
INVESTIGATION OF HYDROGENATION IN LIQUID PHASE. XVIII.*
EXPERIMENTAL VERIFICATION OF A THEORETICAL MODEL
OF A TRICKLE BED REACTOR

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The assumption of a theoretical model of a trickle bed reactor (plane wall) and the solution of relevant partial differential equation describing convective-diffusional transport of hydrogen in the flowing film of the reaction mixture have been experimentally verified. The hydrogenation of cyclohexene in methanol and 1-propanol on electrolytically deposited platinum black was chosen for the model reaction. The effect of the feed rate, partial pressure of hydrogen, temperature and physical properties of the reaction mixture on the reaction conversion were also studied on a laboratory trickle bed reactor.

In the preceding communications^{1,2} we solved a plane and a spherical model of a trickle bed reactor. The aim of this study is to verify experimentally the plane model¹ on a simple laboratory reactor and to provide further insight into the convective-diffusional transport of the dissolved hydrogen through the film of the reaction mixture flowing down the surface of a catalyst. As a model reaction we have selected hydrogenation of cyclohexene in the solution of methanol or 1-propanol on electrolytic platinum black.

Although the applicability of trickle bed reactors has been known for a longer period of time^{3,4}, there are few papers studying their properties, particularly the diffusional transport of hydrogen as a reaction component to the surface of a catalyst. An exception in this sense are the papers^{5,6}, which on the basis of experimental data examine the problem of mass transfer in a reactor consisting of a vertical column of spherical particles of porous catalyst. It has been established in these studies that the reaction rate is controlled by the diffusional transport of hydrogen through the flowing film of the reaction mixture and the mass transfer in the pores of the catalyst.

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In the presented work attention will be paid to the first of these phenomena. We start with the same assumptions used in the solution of the plane model of a trickle bed reactor¹:

1. The reactor is operated under the steady, isothermal, isobaric regime (physical parameters are constants). 2. The flow of liquid over the surface of the catalyst is laminar and no rippling occurs on the surface of the film. 3. The liquid enters the wall perfectly mixed with initial concentration of hydrogen c_0 . 4. The resistance to mass transfer in the gas phase is negligible, *i.e.* the concentration of the dissolved hydrogen in the film at the gas-liquid interface equals the equilibrium value everywhere (for the temperature and pressure of measurement). 5. The reaction taking place on the surface of the catalyst is irreversible, first order with respect to the dissolved hydrogen, and zero order with respect to the concentration of the hydrogenated substrate.

The fulfilment of these assumptions will be judged on the basis of obtained experimental results.

EXPERIMENTAL

Chemicals Used

Hydrogen, technical purity grade (electrolytic, Technoplyn Pardubice), before use purified on Ni/SiO₂ catalyst (Czechoslovak patent 111 791) and Cu/SiO₂ catalyst (Czechoslovak patent 91 868). Nitrogen, grade used for production of light bulbs (MCHZ Ostrava). Chloroplatinic acid, reagent grade (Safina Vestec). Lead(II) acetate, pure grade (Lachema Brno). Methanol, reagent grade (Lachema Brno), before use rectified on a laboratory bubble-cap column (10 theor. plates, reflux 1 : 10). 1-Propanol, reagent grade (Lachema Brno). Cyclohexane, pure grade (Lachema Brno). Cyclohexen, prepared by dehydration of cyclohexanol on γ -alumina⁷ (b.p. 82–83°C); before every use treated by sodium amalgam to remove cyclohexene hydroperoxide^{8,9}, and subsequently distilled on a laboratory distillation column. *trans*-4-Methyl-2-pentene, pure grade (Koch-Light, G. Britain). 2,4-Dimethylsulpholan, pure grade (Lachema Brno). Chromaton N-AW, (Lachema Brno), granularity 0.2–0.25 mm.

Preparation and Properties of the Catalyst

A similar type of the catalyst has been used earlier^{10,11}. The platinum black was deposited on a glossy surface of a cylindrical platinum cathode from 2% (weight) solution of chloroplatinic acid and 0.02% (weight) of lead(II) acetate. The anode was a coil of platinum wire (0.8 mm in diameter). On completion of electrolysis the surface of the platinum black was rinsed with distilled water and subsequently with a solvent used for hydrogenation.

