

## THE HYDROGENATION OF CYCLOHEXENE IN A LABORATORY TRICKLE-BED REACTOR

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The paper deals with the study of a laboratory trickle-bed reactor randomly packed with porous catalyst. The hydrogenation of benzene and cyclohexane solutions of cyclohexene on a palladium and platinum catalyst was chosen for measurement. The effect was studied of the catalyst pellet and the reactor diameter on the efficiency of the system with regard to the external and internal diffusion of the reaction species.

An important problem for the efficiency and research of trickle-bed reactor used particularly in large-scale units for hydrogenation of intermediate petroleum products is the mass transfer between the phases of the system dealt with in the preceding paper<sup>1</sup>. The aim of this study is to investigate the properties of a laboratory trickle-bed reactor randomly packed with catalyst. There are very few papers in the literature examining the mass transfer in trickle-bed reactors in detail; the effort has been focused mostly on simplified models of a trickle-bed reactor, *e.g.*<sup>2-6</sup>. As follows from the previous paper an exact determination of the total external resistance to mass transfer is very difficult owing to the complexity of the system (presence of three phases). The simplest and perhaps so far the only method is based on experimental study of the efficiency of the trickle-bed reactor. This means in practice that the reaction rate measured in the trickle-bed reactor is compared with that obtained with the catalyst of the same grain in a mixed reactor. The latter reactor permits a relatively safe elimination of the effect of external diffusion on the reactor rate, *i.e.* diffusion in the trickling film of liquid and in the point of contact of catalyst pellets as well as eventual non-uniformity of the liquid distribution in the system. The effect of the internal diffusion may be assessed conveniently by measuring the dependence of the reaction rate on the dispersion of the catalyst in the mixed reactor. The total resistance is then, of course, given by combined effect of the external and internal diffusion of the reaction species and may be obtained from comparison of the reaction rates in the trickle-bed reactor and the rate of hydrogenation measured in a mixed

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reactor with powdered catalyst in the so called kinetic region. The conditions for the diffusion in the kinetic region for a given case were defined in the previous paper<sup>7</sup>.

## EXPERIMENTAL

**Chemicals.** The traces of catalyst poisons were removed from cyclohexane (Lachema, pure) by boiling with Ni/SiO<sub>2</sub> catalyst<sup>8</sup> and activated carbon. Cyclohexene was prepared by dehydrating cyclohexanole on  $\gamma$ -alumina in the gas phase<sup>9</sup> at 330°C and atmospheric pressure (b. p. 82–83°C). Chloro-platinic (IV) acid and acetic acid were p.a. chemicals; benzene was of pure grade. The activated carbon used was Supersorbon (Degussa). Hydrogen and nitrogen were purified on Ni/SiO<sub>2</sub> (ref.<sup>8</sup>), or Cu/SiO<sub>2</sub> (ref.<sup>10</sup>), catalyst.

**Catalysts.** Catalyst I was 3% of palladium on activated carbon (CHZ ČSSP Záluží, No 4100) molded into cylindrical pellets 4 mm diameter. Smaller grain was prepared by crushing and screening the original catalyst. Catalyst II was 5% platinum on activated carbon prepared by soaking 4 mm cylindrical pellets of activated carbon (Supersorbon, Degussa) in chloro-platinic (IV) acid. The dried pellets were then reduced in hydrogen<sup>11</sup>.

**Hydrogenation in a mixed reactor.** The measurement of the catalyst activity in the kinetic region (from the viewpoint of external mass transfer) was carried out in a perfectly stirred glass reactor<sup>12</sup>. The reaction rate was being determined in regular time intervals from the loss of volume of hydrogen in a gas burette. The uncrushed catalyst pellets were held in a wire basket to prevent their abrading due to mixing<sup>13</sup>. The measurements were carried out in 20 ml of solvent at 25°C and atmospheric pressure.

