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Absorption accompanied with chemical reaction in trickle-bed reactors

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Abstract—A new development in the field of internals in packed columns is the use of structured packing types. Recently, a new structured packing type coated with a thin alumina layer (KATAPAK™) has been developed. In this report, the results of an experimental and theoretical study concerning the possible applicability of this new packing material for hydrogenation processes in a trickle-bed reactor is presented. The palladium catalyzed hydrogenation of x-methylstyrene is used as a model reaction to study hydrodynamics and mass transfer characteristics in a trickle-bed reactor under reactive conditions. Conversions at several process conditions are measured in a pilot plant in which 3 mm spheres as well KATAPAK™ is applied as packing materials. A comparison of the results of some physical absorption experiments with the results of hydrogenation experiments showed that the resistances in series model—in which the total resistance against mass transfer is calculated from the separate resistances—is not valid in systems where heterogeneous reactions at the solid surface can enhance the mass transfer-rate at the gas–liquid interphase. With the aid of a developed trickle-bed reactor model, based on liquid diffusion, simultaneous reaction at the solid surface and zero volume mixing points, the mass transfer phenomena in trickle-bed reactors in conditions where the resistances in series model fails can be explained and described. The numerically solved model calculates the hydrogen profiles in the liquid films of the reactor and over all single pass conversions at several process conditions. These conclusions are confirmed by the results of the simulation of a model reactor, i.e. the laminar film reactor with a catalytically active wall. From the results of the measurements it could be concluded that in trickle-flow conditions, the application of KATAPAK™ does not significantly improve on the overall performance of trickle-bed reactors. The increase of the physical absorption rate due to better mass transfer characteristics of structured packings compared to dumped packing types—as reported in literature—will be eliminated to a certain extent in reactive systems due to the enhancement effect of heterogeneous reactions in trickle-flow operation. © 1997 Elsevier Science Ltd

Keywords: Structured packing; trickle-bed reactor; hydrogenation.

1. INTRODUCTION

In process industry, the cocurrent gas–liquid trickle-bed reactor is widely used for heterogeneously catalyzed gas–liquid reactions. The earliest antecedent probably was the so-called 'trickling filter' which has been used for removal of organic substances from waste water streams by aerobic bacterial action. This study presents the results of an experimental and theoretical investigation concerning the possible applicability of a structured metal-based packing as substitute for dumped packings in trickle-bed reactors. If, by means of structured packing, mass transfer can be increased, conversions will be higher.

A possible application of catalytically active structurized packing could be the catalytic hydrogenation of olefines in a cocurrently operated trickle-bed reactor. Main objective is to investigate whether catalytically active structured packing, e.g., KATAPAK™, could be an attractive alternative in these hydrogenation processes. Therefore the results are presented of an experimental study on the influence of KATAPAK™ on the mass transfer/conversion rates in a cocurrent gas liquid trickle-bed reactor compared to a reactor filled with spheres. For this

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purpose a model reaction was selected: the (fast) irreversible hydrogenation of α-methylstyrene to cumene over palladium.

Usually chemical processes in three-phase reactors are described with the resistances in series model in which the overall mass transfer rate is calculated from the individual resistances respectively. From results presented in literature, however, it can be concluded that this model may lead to substantial deviations for fast heterogeneous reactions at solid surfaces in trickle-bed reactors. Among others, Turek and Lange (1981) reported of values for the overall mass transfer coefficient obtained for the hydrogenation experiments to be an order of magnitude larger than those observed for physical absorption. It seems that the mass transfer-rate is enhanced. Therefore a 'trickle-bed reactor model' is developed based on liquid diffusion, simultaneous reaction at the solid surface and zero volume mixing points which is able to describe and explain mass transfer phenomena in trickle-bed reactors at conditions where the resistances in series model fails.

2. RESISTANCE IN SERIES MODEL

When a heterogeneous gas–liquid reaction takes place in a three phase reactor, several transport steps can affect significantly the overall reaction rate. The gaseous species must first be transferred from the gas to the liquid, then through the liquid and, together with the liquid species, toward the solid catalyst surface. In case of a porous catalyst in combination with a relatively slow reactions, the reactants may diffuse inside the porous structure of the catalyst, reacting on its surface. The description of mass transfer according to these sequential transport steps is called the resistances in series model, see, e.g. Westerterp *et al.* (1984).

The overall volumetric mass transfer coefficient according to the resistances in series model is expressed by

$$\frac{1}{k_{ov}a} = \frac{m}{k_G a} + \frac{1}{k_L a} + \frac{1}{k_p a_p} + \frac{1}{R}. \qquad (1)$$

For slightly soluble gases such as hydrogen the value of m ($= C_L/C_G$) will be significantly less than unity. For the hydrogenation of α-methylstyrene the reactants will only react on the outer surface of the catalyst because of the high intrinsic reaction rate of the system. Therefore the first and last term in eq. (1) can be neglected. Moreover, if a pure gas phase is used no gas-phase resistance occurs. The liquid side mass transfer coefficient, $k_L a$, may be obtained by absorption measurements with or without chemical reaction in the liquid phase.

3. EXPERIMENTAL SETUP

The experimental setup consists of different sections: gas-mixing, liquid circulation, analytical and reaction. The flow rates of the gas were determined and kept constant with the aid of thermal mass flow controllers. The gas can be saturated with the solvent before entering the column and will not be recycled.
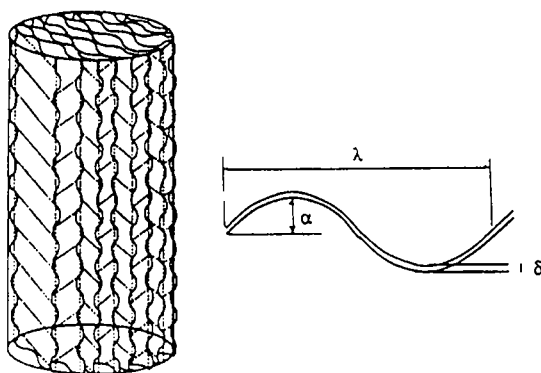

Fig. 1. Schematic representation of KATAPAK™.