The catalytic activity of the platinum black (defined by the reaction rate constant of the hydrogenation of cyclohexene in a selected solvent and related to the geometric surface of the cathode) was measured in a standard apparatus¹² at 25°C and the barometric pressure. The agitated reactor used¹³ was provided with a screw connecting piece mounted in the throat of the reactor to which a cylinder (8.3 mm in diameter, 40 mm long) was attached. The cylinder had a platinum coating 0.3 mm thick, on which the platinum black was deposited.

The conditions of electrolysis were chosen on the basis of experimental results shown in Figs 1 and 2. The figures show the dependence of the reaction rate constant on the current density I ,

and the duration of electrolysis t . The current density is expressed as a ratio of the current in the electrolyzer and the surface area of the cathode. The reaction rate constant in Fig. 2 for $t = 0$ corresponds to the activity of a glossy metal platinum. The conditions in further experiments were selected as follows: Duration of electrolysis $t = 6$ minutes, current density $I = 6 \cdot 10^{-3} \text{ A cm}^{-2}$.

Reaction Kinetics

The hydrogenation of cyclohexene on mentioned catalyst was carried out in methanol and 1-propanol. The reaction order with respect to the dissolved hydrogen in the reaction mixture was considered unity¹². The reaction order found under the conditions of measurement with respect to the hydrogenated substrate was in both cases zero for concentration of the substrate greater than 0.25% (weight). This assessment is demonstrated in Fig. 3, showing a typical example of the time dependence of the reaction rate constants K . The rate of hydrogenation, r , can be expressed by the relation:

$$r = \frac{dx}{d(W/F)} = Kc^* \quad (1)$$

Thus the selected model reaction fulfils assumption 5.

Apparatus

The verification of the plane model of a trickle bed reactor¹ was carried out on an apparatus formed by a vertical column, provided on its outer surface by an active layer of catalyst and wetted

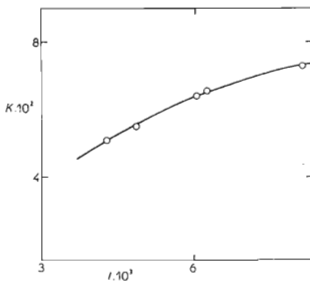


FIG. 1

Dependence of the Reaction Rate Constant of Hydrogenation of Cyclohexene in Methanol at 25°C and Barometric Pressure on the Current Density
Duration of electrolysis $t = 6$ min.

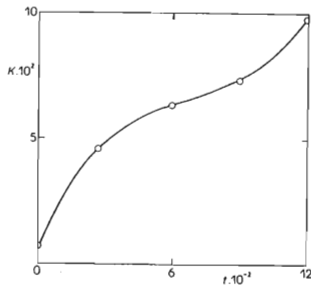


FIG. 2

Dependence of the Reaction Rate Constant of Hydrogenation of Cyclohexene in Methanol at 25°C and Barometric Pressure on Duration of Electrolysis
Current density $I = 6 \cdot 10^{-3} \text{ A cm}^{-2}$.

by the reaction mixture. This arrangement eliminated the disadvantages of the wetted wall (particularly the disturbing effects of the edges of the wall). In measurements, however, the assumption of the film thickness, s , being substantially smaller than the radius of the wetted column, R , had to be fulfilled. In the opposite case, the solution of the diffusion equation for the plane model could not be applied. This condition was fulfilled in all experimental runs. The maximum value of s/R ratio was 10^{-2} .

Reactor

A vertical cut through the reactor used is shown in Fig. 4. The reactor consisted of a top flange with a feed chamber, a glass temperature-controlled jacket, a bottom flange with a collecting device, adjusting screws and the wetted column itself. The amount of feed brought on the column (or the density of wetting) was determined by the size of the cone-shaped slit in the bottom part of the feed chamber (the thread on the top of the column served for its regulation) and the hydrostatic pressure between the slit and the overflow in the upper part of the feed chamber.

