concentrations of very small catalyst particles ($d_p$<10 µm). The foam dissapears when the catalyst concentration is increased to approximately 3 wt% or higher. With larger particles the production of foam is not significant, irrespective of the concentration.

## 4.6 Experimental

### 4.6.1 Materials and catalyst

All the gases used (ethene, helium, hydrogen and nitrogen) were obtained from cylinders (purity>99.5%). The cylinder with ethene (polymer grade) contained a maximum of 0.05% ethane, which was experimentally veryfied. Nitrogen, used as carrier gas, was dried with molsieves. The reactant gases were not purified. The catalyst, a prereduced hydogenation catalyst, was supplied by Degussa Nederland B.V. It consists of 5 wt% $Pd/\gamma\text{-}Al_2O_3$ and was designated as E 207 R/D. The specific surface area was $400 m^2/g$. Fractions with a mean diameter of 35 and 45 µm were obtained after sieving. A 7 µm mean diameter fraction was obtained by crushing a sieve fraction with a diameter smaller than 25 µm. Fresh catalyst particles were added to the reactor without further treatment. Used catalyst particles were washed and reduced with hydrogen at 250°C.

The liquid phase, squalane, was equal to that used for the kinetic investigation (see Chapter 2). Squalane was recycled by separation of catalyst particles and vacuum destillation at 70°C.

### 4.6.2 Apparatus

A schematic diagram of the apparatus is shown in Fig. 4.4. The reactor consists of a glass tube, (height 1.6 m and diameter 0.050 m) which is heated externally by electric wire. The amount of heat is regulated by a PID temperature controller (Eurotherm 070) which holds the reactor temperature constant at 250°C within 0.5°C. The temperature is measured by a thermocouple type K which is inserted in the liquid phase. The gas distributor is a porous plate with a pore diameter range of 16-40 µm or a perforated plate with 19 300 µm diameter holes. Only for holdup experiments porous plates with different pore size ranges were used.

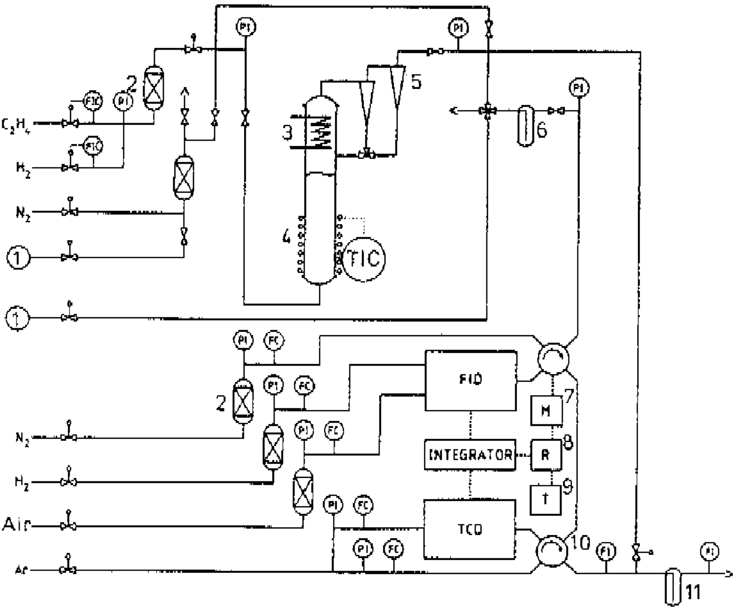

*Fig. 4.4 Experimental setup:*

*(1) calibration mixture; (2) molsieves; (3) cooling; (4) electric heat wire; (5) cyclones for entrained squalane; (6) oil filter; (7) magnetic valve; (8) relais; (9) time switch; (10) sample valve; (11) water saturator*

Ethane and ethene were analysed on-line by a Pye 104 gas chromotograph equipped with a flame ionization detector. The GLC signal was integrated by a HP 3392A integrator. Initially, the concentration of hydrogen was also measured for the sake of controlling. Since both analyses agreed closely, only ethane and ethene were measured during most of the experiments. The traces of ethane present in the ethene feed were measured before the start of each experiment. The fraction of ethane in the reactor outlet gas originating from the ethene cylinder was usually below 10 vol%.