Table 1. Geometry and properties of the packing types

Glass spheres		KATAPAK™	
d_p	3.0 mm	λ	7.7 mm
		α	2.5 mm
		δ	0.5 mm
ε	0.40	ε	0.84
a_g	1200 m^{-1}	a_g	656 m^{-1}

After the gas leaves the reaction section it will pass a cold trap to remove traces of organic compounds before venting. The liquid will be introduced and kept in the experimental setup in two 60 l storage vessels which are stored at a desired temperature (< 370 K). The liquids are kept under a nitrogen atmosphere (99.9 vol%). The composition of the liquid phase was analyzed by means of gaschromatography. A flame ionization detector (FID) was used to measure the concentrations of the occurring liquid compounds. The reaction section consists of three parts. On top of the actual reactor, a fixed bed of about 10 cm is placed (3 mm glass spheres) in order to assure a uniform distribution. This section also contributes in heating up the gas phase to the desired reactor temperature. For detailed information on the reactor configuration the reader is referred to Versteeg and van Swaaij (1988a). To avoid wall channeling of the liquid phase when applying KATAPAK™ (supplied by Sulzer and presented schematically in Fig. 1), the elements were tight covered by sheets of Kapton. The geometry and properties of the packing types are summarized in Table 1.

4. EXPERIMENTAL RESULTS

4.1. *Physical absorption of* CO_2 *in water*

For this purpose the reactor was filled with 3 mm glass spheres. Using pure CO_2 as gas and distilled water as liquid, pure physical absorption occurs and the net decrease in gas flow is measured. Gas and liquid phase were assumed to pass through the reactor in ideal plug flow mode. From the combined material balances for gas and liquid phase the $k_L a$-value can be

Table 2. Experimental conditions physical CO_2 absorption in distilled water at 313 K

Packing: Glass spheres

d_p	3.0 mm
$V_{s,L}$	3.31–9.33 mm s^{-1}, pure water
$V_{s,G}$	9.1–81.7 mm/s^{-1}, pure carbon dioxide
L	400 mm
d_t	36.2 mm

calculated according to

$$k_L a = -\frac{\phi_l}{LS} \ln\left[1 - \frac{\phi_{g,\text{in}} - \phi_{g,\text{out}}}{m\phi_l} \right]. \qquad (2)$$

The solubility was calculated from the data summarized by Versteeg and van Swaaij (1988b). The decrease in flow rate of a carbon dioxide flow due to absorption in water was measured at 313 K in a trickle-bed reactor filled with glass spheres with an average diameter of 3 mm. The packing height in these experiments was 400 mm. The flow regime that occurred was trickle flow for all gas and liquid loads. In Table 2 the experimental conditions used are presented. The main goal of these experiments was to obtain an impression of the order of magnitude of the value of $k_L a$ in the trickle bed reactor at operating conditions.

The results of the absorption experiments are presented in Fig. 2 and $k_L a$ varies between

$$0.006 < k_L a < 0.014 \text{ s}^{-1}. \qquad (3)$$

An increase of the value for $k_L a$ can be observed at decreasing gas velocity due to rimpling phenomena and at increasing liquid velocity probably caused by a better wetting efficiency of the solid (glass) phase at higher liquid velocities. The pressure drops during all experiments were about 10–50 Pa over the packed bed height of 0.5 m and therefore very difficult to
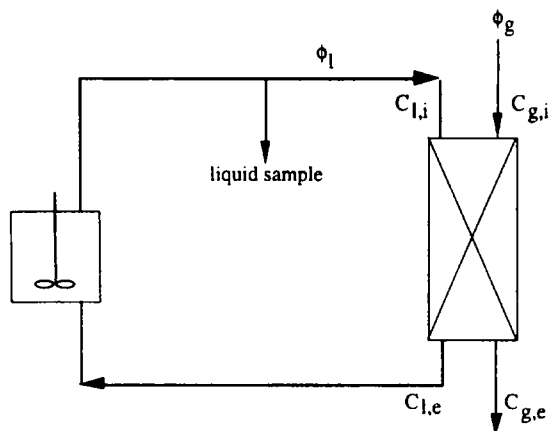

Fig. 3. Full liquid recycle configuration.

determine very accurately. Measurements at liquid velocities below 0.003 m s^{-1} were also performed but resulted in inaccurate data due to the fact that almost complete saturation (over 85%) of the liquid phase occurred.

4.2. Hydrogenation of α-methylstyrene

Because of the small conversions obtained in single pass operation, for the benefit of accuracy in analysis, the experiments were performed with full recycle of the liquid, see Fig. 3. If the concentration of the reactant will be monitored at the entrance of the tricklebed reactor, from the slope of the conversion-time plot $k_{ov} a$ can be estimated with eq. (4):

$$C_{\text{ams},t=t} = C_{\text{ams},t=0} - \left(\frac{k_{ov} a m C_g}{k_{ov} a + k'}\right)$$

$$\times \left\{ L + \frac{\phi_l}{S(k_{ov} a + k')} \right.$$

$$\times \exp\left[-\frac{(k_{ov} a S + k' S)}{\phi_l} \right] L \left. \right\} \left(\frac{Sk'}{V_R}\right) t. \qquad (4)$$
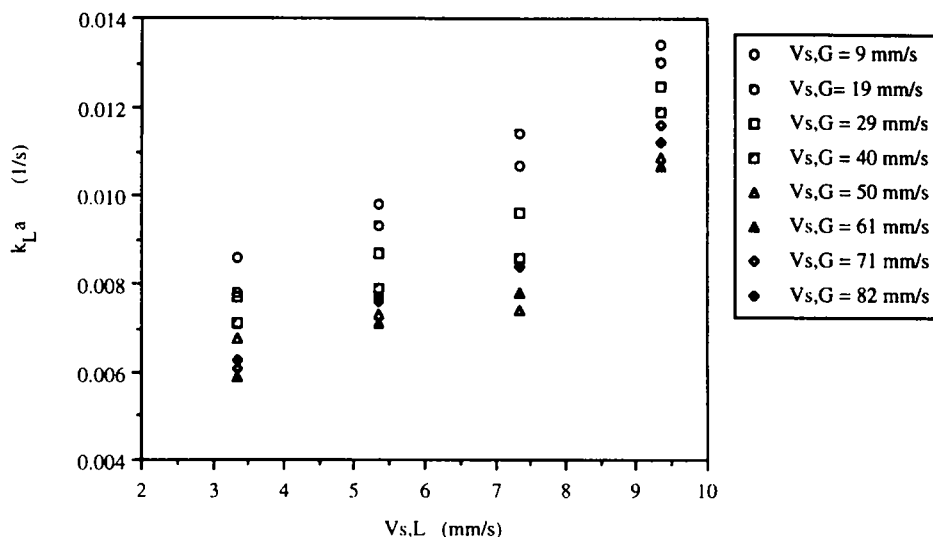
Fig. 2. Mass transfer results physical CO_2 absorption in distilled water at 313 K.