The wetted column was formed by inside temperature controlled tube (2 cm in diameter, 25 cm long) plated with platinum 0.3 mm thick. Similar platinum plating had a cylinder designed for the measurement of the reaction rate constant. The platinum surface was polished, degreased and rinsed with nitric acid and aqua regia prior to every experiment. An active layer of the plati-

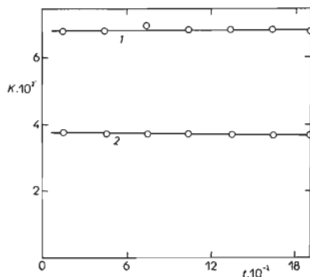


FIG. 3

Time Dependence of the Rate of Hydrogenation of 1% Solution of Cyclohexene in Methanol (1) and 1-propanol (2), in Mixed Reactor at 25°C and Barometric Pressure

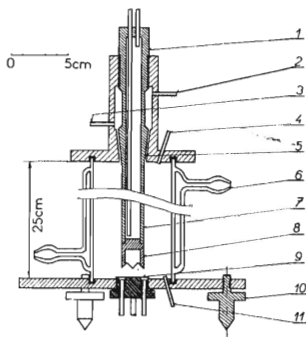


FIG. 4

Cut through the Reactor

1 Slit control; 2 overflow; 3 liquid phase inlet; 4 hydrogen inlet; 5 cone shaped slit; 6 temperature-controlled glass jacket; 7 wetted column with catalyst and inner temperature control; 8 collecting segment; 9 collecting device; 10 adjusting screw; 11 gas outlet.

num black was electrolytically deposited on the clean surface of the column. In experimental runs when the platinum black was not deposited on the whole wetted surface, of the column, the remaining portion of the surface was covered by a thin film of methylmethacrylate varnish. The varnish affected neither the reaction itself, nor the hydrodynamics of the film flow of the reaction mixture.

At the bottom end, the column was terminated by a collecting segment enabling samples from each of the four quadrants of the circumference of the column to be taken and thus, at the same time, to determine the uniformity of wetting on the whole circumference. The collecting device in the center of the bottom flange was formed by a nut with four channels located under the tips of the collecting segment and connected with the measuring vessels. Both flanges were equipped with inlet and outlet openings for gas and were cemented to the glass jacket.

Scheme of Apparatus

The arrangement of the apparatus is depicted in Fig. 5. Hydrogen (respectively nitrogen) was supplied from a pressure cylinder through a flow stabilizer S 2 (ÚAČHP Satalice), flow-meter, catalytic purifier and a saturator (saturating the gas with the vapors of solvent at the temperature of measurement) into the reactor. The reaction mixture (respectively pure solvent) was fed from

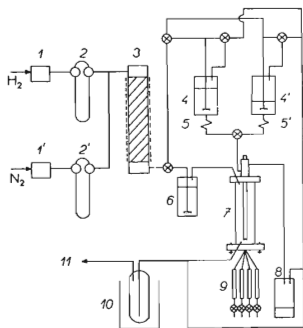


FIG. 5

Scheme of Apparatus

1, 1' Gas flow-rate stabilizer; 2, 2' flow-meters; 3 catalytic gas purifier; 4 reaction mixture storage tank; 4' pure solvent storage tank; 5, 5' temperature control; 6 presaturator of gas with vapors of solvent; 7 reactor; 8 storage tank; 9 measuring vessels; 10 freezing trap; 11 gas outlet.

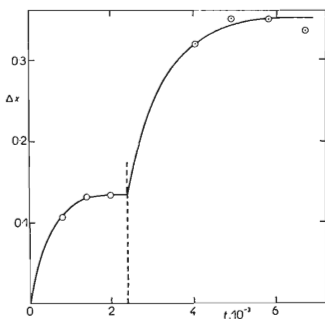


FIG. 6

Steadying of the Regime in the Reactor at 25°C and Barometric Pressure; Solvent Methanol

○ $N_{Re} = 6.24$; ◻ $N_{Re} = 13.2$.

the upper storage tank through a temperature control into the reactor. A part of the reaction mixture returned *via* overflow into the lower storage tank, thus keeping the flow rate of the reaction mixture into the column constant. The value of the flow rate was measured from time differences of volume of the reaction mixture passing through the reactor.