## 4.7 Results and discussion

### 4.7.1 Effect of the gas distributor

Production of small bubbles by a porous plate distributor with small pore diameters makes sense only, if the diameter of bubbles remains small during a considerable part of their residence time. In that case gas holdup and gas-liquid mass transfer will be noticeably larger than in case initally larger bubbles are formed. The influence of the gas distributor type thus provides information on the tendency of bubbles to coalesce. This section deals with the influence of the type of the gas distributor on the gas holdup followed by the effect on the gas-liquid mass transfer.

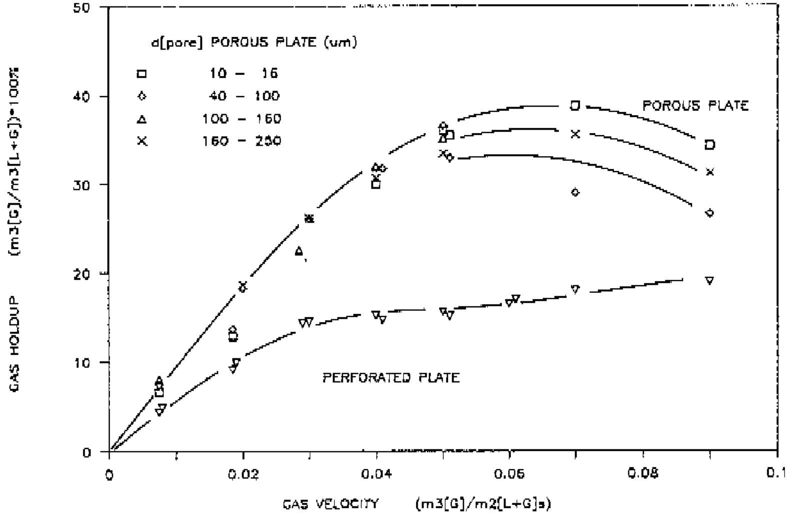

*Fig. 4.5 The gas holdup as a function of the gas velocity in the absence of solids for various gas distributors. The liquid column height is 0.80 m*

The gas holdup observed in a bubble column filled with squalane only is considerably larger with a porous plate than with a perforated plate as gas distributor as shown in Figure 4.5. The larger gas holdup observed with a porous plate can be attributed to the visibly smaller gas bubbles. The pore diameter of the porous plate hardly affects the gas holdup in the bubble flow regime (up to 4-5 cm/s). In the transition range, however, the porous plate with the smallest pore diameter produces the largest gas holdup as shown in Figure 4.5. Especially at higher gas velocities (>4cm/s) relatively large bubbles are formed which have a low contribution to the gas holdup due to their high rising velocity. These (large) bubbles are formed more easily at a distributor with larger pore or orifice diameter. Consequently, the maximum gas holdup and the change

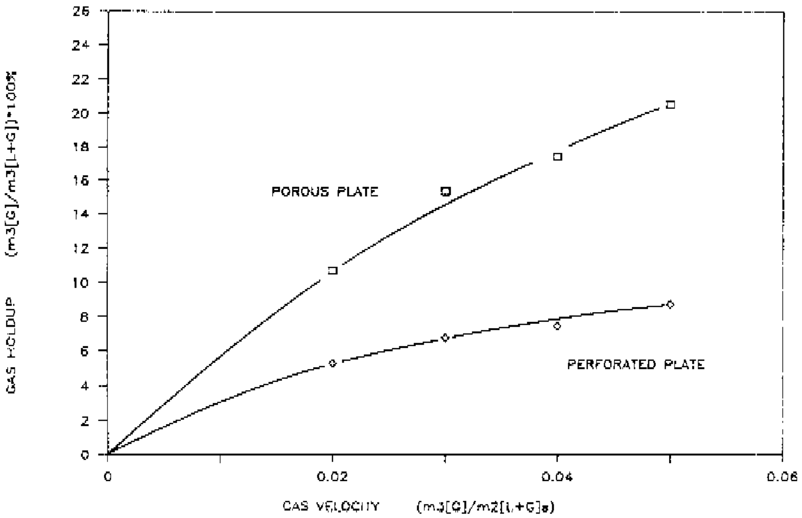

*Fig. 4.6 The gas holdup as a function of the gas velocity in the presence of solids. The liquid level is 0.13 m. The particle diameter and catalyst concentration are 45 µm and 120 kg/m$^3_L$ (15.4 wt%) respectively*

from bubble to heterogeneous flow is reached at a lower gas velocity when the perforated plate is used as shown in Figure 4.5. The large difference between the gas holdup obtained with a porous plate and that with a perforated plate as gas distributor indicates that small bubbles coalesce slowly in a bubble column with squalane as liquid.