4.2.1. Mass transfer parameters spheres. The experimental conditions applied are presented in Table 3. Before the experiments were performed the catalyst was activated *in situ* for 2 h 110°C in a hydrogen atmosphere. Batch experiments in which several activation experiments were tested showed that this procedure resulted in a sufficiently activated catalyst.

In Fig. 4 the results of the mass transfer determination at several gas and liquid velocities are presented graphically. Part of the results were obtained in the non-foaming regime. At these lower liquid velocities a slight decrease of the overall mass transfer coefficient with increasing liquid velocity is observed. This may be caused by an increase in the total liquid hold-up resulting in an increase in thickness of the liquid layer flowing over the solid phase (if complete wetting is assumed at all conditions). At velocities above the transition zone where foaming occurs no consistent correlation of the overall mass transfer parameter with increasing liquid velocity can be determined. Since the value of the specific area, a (m^{-1}), will increase due to foaming, no increase of the value k_{ov} is to be expected from the results.

The most remarkable result is that the values for the overall mass transfer coefficients measured with reaction for the region without foaming, i.e. in the trickling flow-regime, are significantly higher (6–8 times) than those obtained for physical absorption experiments:

$$0.036 < k_{ov}a < 0.090 \text{ s}^{-1}. \tag{5}$$

It should be noted that the experimental conditions are identical and that the differences in physical properties between the two systems (water; viscosity $= 0.653 \text{ kg m}^{-1}\text{s}^{-1}$ and diffusivity $= 2.7 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ (Versteeg and van Swaaij, 1988b) and organic system; viscosity $= 0.60 \text{ kg m}^{-1}\text{s}^{-1}$ and diffusivity $= 1.6 \times 10^{-8} \text{ m}^2\text{s}^{-1}$ (Satterfield *et al.*, 1968)) are relatively small (according to the penetration-model only a difference of a factor of about 2.5 is to be expected for k_L), therefore a semi-quantitative comparison is allowed.

4.2.2. Mass transfer parameters KATAPAK™. Katapak™ was used as an example for the new type of structured packing material to perform similar hydrogenation experiments. Using similar conditions

Table 3. Experimental conditions of hydrogenation for spheres

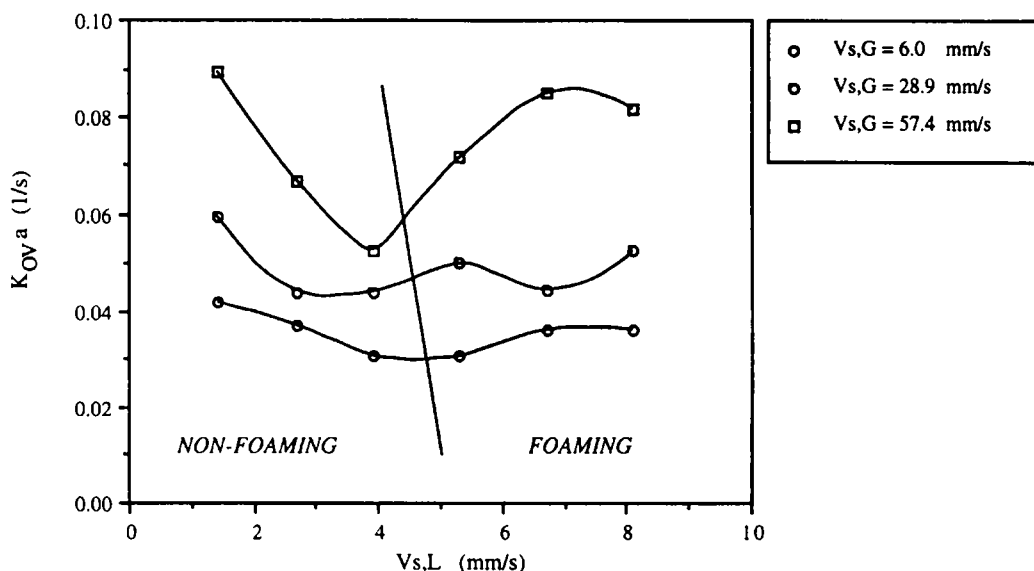| Packing	P_d on γ-alumina spheres	
	$d_p = 3$ mm	
	palladium content: 3.0%	
	palladium surface: 70 $m^2 g^{-1}$	
$V_{s,l}$	1.3–8.1 (10^3 m s^{-1})	
$V_{s,g}$	6.0 57.4 (10^3 m s^{-1})	
C (α-methylsytrene)		0.512–2.107 kmol m^{-3}
Fraction (hydrogen)		1.00, dimensionless
L (active bed)		400 mm; L (inert): 90 mm
d_t		36.2 mm
T (reactor)		313.0 K

Fig. 4. Full liquid recycle configuration for the hydrogenation of α-methylstyrene with spherical catalyst.

a direct comparison with the results of the hydrogenation experiments obtained for the conventional 3 mm spheres packing is justified. Although the porous spheres have a much higher (catalytically active) surface to volume ratio compared to KATAPAK™, preliminary calculations (Thiele moduli), however, showed that owing to the fast reaction only the outer surfaces of both packing types contribute to the reaction rate. The palladium content in KATAPAK™ is significantly lower but the palladium is most likely concentrated at the most outer surface of the alumina coated structured packing. Based on these assumptions, both types of catalyst are comparable concerning their contribution to the overall performance of the trickle-bed reactor. Operating conditions are presented in Table 4.

The results concerning the overall mass transfer coefficients for several process conditions are presented graphically in Fig. 5. Contrary to the results with conventional packing no foaming was visually observed over the complete range of process conditions.