Method of Measurement

Having placed the column with deposited platinum black into the reactor, the whole apparatus was flushed with hydrogen (respectively a mixture with nitrogen). At the same time, the reaction mixture (1% solution of cyclohexene in the solvent) was saturated with hydrogen in the upper tank fulfilling thus assumption 3. In all experiments the initial concentration, c_0 , was equal to the equilibrium solubility of hydrogen in the reaction mixture at a given temperature and pressure. In the process of saturation the column was wetted with the pure solvent. The solvent was then switched to a solution of cyclohexene and after establishment of a steady state in the reactor, samples were taken for analysis. At least two samples were taken in each experiment.

Fig. 6 shows a typical course of the time dependence of the conversion at the beginning of the experiment and after the exchange of the feed (the instant of the exchange is marked in Fig. 6). The figure enables the rate of the transition of the system into the steady state to be estimated. The time necessary for the attainment of the steady state was in both cases 30–40 minutes. The attainment of the steady state, checked as has been mentioned, is the most important factor for the fulfilment of the assumption 1, since the isothermal and isobaric regime of the system can be easily ensured.

The experimental conversions of the reaction were compared in all cases with the values of the theoretical conversions, calculated using the solution of the model reactor (see Fig. 8 of the preceding paper)¹. In the calculation it was assumed that the properties of the reaction mixture are identical with those of the pure solvents. The values of the dimensionless groups (Sherwood number N_{Sh} , Peclet number N_{Pe} , geometric simplex P) and the theoretical conversions of the reaction were evaluated from physical constants of methanol and 1-propanol^{14–16}.

Analytical Method

The reaction mixture sampled from the reactor was analyzed by means of a gas chromatograph Chrom-2 with flame-ionization detection, operated under following conditions: stationary phase 10% of 2,4-dimethylsulpholane on Chromaton N-AW, the length of the column 1.6 m, the diameter of the column 0.6 cm, the carrier gas nitrogen (flow rate 0.8 ml min^{-1}), the temperature 50°C , the samples $3 \mu\text{l}$, the sensitivity 1 : 1000.

The degree of conversion was determined from the integral curve of the chromatographic chart. It has been established in the analysis, that the response of the detector for cyclohexene and cyclohexane are identical, and, under given conditions, it depends linearly on the amount of the sample injected into the column. The absolute value of concentration of cyclohexene in the reaction mixture was determined by means of an inner standard *trans*-4-methyl-2-pentene.

RESULTS AND DISCUSSION

Our experimental set-up enabled to examine the effect of the feed rate, the partial pressure of hydrogen and of the temperature on the reaction conversion, and to compare the results with the theoretical value of the conversion given by the solution of our verified mathematical model¹.

TABLE I

Ranges of System Parameters and of Some Quantities During Experiments

Parameter or quantity	Range of values	Parameter or quantity	Range of values
N_{Sh}	0.348 — 4.26	ΔX_{red}	0.70 — 0.28
$N_{Pe} P$	0.0478 — 14.8	K	0.753 — 6.83
N_{Re}	1.36 — 19.2	L	0.5 — 2.5
		Δx	0.0048 — 0.59

The result of this comparison is shown in Fig. 7. The figure plots the experimental conversion of hydrogenation of cyclohexene, Δx_E , at 25°C and the barometric pressure in the dependence on the values of the theoretical conversion, Δx_T , at the same parameters of the system. The ranges of individual parameters and quantities of the measurement are summarized in Table I. The table indicates that all measurements fell into the laminar region for $N_{Re} < 20$. For this region it is shown in the literature (see *e.g.*¹⁷), that no ripples appear on the surface of the film. Indeed, no rippling was

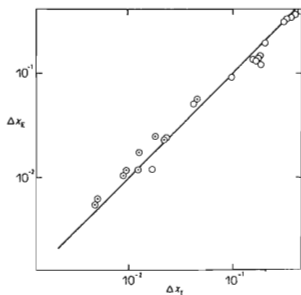


FIG. 7

Comparison of Experimental and Theoretical Values of Conversion at 25°C and Barometric Pressure

○ Methanol, ⊙ 1-propanol.