**Hydrogenation in a laboratory trickle-bed reactor.** The measurements were carried out in an apparatus schematically shown elsewhere<sup>14</sup>. The trickle-bed reactor consisted of a standard glass column NZ 14 or 29 with ground joints. The inner diameter of the column was 1.33, 1.50 or 3.04 cm. The column was thermostated by a jacket. The volume flow rates of hydrogen and nitrogen were measured by flow meters; the flow rates were stabilized. The gas mixture was purified catalytically, dried and saturated by vapours of the used solvent (benzene or cyclohexane) before entering the reactor. The purified gas entered the reactor at the column top. The liquid mixture was driven by a piston pump from storage bottles and discharged on the top of the column through a central nozzle. The reactor was filled to a given height of the catalyst, the liquid flow rate was set and the supply of the pure solvent turned on. After setting the flow rates of gases and perfect wetting of the catalyst surface the supply of the pure solvent was changed for the solution of cyclohexene in the given solvent. The reaction mixture was then sampled and analyzed in twenty minute intervals. The amount of cyclohexene was determined by Hanuš' method<sup>15</sup> based on addition of bromine iodide on the double bond. Having reached the steady state the flow rate of the liquid phase was changed and the measurement continued in an analogous way. It was established that the maximum over-all experimental error of the reaction rate was 10% rel.

## RESULTS AND DISCUSSION

The mass transfer in a random trickle-bed catalytic reactor was studied on hydrogenation of benzene solution of cyclohexene on the palladium catalyst (*I*), and of cyclohexane solution of cyclohexene on the platinum catalyst (*II*). Zero reaction order with respect to concentration of substrate was found in both cases. The reaction

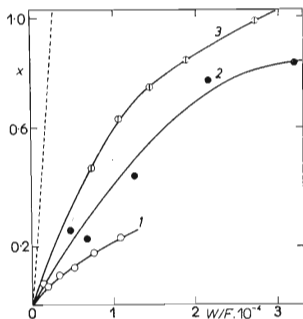


FIG. 1

A Plot of Conversion  $x$  versus  $W/F$   
Catalyst I, solvent benzene,  $d_p = 0.05$  cm,  
1  $L = 1$  cm, 2  $L = 3$  cm, 3  $L = 10$  cm.

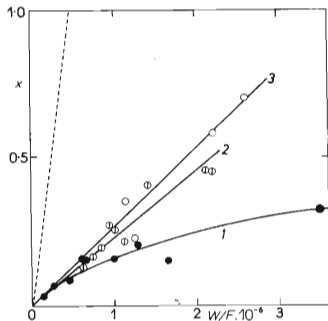


FIG. 2

A Plot of Conversion  $x$  versus  $W/F$   
Catalyst I, solvent benzene,  $d_p = 0.155$  cm,  
1  $L = 3$  cm, 2  $L = 5$  cm, 3  $L = 10$  cm.

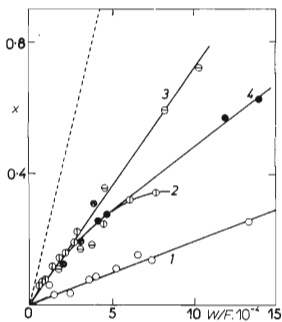


FIG. 3

A Plot of Conversion  $x$  versus  $W/F$   
Catalyst I, solvent benzene,  $d_p = 0.4$  cm,  
1  $L = 2.8$  cm, 2  $L = 5.6$  cm, 3  $L = 11.3$  cm,  
4  $L = 16.9$  cm.

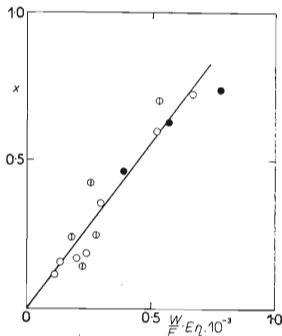


FIG. 4

A Plot of Conversion  $x$  versus  $E\eta W/F$   
Catalyst I, solvent benzene,  $L = 10$  cm,  
●  $d_p = 0.05$  cm, ○  $d_p = 0.155$  cm, ◻  $d_p = 0.4$  cm.

TABLE I  
Reactor Efficiency from the Viewpoint of External and Internal Diffusion and Over-All Effectiveness of the Catalyst

Grain diameter cm	Effectiveness factor of catalyst $\eta$	Effectiveness outside the catalyst grain $E$	Over-all effectiveness $\eta \cdot E$
0.052	0.20	0.15	0.73
0.155	0.095	0.16	0.015
0.40	0.022	0.24	0.005

Catalyst I; solvent benzene;  $d_t = 1.33$ ;  $L = 10$  cm;  $V_L = 3.5$  cm<sup>3</sup> min<sup>-1</sup>.