The pressure drops during all experiments were so low that could be determined. An increasing overall mass transfer coefficient with the liquid velocity is observed. A better wetting efficiency at higher liquid loads was noticed and is probably the main reason for this increase due to a higher value for the specific area.

$$0.04 < k_{ov}a < 0.09 \text{ s}^{-1}. \tag{6}$$

The results also show an increase of mass transfer with superficial gas velocity due to rimpling effects. In the non-foaming regime with spheres a slight decrease of mass transfer with increasing liquid velocity was determined while with KATAPAK™ a more pronounced increase was observed. Therefore the largest difference in the overall mass transfer parameter is found at higher liquid velocities (disregarding the measurements in the foaming regime). In the most favorable case the overall mass transfer is increased by a factor 1.5 when applying KATAPAK™. Furthermore, it is concluded that at moderate liquid loads $(V_{s,L} \leqslant 8 \text{ mm s}^{-1})$ complete wetting does not occur in

Table 4. Experimental conditions of hydrogenation for KATAPAK™

Packing	KATAKAP™ (palladium coated)
	Palladium content: 0.55%
	Palladium surface: 0.35 m^2 g^{-1}
$V_{s,L}$	$2.7 - 9.8 \times 10^3$ m s^{-1}
$V_{s,g}$	$5.0 - 48.2 \times 10^3$ m s^{-1}
C (α-methylstyrene)	$0.478 - 2.201$ kmol m^{-3}
Fraction (hydrogen)	1.00, dimensionless
L (active bed)	400 mm; L (inert): 90 mm
d_t	39.0 mm
T (reactor)	313.0 K
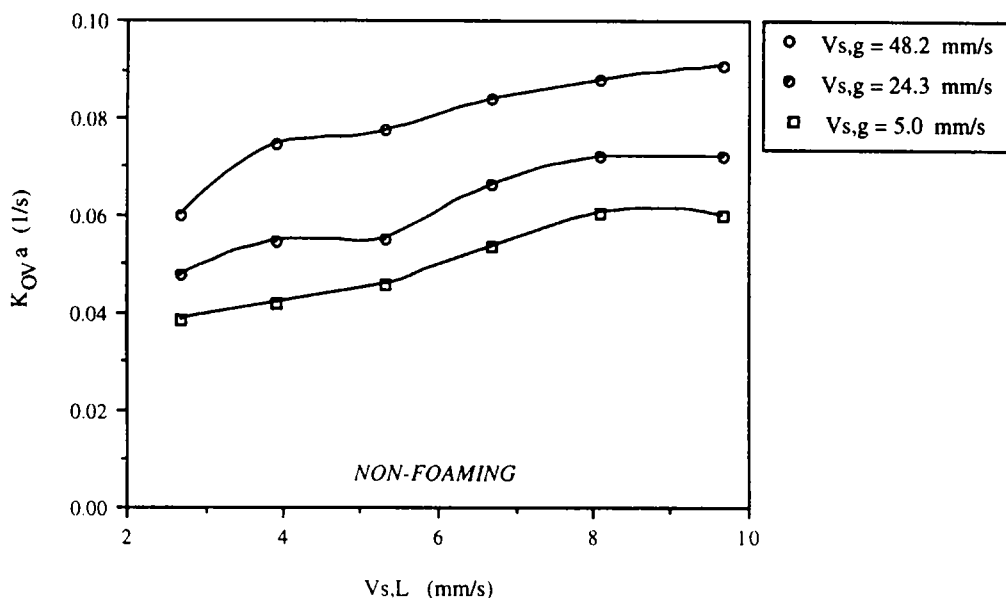
Fig. 5. Full liquid recycle configuration for the hydrogenation of α-methylstyrene with the KATAPAK™ catalyst.

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the upper part of the active packing. Visual observations supported this conclusion. This result can be described as disappointing in comparison to literature data where structured packing is used for distillation processes (Bravo et al., 1985). In these countercurrent, pure physical operations an increase with a factor 5–10 were reported caused by new structured packing types. It should be noted, however, that in the present study the geometrical area of the spheres is about a factor two higher that of KATAPAK™ which affects the possible increase owing to use of the structured packing substantially.

4.3. Discussion

In the resistances is series model in which the total resistance against mass transfer is calculated as the sum of the separate resistances, the overall mass transfer coefficients should by definition be smaller than (or at maximum equal to) either one of the individual coefficients. In the physical absorption experiments only the resistance against mass transfer near the gas–liquid interphase is present and equal to the reciprocal value of $k_L a$. In the hydrogenation experiments the resistance near a catalyst particle, the reciprocal value of $k_S a_p$ is added. Therefore it should be concluded that the resistances in series model fails in explaining the mass transfer characteristics observed in the present study.

Turek and Lange (1981) performed comparable experiments also with and without reaction in trickle-beds. Identical results were presented in which the overall mass transfer coefficients were found to be 10 times higher than the separately measured values for $k_L a$. In their experiments no difference in physical properties were present due to the use of identical systems. In a first explanation Turek and Lange stated that in the absorption process, the active interfacial area between gas and liquid is formed mainly by the dynamic part of the fluid phases, as the static part is almost saturated by gas (hydrogen). The area between gas and static hold-up is not at all significant to contribute for the mass transfer process. However this area plays an important role under the conditions of reaction, as the hydrogen is in this case consumed by reaction and accordingly a transport of gas takes place through this area. Their second explanation is microturbulence in the liquid film formed by reaction (thermo-convection and increased back diffusion of the products). The effective thickness of the boundary layers are decreased by microturbulence, which results in an increase of the $k_L a$- and $k_p a_p$-values. Despite the fact that these explanations contribute towards the observed effect, none of these reasons can completely explain the substantial differences in the values observed for the overall mass transfer coefficients.

5. ABSORPTION SIMULATION MODELS

In order to qualitatively understand the observed experimental phenomena, two theoretical routes have

been studied. In the first route a simulation model is developed that describes the present hydrogenation process in an idealized reactor, the laminar film reactor. The second route consists of a model simulating the overall process occurring in trickle bed reactors. The objective is to estimate the absorption rates that can be expected for processes with catalytic chemical reactions.

