction over stereoselective Rh catalyst was reported in [1,3]. There is, however, an industrial need to develop a continuous process, which would utilize less expensive, but still active and reasonably stereoselective nickel catalysts. These catalysts due to lower activity would operate at higher temperatures, leading to an increase of thermodynamically more stable *trans*- isomer. For instance, the *cis*/*trans* ratio close to 1:2 was obtained [4,5] in 4-TBP hydrogenation over a nickel chromium catalyst at 438 K, when the reaction was performed in ethanol in a slurry reactor.

Although catalytic three-phase slurry reactors are predominantly used for production of fine chemicals in a batch operation mode, the necessity to intensify the manufacturing process is behind the recent attempts to conduct these reactions in a continuous mode with a fixed bed of catalysts particles. Although somewhat new to production of fine chemicals, three-phase catalytic reactors with fixed bed of catalyst particles are widely used in petrochemical and chemical industries

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Nomenclature

a	the specific area
D	diffusion coefficient
h	thickness of the liquid film
L	volumetric flow rate per unit of reactor cross-section
p_1	parameter, defined in Eq. (7)
p_2	parameter, defined in Eq. (7)
U	the linear flow rate
v	relative retaining volume

Greek letters

β	parameter, defined in Eq. (7)
ε	porosity of the bed
σ	relative wetted surface area
ψ	adjustable parameter

for bulk chemicals. The majority of studies are devoted to cocurrent downflow reactors (trickle-bed) [6], while cocurrent upflow reactors received less attention. The upflow mode of operation have advantages of uniform liquid distribution, reliable scale-up, selectivity and temperature control [7]; at the same time significant back-mixing could possible worsen the reactor performance. Several reaction systems were compared in [7] and the controversy still remains which mode of operation (trickling or upflow mode) is advantageous.

The purpose of this study was to investigate three-phase hydrogenation of 4-TBP in a cocurrent upflow reactor over a commercial nickel-chromium catalyst, while comparison with a trickle-bed reactor was outside of the scope.

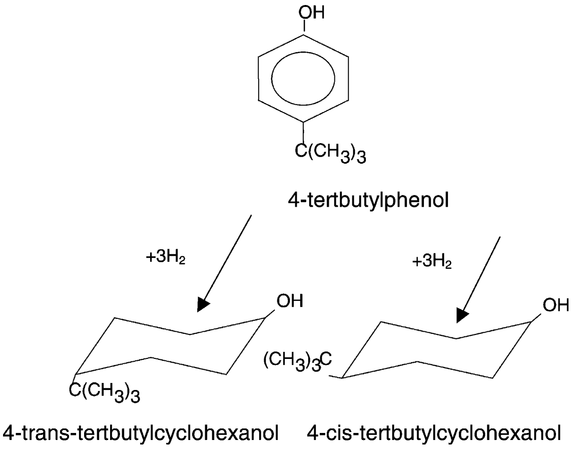

Fig. 1. Reaction scheme.

2. Experimental

The experiments were carried out in a packed bed reactor, operating in a cocurrent upflow regime. The reactor had the following characteristics: inner diameter 14 mm and maximum height of the bed 300 mm. Commercial Ni/Cr_2O_3 catalyst (50% Ni) was used. The catalyst granules of 2 mm × 2 mm size were applied. The reaction was carried out at 433 K and 1–2 MPa of hydrogen pressure. The flow rate was kept constant and equal to $1.5\,h^{-1}$. The substrate 4-TBP was diluted with isopropanol (molar ratio 2:1). Analysis of products was performed by GC.

3. Results and discussion

It was found that 4-TBP could be successfully hydrogenated in an upflow three-phase reactor. Overall conversion of the substrate at the reactor outlet was 90–97% depending on hydrogen pressure. The selectivity to the final hydrogenation product was around 100%, which means that formation of 4-*tert*-butylcyclohexanone was not detected. The *cis*/*trans* ratio of 4-*tert*-butylcyclohexanol was 1:2.3, which is very similar to the one reported for the same reaction over almost the same nickel chromium catalyst in a slurry reactor [4,5]. This ratio at 433 K is close to the value, which would be expected from thermodynamic considerations [4].

The amount of experimental data is somewhat limited, however, an attempt was made to utilize a rather simple model for the analyzing of the upflow reactor performance. Rather rigorous modeling of a three-phase catalytic upflow reactor was conducted in [8] for catalytic hydrogenation of 1,5,9-cyclododecatriene. A mathematical description was based on an one dimensional heterogeneous model and led to a system of 12 combined algebraic–differential equations involving up to 24 parameters [8]. Dynamic behavior of the upflow fixed bed reactor was considered in [9,10]. However, for the purpose of reactor modeling in the present study another approach was adopted, which was originally developed for three-phase glucose hydrogenation [11].