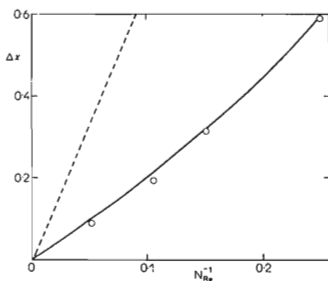


FIG. 8

Effect of the Feed Rate on the Reaction Conversion at 25°C and Barometric Pressure

Length of the active layer of catalyst $L = 4.3$ cm; feed 0.84% solution of cyclohexene in methanol.

observed during the measurements and the surface of the film was smooth in accord with assumption 2.

In experimental runs with a short wall of active catalyst (less than 1 cm), the wetted column held several equally spaced rings of the platinum black. In this manner, the conversion of hydrogenation was proportionally increased and hereby the accuracy of its determination. In our experimental arrangement it was necessary to make sure that the reaction mixture is again perfectly saturated with hydrogen before entering the following ring of the catalyst. The necessary spacing of the rings was calculated from an equation given by Sherwood and Pigford¹⁸:

$$1 - \varepsilon = 0.7857 \exp(-5.121D\tau/s^2), \quad (2)$$

where ε is the degree of saturation of liquid by gas, τ is the time of contact of phases. The calculation of the time of contact was performed for $\varepsilon = 0.95$ and the required distance between the rings amounted to 2 cm.

A good agreement of the experiment with the model is evident from Fig. 7. By a linear regression it has been established that the relation between the experimental and calculated values of the reaction conversion can be expressed by equation:

$$\log \Delta x_E = (1.021 \pm 0.047) \log \Delta x_T. \quad (3)$$

The presented result can be regarded as a very good agreement of the experimental values and the theoretical model. This agreement was found for both solvents used, so that the different physical properties of the reaction mixture (primarily the viscosity¹⁴ and the diffusion coefficient¹⁶) generalize even more the experimental verification of the model.

The effect of the feed rate, F , on the reaction conversion is shown in Fig. 8, where the feed rate is expressed by the Reynolds number of the film flow of the reaction mixture N_{Re} . There is a direct proportionality between both quantities according to the relation:

$$N_{Re} = F(4M_V/\pi aR\mu). \quad (4)$$

The solid line indicates the numerical solution of the diffusion equation for given parameters of the reactor. From the figure it follows, that the experimental points also comport well with this dependence. Apart from that, the broken line is a straight line belonging to a hypothetical kinetic regime of the reactor (according to Eq. (1)), with the absence of the diffusional resistance to the hydrogen transfer through the flowing film of the reaction mixture. The slope of the straight line equals rW .

The existence of the diffusional resistance to the hydrogen transfer in the flowing film of the reaction mixture has been, similarly as in the preceding papers^{5,6}, confirmed.

Its magnitude can be estimated from the value of the Sherwood number¹. For given conditions, the diffusional resistance is obviously small in the case of a slow reaction (low value of the reaction rate constant) and intermediate wetting densities (small thickness of the flowing film). From this follows, that it is not always possible to ensure such a regime in a trickle bed reactor (requested by Acres¹⁹), when the diffusional transfer of the reacting component in the film is without effect on the reaction rate.

Thus, from Fig. 8 shown, one can judge the magnitude of the diffusional resistance, or, in other words, the effectiveness of the model reactor for given conditions. The effectiveness can be characterized by the reduced conversion, ΔX_{red} , defined¹ as a ratio of the actual conversion to the maximum conversion attainable, provided that the concentration of hydrogen near the catalyst along the whole column equals the equilibrium value. The value of this quantity in Fig. 8 amounts to 0.287–0.358.