5.1. Laminar film model

The liquid flow over the catalyst materials inside the trickle-bed reactor can be simulated by a model reactor; the laminar film reactor with a catalytically active wall. In the film reactor no disturbing effects owing to the hydrodynamics, e.g. dynamic vs static hold-up, partial wetting and liquid-film break-up, occur. Therefore the description of the hydrogenation process from fundamentals is simple and straightforward and may possibly give additional information on the experimental results.

The absorption of a gaseous reactant into a laminar film can be described by

$$v_{max}\left(1 - \left(\frac{y}{\delta_{film}}\right)^2\right)\frac{\partial C}{\partial x} = D_L \frac{\partial^2 C}{\partial y^2}. \qquad (7)$$

The x-direction is the vertical downflow and the y-direction, the liquid film perpendicular to the flow, respectively. Moreover, it is assumed that the entrance length for the hydrodynamic velocity profile is negligible. For more detailed information on the hydrodynamics the reader is referred to Bird et al. (1960).

Equation (7) is subjected to the following boundary conditions:

$$x = 0 \text{ (i.e. the gas–liquid interface)}$$

and

$$y \geqslant 0: C = C_{sat} \qquad (8a)$$

$$y = 0 \quad \text{and} \quad x \geqslant 0: C = C_i \qquad (8b)$$

$y = \delta$ and $x \geqslant 0$ (the catalytically active wall):

$$-D_L \frac{\partial C}{\partial y} = \frac{R}{W} = k''C. \qquad (8c)$$

By means of changing the value of k'' in eq. (8c) the regime of the absorption process can be varied, i.e. $k'' = 0$ is similar to physical absorption in a laminar falling film and in case $k'' = \infty$ the catalytic reaction is instantaneous compared to the absorption rate respectively. With the aid of a numerical technique (Baker and Oliphant, 1960) eqs (7) and (8) can be uniquely solved, resulting in absorption rates as function of among others the reaction rate and contact time (i.e. film length).

5.2. Trickle bed model

The model is based on the work of Astarita and Beek (1967). It is assumed that the flow geometry of the model is represented by a series of zero volume mixing points separated by relative short lengths of vertical flat plates over which the liquid flows. These

plates (e.g. dumped or structured packing) can either be catalytically active or inert. These small sections can be regarded as very short (laminar or turbulent) falling film contactors. The expected number of mixing points per unit bed length is dependent of the type, shape and size of packing used.

The basic model assumptions are

1. The liquid in the bed is equally distributed over the entire external area of the packing and the reactor wall.
2. The gas phase resistance is negligible.
3. The bed and the fluids are isothermal.
4. Entrance and exit effects of the mixing points are negligible.
5. An uniform distribution of the liquid of the cross-sectional area.

The model used for this simulation is shown schematically in Fig. 6. It consists of a liquid film flowing vertically downward between two mixing points along a wall. A mixing point is a zero hold-up, perfect mixer in which no absorption or reaction occurs. The solid may be catalytically active, in that case absorption occurs at the gas–liquid interface and reaction occurs at the liquid–solid interface, or the solid may be inert.

A steady state mass balance over the micro element of liquid as shown in Fig. 7 is

$$D_L \frac{\partial^2 C}{\partial y^2} = v(y) \frac{\partial C}{\partial x} \qquad (9)$$

in which $v(y)$ represents the axial velocity (function of radial coordinate). Since the output of each mixing point is perfectly mixed, the concentration across the liquid film is fixed as some initial value yielding the first boundary condition:

$$x = 0, \quad y > 0: \quad C = C_i. \qquad (10)$$

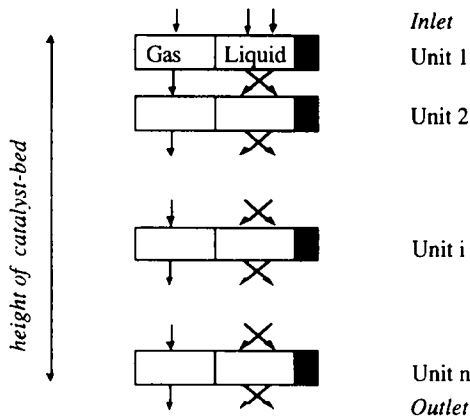For the first unit, this is the concentration already present in the liquid.

Fig. 6. Schematic presentation of the trickle bed simulation model.
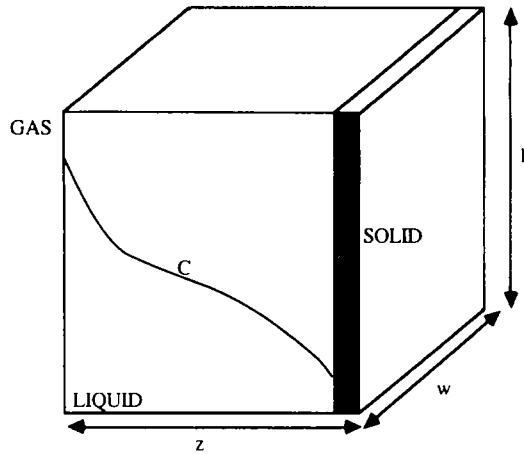

Fig. 7. One unit of the simulation model of a trickle-bed reactor.

Next it is assumed that equilibrium exists between gas and liquid phase at the interface:

$$x > 0, \quad y = 0: \quad C = C_{sat}. \qquad (11)$$

For catalytically active solids, the rate of mass transfer through the interface equal the reaction rate in the solids:

$$x = 0 \text{ and } y = \delta: \quad -D_L \frac{\partial C}{\partial y} = \frac{R\rho_B}{a}. \qquad (12a)$$

For an inert solid, no transfer will occur through the liquid–solid interface which gives

$$x = 0 \text{ and } y = \delta: \quad \frac{\partial C}{\partial y} = 0. \qquad (12b)$$

Before eq. (9) can be solved uniquely, the liquid velocity profile, $u(y)$, must be defined. In case the reactor is operated in the continuous flow regime it reasonable to assume that the liquid flows laminar. Therefore a parabolic velocity profile must be implemented for a fully developed flow:

$$v = v_{max}(1 - y^2). \qquad (13a)$$

The influence of the velocity profile can be studied by using the opposite asymptotic case: ideal plug flow:

$$v = v_{ave}. \qquad (13b)$$

In order to solve eqs (7) and (9) with the corresponding set of boundary conditions a numerical technique must be used. The partial derivatives are approximated by finite differences. The discretization of the differential equation results in a set of equations in a form that allows convenient method of solution to be used (tridiagonal matrix). The system of equations to be solved has $n - 2$ equations the same number unknowns for each increment of i (along the axial, x direction). The structure of these equations fits that of the tridiagonal system. This structure allows to use the efficient Thomas Tridiagonal Algorithm (LU decomposition) for the solution of the equations (Lapidus, 1962).