rate with respect to hydrogen was not of the first order on either of the catalysts even in the kinetic region (the apparent reaction order was about 0.64), a fact that was attributed to the specific behaviour of the used catalysts. All experimental data were plotted in the usual kinetic coordinates, *i.e.* conversion  $x$  versus  $W/F$ . Typical examples of these plots for various conditions are shown in Figs 1–3. To facilitate analysis of the effect of mass transfer outside the pellet on the reaction rate and hence on the efficiency of the system each graph shows also by broken straight line the situation in which the above effect is zero (the experimental results were obtained from measurements in the mixed reactor using catalyst of identical grain). The linear

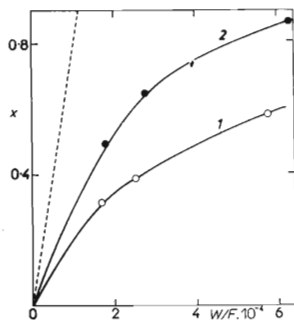


FIG. 5  
The Effect of Reactor Diameter on the Relation between Conversion  $x$  and  $W/F$

Catalyst II, solvent cyclohexane,  $d_p = 0.4$  cm,  $L = 10$  cm 1  $d_t = 1.50$  cm, 2  $d_t = 3.04$  cm.

character suggests the zero-th order of the reaction with respect to the hydrogenated substrate. Figs 1—3 further indicate that the increasing height of the catalyst bed increases the reaction rate and hence the efficiency of the system. This fact is apparently associated with the non-uniformity of the flow of liquid near the top of the column<sup>16</sup>; this effect, of course, becomes more manifest in short beds.

Selected values of the efficiency of the reaction system from the viewpoint of external mass transfer are summarized in Table I together with the effectiveness factor of the catalyst (necessary values of  $\eta$  which are limited mainly by diffusion of hydrogen were taken from previous work<sup>13</sup>). The over-all effectiveness of the catalyst is then, of course, given as a product of both quantities and it is also indicated in this table. While the effectiveness of internal catalyst surface (effectiveness factor) increases with decreasing size of the catalyst grain, the efficiency of the trickle-bed reactor from the viewpoint of external mass transfer decreases. This result leads to a conclusion that there exists apparently an optimum value of the size of catalyst grain for which the reaction rate reaches a maximum. In practical application, however, one has to take into account the pressure drop of the gas passing through the reactor; this depends considerably on the size of the catalyst grains. From the data given in Table I it thus follows that the external diffusion of the reaction components plays expectedly an important role in total resistance to mass transfer in a trickle-bed reactor.

The consistency of the experimental data and the fit of the kinetic equation was tested by plotting the reaction conversion *versus*  $EnW/F$ , *i.e.* the volume rate, corrected by the factor of external and internal diffusion (see Fig. 4). The slope of the best straight line through the experimental points equals in this case the value of the reaction rate on powdered catalyst.

The effect of the diameter of the reactor used is apparent from Fig. 5. The measurements were carried out in this case in two reactors of different diameter packed with the platinum catalyst II. The broken straight line in the figure corresponds again to the kinetic region. From the results it is seen that larger diameter reactor displays higher efficiency of the system which can be apparently attributed to the fact that the distribution of liquid in such a reactor is more favourable, *i.e.* a smaller portion of liquid trickles down the wall. The magnitude of the wall flow is the smaller the greater the ratio of the simplex  $d_t/d_p$  (ref.<sup>16</sup>). The non-uniformity of liquid flow in the axial and radial direction caused that even a simple model of the reactor could not be found which would characterize its properties.

It may be concluded that the proposed method of determining the effect of mass transfer in a trickle-bed reactor on the reaction rate is so far the most reliable since there has been no method available to date enabling the intensity of this effect to be determined.

## LIST OF SYMBOLS

$d_p$	diameter of catalyst grain (cm)
$d_t$	reactor diameter (cm)
$E$	effectiveness outside the catalyst grain
$F$	feed rate (mol min <sup>-1</sup> )
$L$	length of bed (cm)
$P_H$	partial pressure of hydrogen (Torr)
$r$	reaction rate (mol min <sup>-1</sup> g <sub>cat</sub> )
$V_L$	liquid flow rate (cm <sup>3</sup> min <sup>-1</sup> )
$W$	weight of catalyst (g)
$x$	conversion
$\eta$	effectiveness factor

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