The effect of the partial pressure of hydrogen on the reaction conversion in given experimental set-up is shown in Fig. 9. Considering that the variation of the partial pressure of hydrogen was realized by dilution with an inert gas (nitrogen), a concentration gradient of hydrogen formed near the gas-liquid interface, making thus the concentration of the dissolved hydrogen lower than that corresponding to the composition of the gas phase. The experimental values marked with open circles were therefore corrected in the same way as in the work^{5,6}, using equation²⁰. The corrected values are marked with full circles. The correction applied amounts to about 8%, which is within the accuracy of the experiment and no unambiguous inference can be drawn about the character of the mass transfer in the gas phase. From the result it is obvious that the reaction is of the first order with respect to hydrogen and that the equilibrium value of concentration of the dissolved hydrogen is reached at the gas-liquid interface. This finding is identical with that of the preceding papers^{5,6} and confirms the validity of assumption 4.

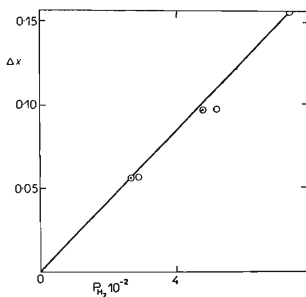


FIG. 9

Dependence of the Reaction Conversion on Partial Pressure of Hydrogen

Feed 1.07% cyclohexene in 1-propanol, $N_{Re} = 2.60$, temperature 25°C, length of the active layer of catalyst 9×0.5 cm. ○ Experimental values; ● corrected values.

The effect of the temperature on the reaction conversion was also examined. The value of the activation energy of hydrogenation of cyclohexene on the selected catalyst, $\Delta E = 3.2 \text{ kcal mol}^{-1}$, in the kinetic region was determined in a mixed reactor. The apparent value of the activation energy measured in the trickle bed reactor was $\Delta E' = 2.8 \text{ kcal mol}^{-1}$. It is obvious that the measured activation energy is lower in the case of the trickle bed reactor, since the activation energy of diffusion of hydrogen in methanol²¹ is, in given temperature range, smaller than the activation energy of hydrogenation. However, a considerable error of determination of the apparent activation energy (about $0.9 \text{ kcal mol}^{-1}$), brought about by a low value of the energy of hydrogenation of cyclohexene and by a narrow temperature range in which the experiments were carried out ($15 - 35^\circ\text{C}$), render the quantitative evaluation of the experimental data impossible.

It can be concluded that the published solution of the theoretical model of a plane trickle bed reactor¹ has been experimentally verified. The mass transfer in a flowing film of the reaction mixture can thus be described by differential equation expressing this convective-diffusional process. The assumptions made in the derivation of the model were also fulfilled to the full extent.

LIST OF SYMBOLS

a	weight content of substrate in the reaction mixture (—)
c_0	initial concentration of hydrogen in the reaction mixture (mol cm^{-3})
c^*	equilibrium concentration of hydrogen in the reaction mixture (mol cm^{-3})
D	diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)
F	feed rate of substrate (mol s^{-1})
I	current density (A cm^{-2})
K	reaction rate constant of hydrogenation ($\text{cm}^3 \text{ s}^{-1} \text{ cm}_{\text{cat}}^{-2}$)
L	length of wetted wall or column (cm)
M_v	molecular weight of substrate (g mol^{-1})
$N_{\text{Pe}} = w_{\text{max}}s/D$	Peclet number (—)
N_{Re}	Reynolds number (see Eq. (4)) (—)
$N_{\text{Sh}} = Ks/D$	Sherwood number (—)
$P = s/L$	geometric simplex (—)
r	reaction rate ($\text{mol s}^{-1} \text{ cm}_{\text{cat}}^{-2}$)
R	radius of wetted column (cm)
s	thickness of film (cm)
t	time (s)
w_{max}	velocity at the surface of film (cm s^{-1})
W	amount of catalyst (cm_{cat}^2)
Δx_E	experimental conversion (—)
Δx_T	theoretical conversion (—)
ΔX_{red}	reduced conversion (—)
ε	degree of saturation of liquid with gas (—)
μ	viscosity of liquid ($\text{g cm}^{-1} \text{ s}^{-1}$)
τ	time of contact of phases (s)

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