6. MODEL SIMULATIONS

6.1. *Laminar film reactor*

From the results obtained form the model simulations it can be concluded that the ratio:

$$\text{Ratio} = \frac{\text{Absorption flux for } k'' = \infty \ (\text{mol m}^{-2}\text{s}^{-1})}{\text{Absorption flux for } k'' = 0 \ (\text{mol m}^{-2}\text{s}^{-1})}$$

(14)

is an unique function of the local Fourier-number, Fo:

$$Fo = \frac{D_L H}{u_{max}\delta^2}$$

(15)

where H is the height of the laminar film. The results are presented in Fig. 8.

In Fig. 8 it is demonstrated that at small values of the Fo-number (e.g. short film lengths or contact times) the influence of a catalytically active wall (i.e. the presence of a catalyst in a trickle-bed reactor) can be neglected. However, for higher Fo-numbers the absorption rate for the process with chemical reaction increases substantially compared to the physical absorption case. This pronounced increase must be attributed to the effect of the heterogeneous reaction at the wall on the concentration gradient at the gas–liquid interface which is proportional to the
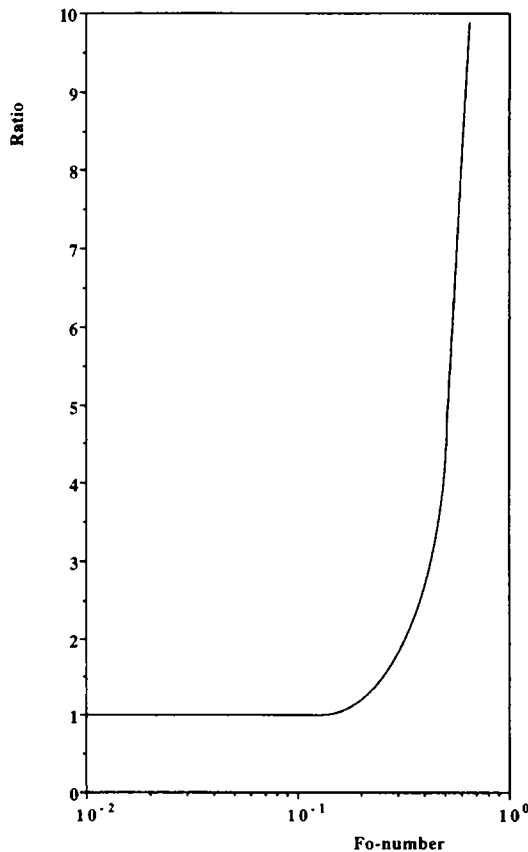

Fig. 8. Effect of the presence of a catalytically active wall in a laminar film reactor on the absorption rate as function of the Fo-number.

absorption rate. Overall it must be concluded that owing to the chemical reaction the absorption rate is higher than that estimated from the (pure) physical gas–liquid and liquid–solid mass transfer coefficients respectively.

$$\frac{C_i V_{bulk}}{\frac{1}{2}(C_i + C_{sat})V_{film}} \gg 1.$$

(16)

Therefore in three-phase reactors in which a kind of liquid film is flowing over a catalytically active packing (either dumped or structured) the applicability of the resistances in series model becomes questionable because condition (16) (Westerterp *et al.*, 1984) is not any more fulfilled. This implies that mass transfer and the catalytic reaction are no longer in series but partially parallel which may result in some kind of enhancement of the absorption rate similar to homogeneous gas–liquid processes.

6.2. *Trickle-bed reactor*

Previous presented results concerning mass transfer parameters were obtained using the plug flow model for trickle-bed reactors as described in Section 4.2. From the conversion-time plots also single pass conversions can be calculated. These single pass conversions can be used in combination with the 'trickle-bed reactor model' to fit average depths of the liquid layer flowing over the solid particles and reactor wall. The results are presented in Fig. 9.

Assuming complete wetting of the catalyst and an uniform thickness of the liquid layer at every point in the reactor, the total liquid hold-up data can also be converted to average depths of the liquid layer. This procedure was followed to obtain literature data concerning the thickness of the liquid layer. In Fig. 9 the literature data of Specchia and Baldi (1977) show a fairly good agreement with the non-foaming fitted data in the present system. Less influence of the gas superficial velocity, however, is assumed in their empirical correlations.

Because for KATAPAK™ no complete wetting was observed, it was decided not to use the absorption model to fit the thickness of the liquid layer because for these calculation complete wetting must be assured.