The modeling of the upflow fixed bed reactor was based on the following assumptions:

(a) Radial gradients are negligible.
(b) Reactor operated under isothermal conditions.
(c) Hydrogen pressure is constant throughout the catalyst bed.
(d) Liquid distribution is uniform and the liquid flow has laminar character with the same velocity along the bed.
(e) Plug flow conditions prevail both in the liquid and in the gas phase. This is somewhat a simplification with respect to the liquid phase, as it was demonstrated [12], that at lower liquid velocity backmixing could be enhanced, leading to a necessity for utilization of more complicated axial dispersion model [8]. However, in the present study the liquid velocity was sufficiently high to neglect backmixing.
(f) Gas–liquid mass transfer is supposed to be fast, thus dissolution of hydrogen is not the limiting step.
(g) The film around the catalyst particle is divided into a dynamic and static zones. This concept was introduced [11] to average the impact of all the stagnant liquid zones, which could be in the reactor, including those inside the catalyst pores.

The mass balances in the liquid and gas phases are given by

$$D_{\mathrm{L}}\frac{\partial^2 C_{4-\mathrm{TBP}}}{\partial x^2} - U(x)\frac{\partial C_{4\text{-}\mathrm{TBP}}}{\partial y} = 0 \qquad (1)$$

$$D_{\mathrm{g}}\frac{\partial^2 C_{\mathrm{H}_2}}{\partial x^2} - U(x)\frac{\partial C_{\mathrm{H}_2}}{\partial y} = 0 \qquad (2)$$

where U is the linear flow rate, $U(x) = u(0 \le x \le \delta)$; $U(x) = 0(\delta < x \le h)$ (see Fig. 2).

Following [11], boundary conditions are defined. At the boundary conditions ($y = 0$), concentration of the substrate is equal to the initial concentration C_0 and the gas concentration has an equilibrium value C_{e}. At $x = 0$, $\partial C_{4\text{-}\mathrm{TBP}}/\partial x = 0$ and $C_{\mathrm{g}} = C_{\mathrm{e}}$.

Due to the chemical reaction it is supposed that the fluxes of reagents (4-TBP and hydrogen) are equal:

$$D_{4\text{-}\mathrm{TBP}}\left.\frac{\partial C_{4\text{-}\mathrm{TBP}}}{\partial x}\right|_{x=h} = D_{\mathrm{H}_2}\left.\frac{\partial C_{\mathrm{H}_2}}{\partial x}\right|_{x=h} \qquad (3)$$

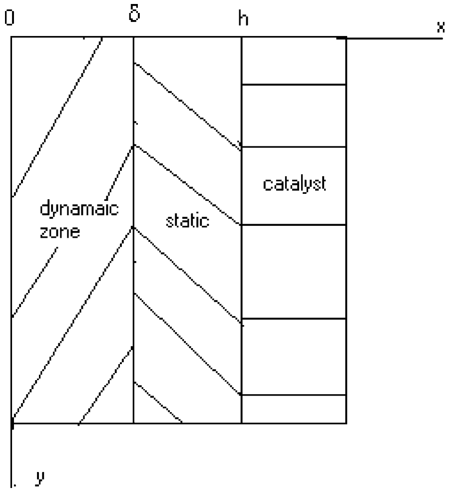

Fig. 2. Phase pattern (see explanation in the text).

If mass transfer is rate limiting one can assume the instantaneous chemical reaction leading to the surface concentration of the limiting substrate equal to zero on the surface.

Typically the equilibrium concentration of dissolved hydrogen is much less than the concentration of the organic substrate, hence up to a certain value of $y = y^*$:

$$C_{\mathrm{H}_2}|_{x=h} = 0, \quad y^* \le y \qquad (4)$$

after which diffusion of the substrate (4-TBP) is no longer compensated by its disappearance due to reaction, leading to

$$C_{4\text{-}\mathrm{TBP}}|_{x=h} = 0, \quad y^* \le y \qquad (5)$$

The reaction rate is thus determined by hydrogen diffusion at high substrate concentration and by 4-TBP diffusion at low concentrations. The analytic solution of the essentially simplified model of the upflow reactor is given as follows:

$$C(y) = C_0 - p_1 y, \quad y \le y^*;$$
$$C(y) = C^* \exp(-p_2(y - y^*)), \quad y \succ y^* \qquad (6)$$

where the parameters are defined [11] as follows:

$$p_1 = C_{\mathrm{e}} D_{\mathrm{H}_2} \Phi;$$

$$p_2 = \beta D_{4\text{-}\mathrm{TBP}} \Phi;$$

$$\beta = (1 - \tfrac{2}{3}\alpha)^{-1};$$

$$C^* = \frac{p_1}{p_2};$$

$$y^* = \frac{C_0 - C^*}{p_1};$$

$$\alpha = \frac{\delta}{h}. \qquad (7)$$

Parameter Φ is expressed in the following way:

$$F = \frac{\sigma^2}{Lv},$$

where σ is the relative wetted surface area (the ratio of the wetted surface to the catalyst volume), L the volumetric flow rate per unit of reactor cross-section, and v is the relative retaining volume, $v = \alpha\sigma h$. Molecular diffusion coefficient of hydrogen was taken to be $53 \times 10^{-5}\,\text{cm}^2/\text{s}$, while the diffusion coefficient of 4-TBP in isopropanol was calculated from the Wilke–Chang [13] equation. Diffusion coefficients of 4-TBP were found to be slightly dependent on the isopropanol mole fraction. For the purpose of modeling, the average value $14 \times 10^{-5}\,\text{cm}^2/\text{s}$ was used. The thickness of the liquid film h was estimated to be equal to 0.02 cm following the Satterfield method, $h = \varepsilon/2a$, where ε is the porosity of the bed (0.25) and a is the specific area ($6.35\,\text{cm}^2/\text{cm}^3$). Then the only remaining parameter, which should be calculated is the ratio σ/α. The value of $\alpha = 0.8$ was reported for glucose hydrogenation [14] and is adopted in the present study. However, comparison between experimental data and modeling (using the procedure described above without any adjustable parameters) revealed, that for the proper description the modified value Φ' should be used. This parameter is equal to the theoretically calculated one corrected with a coefficient $\psi = 0.2$ (e.g. $\Phi^* = \psi\Phi$). The necessity to introduce an adjustable parameter ψ is probably associated with the fact that not all the catalyst surface is accessible to reactants. This parameter can be thus considered as some sort of a catalyst effectiveness factor.

The simplified model presented above was applied for modeling of benzene hydrogenation in an upflow three-phase reactor [15]. Reaction was carried out at different liquid flows (0.1–$1.2\,\text{h}^{-1}$) at several temperatures and hydrogen pressures over a nickel catalyst (1.5 mm × 1.5 mm). This reaction was selected for the evaluation of the model as the physical properties of the system, including values of diffusion coefficients can be reliably calculated. The same methodology as discussed above was used to calculate benzene conversion at different conditions and compare them with those reported in [15]. Note that in these calculations there were no additional adjustable parameters and the reactor performance was estimated solely

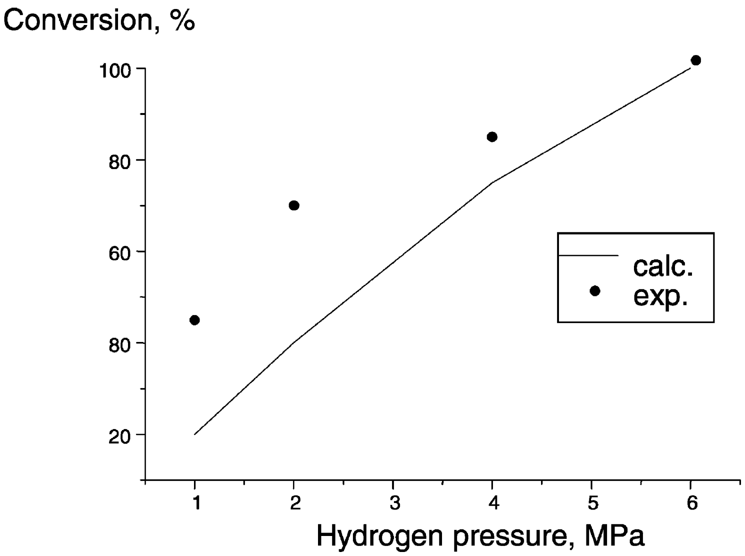

Fig. 3. Comparison between experimental [15] and calculated data on benzene hydrogenation in upflow three-phase reactor.

on the basis of available physico-chemical parameters. Results of calculations at 140 °C and 0.6 h^{-1} and different hydrogen pressures are presented in Fig. 3.

Experimental values at other conditions were reported in [15]. Thus, conversion at 1.2 h^{-1} and 4 MPa at 140 °C is equal to 66%, while the calculated value (note there was no fitting performed) was 65%. Interestingly, that even the conversion dependence on temperature can be quite reasonably explained with the utilized model. For instance, the calculated value of conversion at 0.6 h^{-1} and 4 MPa at 80 °C was equal to 55%, while the experimental one was 30%. Taking into account that the model is extremely simple, neglecting for instance reaction kinetics, the power of the model to describe the experimental data on hydrogenation of organic compounds in upflow three-phase reactor is remarkable.

4. Conclusions

An upflow three-phase reactor was utilized for 4-TBP hydrogenation over a commercial nickel-chromium catalyst. The reaction was selective to 4-*tert*-butylcyclohexanol with overall conversion reaching 97% at 2 MPa of hydrogen pressure. The stereoselectivity towards *cis*-4-*tert*-butylcyclohexanol was around 30%, which is similar to reported previously for the same reaction over Ni/Cr_2O_3 in a slurry reactor. This stereoselectivity value is close to the thermodynamic one. Experimental data were evaluated by a model, which assumes that at low conversion of organic compound the rate of the process is determined by the hydrogen mass transfer in the liquid film, while at high conversions the transfer of the organic compound to the catalyst surface is the limiting factor. The model considers the existence of a dynamic and a static zone of the liquid film as well as the fact, that not all the catalyst surface is accessible. The proposed model with the only one adjustable parameter describes well the experimental data.

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