The absorption simulation model is based on liquid diffusion in a liquid layer flowing over a solid phase accompanied by a simultaneous reaction on the solids. Since this model is not based on separate resistances in series it may be able to give an explanation for the phenomena discussed in the previous sections. In Fig. 10(a) the scheme of the 3D-plots is elucidated and in Fig. 10(b) the results of the model calculations are qualitatively shown in which hydrogen profiles are plotted in the liquid layer for: (a) no reaction and (b) a reaction. For a realistic set of conditions (Table 5) the 3D-plot represents units between two mixing points. It must be noted that the reader should compare qualitatively the differences between the images on the l.h.s. and the r.h.s. in order
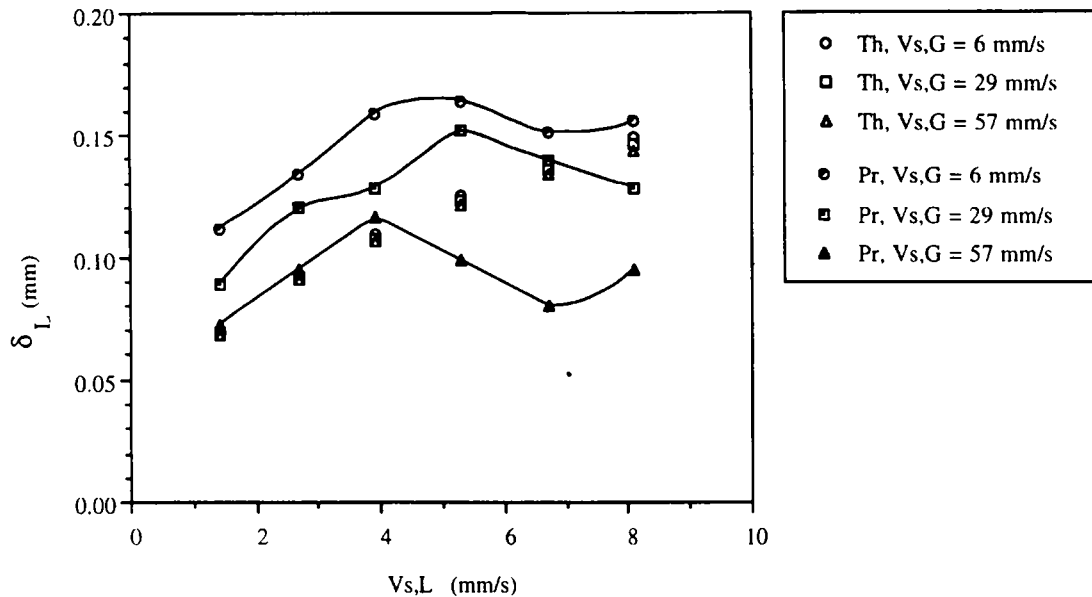
Fig. 9. Fitted depths of the liquid layer with the absorption simulation model for several process conditions [Pr: fitted values from experimental data, Th: estimated values from a hold-up relation of Specchia and Baldi (1977)].

Table 5. Input data for the simulations of the trickle-bed reactor model

System	Hydrogen and pure α-methylstyrene
Temperature	40 C
Bed length	10 cm, devided in 4 units
100 axial and 50 radial steps in the discretization model	
$V_{s,L}$	4 mm s^{-1}
$V_{s,G}$	50 mm s^{-1}
Packing	3 mm spheres
Liquid holdup	0.12
Porosity	0.40

to see the influence of the reaction at the solids interface.

In case of no reaction the gas phase component diffuses into the liquid layer flowing with a certain velocity profile over the solid phase. Already after the first mixing point (second unit) the hydrogen in the liquid phase actually reaches the solids and no further radial transport is possible. In the following units the liquid phase is almost saturated with the gas phase (the top-side of the cube represents the saturation concentration of the gas phase in the liquid phase). Due to this effect the radial gradient at the gas liquid interphase decreases in each successive unit. If complete saturation is reached this gradient will be zero. This gradient is also a measure for the concentration difference for gas–liquid mass transfer. If this difference equals zero, no mass transfer occur.

The plots at the right side of Fig. 10(b) show the gas-phase component profiles in the liquid phase as they would occur with reaction. The first unit is almost identical to the corresponding first unit in case

no reaction occurs. The difference arises when the hydrogen-profile reaches the catalyst. Now a reaction occurs resulting in a radial gradient at this surface and transport is affected by the consumption of hydrogen by reaction. In the successive units a radial gradient at the gas liquid interphase is also present. In the following units a kind of steady state occurs and the hydrogen consumption by reaction is equal to the hydrogen supply via mass transfer.

The conclusion of these simulations should be that in case of the small thickness of the liquid layer (for realistic conditions: 0.1 mm) the reaction at the solid surface prevents the decrease of the mass transfer rate due to the fact that no 'liquid bulk' (as assumed in the resistances in series model) is present in the liquid phase in trickle-bed reactors. This also explains the fact that the overall mass transfer coefficient can be higher than the separate liquid phase mass transfer coefficient at the gas–liquid interphase. Therefore models based on the resistances in series model should not be recommended in describing mass transfer characteristics in trickle-bed reactors.
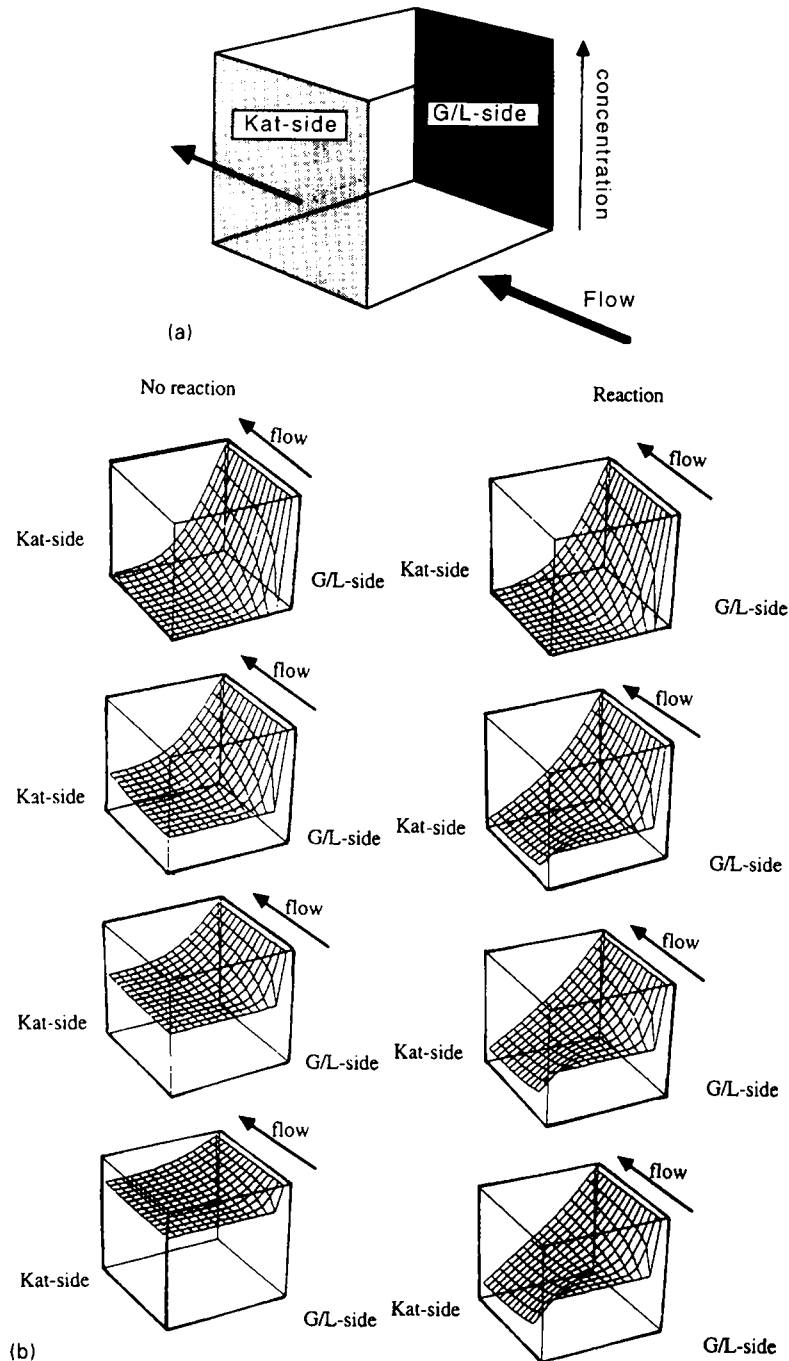
Fig. 10. (a) Scheme of the 3D-plot. (b) 3D-plots of dimensionless hydrogen concentrations is some units of the trickle-bed for two asymptotic cases: without (profiles l.h.s.) and with a reaction at the catalyst surface (profiles r.h.s.). Refer to (a) for additional information.

7. CONCLUSIONS

A comparison of the results of physical absorption experiments with the results of hydrogenation experiments showed that the resistance in series model – in which the total resistance against mass transfer is calculated from the separate resistances — is not valid in systems where heterogeneous reactions at the solid surface can affect the mass transfer-rate through the gas–liquid interphase. The developed laminar film and trickle-bed reactor models, based on liquid diffusion, simultaneous reaction at the solid surface and zero volume mixing points, are able to describe and explain mass transfer phenomena in trickle-bed reactors in conditions where the resistances in series model fails. The numerically solved models calculate the hydrogen profiles in the liquid films of the reactor and overall single pass conversions at several process conditions.

In trickle-flow conditions, the application of KATAPAK™ seems to improve not significantly the performance of the trickle-bed reactors. Contrary to the results reported in literature where a significant increase in the rates for physical absorption is observed in countercurrent operation (distillation). It should be noted, however, that in the present study the geometrical area of the spheres is about a factor of two higher that of KATAPAK™ which affects the possible increase owing to the use of structured packing substantially. The increase of the physical absorption rate due to better mass transfer characteristics of structured packings compared to dumped packing types will, however, be eliminated to a certain extent in reactive systems due to a kind of enhancement effect of the reactions in trickle-flow operations. The advantages of structured packing types is therefore less pronounced.

NOTATION

a	specific surface, m^{-1}
C	concentration, $kmole\, m^{-3}$
D, d	diameter, m
D	diffusion coefficients, $m^2 s^{-1}$
Fo	Fourier-number defined, according to eq. (21), dimensionless
H	height of the laminar film, m
d_t	bed diameter, m
k, K	mass transfer coefficient, $m\, s^{-1}$
k'	pseudo first order kinetic constant, s^{-1}
k''	first order surface based kinetic constant, $m\, s^{-1}$
K	kinetic constant $(-n-)$
L	length of fixed bed, m
l	height of the unit cell, Fig. 6, m
m	dimensionless solubility, dimensionless
R	reaction rate, $kmole\, m^{-3} s^{-1}$
S	circumferential area of fixed bed, m^2
t	time, s
v	superficial velocity, $m\, s^{-1}$
V_R	reactor volume, m^3
W	width of the laminar film, m
w	depth of the unit cell, Fig. 6, m
x	axial axis, m
y	radial axis, m
z	width of the unit cell, Fig. 6, m

Greek letters

α	specific dimension KATAPAK™, see Fig. 1, m
β	hold-up, dimensionless
δ	thickness of liquid layer, m
δ	specific dimension KATAPAK™, see Fig. 1, m
ε	bed porosity, dimensionless
λ	specific dimension KATAPAK™, see Fig. 1, m
ρ	density, $kg\, m^{-3}$
ϕ	flow rate, $m^3 s^{-1}$

Subscripts/superscripts

1, 2	at several constants (c)
ave	average
αms	α-methylstyrene
bulk	liquid bulk
film	mass transfer film
G, g	gas
i	inlet, core, gas liquid interface
in	inlet
L, l	liquid
max	maximum value
ov	overall
out	outlet
p	particle
s	superficial
sat	saturation
tot	total
x, y	directions
bulk	at bulk conditions

REFERENCES

Astarita, G. and Beek. W. J. (1962) *Chem. Engng Sci.* **17**, 665–674.

Baker, G. A. and Oliphant, T. A. (1960) *Quart. Appl. Math.* **17**, 361–373.

Bird, R. B., Stwart, W. E. and Lightfoot, E. N. (1960) *Transport Phenomena.* Wiley, New York.

Bravo, J. L., Rocha, J. A. and Fair, J. R. (1985) *Hydrocarb. Proc.* **64**, 91.

Lapidus, L. (1962) *Digital Computation for Chemical Engineers,* McGraw-Hill, New York.

Satterfield, C. N., Ma, Y. H. and Sherwood, T. K. (1968) *I. Chem. Engng Symp. Series* **28**, 22–29.

Spechia, V. and Baldi, G. (1977) *Chem. Engng Sci.* **32**, 515–523.

Turek, F. and Lange, R. (1981) *Chem. Engng Sci.* **36**, 569–579.

Versteeg, G. F. and van Swaaij, W. P. M. (1988a) *Chem. Engng Process* **24**, 163–176.

Versteeg, G. F. and van Swaaij, W. P. M. (1988b) *J. Chem. Engng Data* **33**, 29–34.

Westerterp, K. R., van Swaaji, W. P. M. and Beenackers, A. A. C. M., Chemical reactor design and operation, Wiley 1984.