The addition of solids does not significantly reduce the large difference in gas holdup between a porous and perforated plate as shown in Figure 4.6, in which the gas holdup is depicted versus the gas velocity for a suspension with 15.4 wt% solids. Generally, the addition of solids leads to a gas holdup decrease as will be shown in section 4.7.3. An exception is the gas holdup at gas velocities above 4 cm/s with a perforated plate as gas distributor as shown in Figure 4.7. The higher

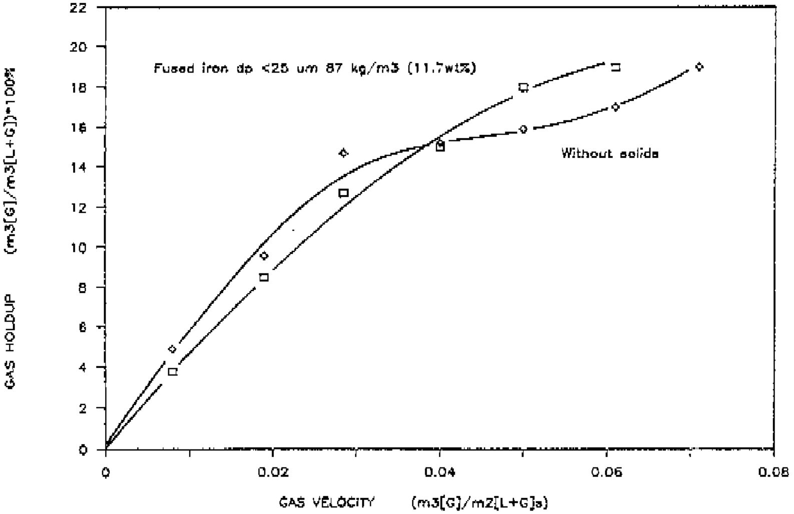

*Fig. 4.7 The gas holdup as a function of the gas velocity in the absence and presence of solids. The liquid level is 0.60 m. The gas distributor is the perforated plate*

gas holdup with 11.7 wt% solids in this figure indicates that the change from bubbling to heterogeneous flow may occur at higher gas velocities by the presence of solids. Probably, the solids inhibit the formation of large bubbles specially bubbles with the dimension of the column diameter.

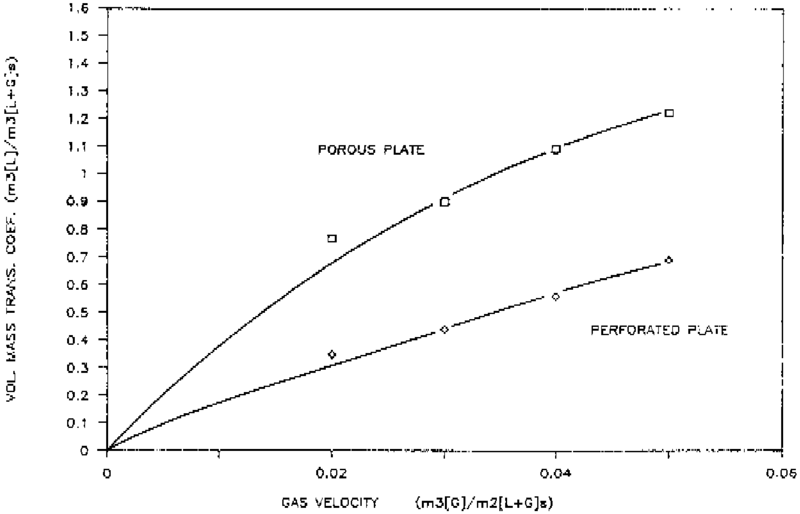

*Fig. 4.8 The value of $k_La$ as a function of the gas velocity. The suspension level is 0.13 m. The catalyst concentration is 80 $kg/m^3_L$ (10.8 wt%).*

In consequence of the higher gas holdup and the smaller gas bubbles, the gas-liquid mass transfer is considerably larger when a porous plate is used instead of a perforated plate as shown in Figure 4.8. The $k_La$ $_{porous}/k_La$ $_{perforated}$ ratio (= 2), however, is smaller than the gas holdup ratio (≃ 3). This may be attributed to an (average) lower $k_L$ value with the porous plate due to the presence of a large amount of small bubbles with a rigid surface. The diameter of these small bubbles is approximately 0.7 mm as this value is reported by Zaidi et al.[12] for gas bubbles in a Fischer-Tropsch wax without solids. Although visible observation in the three phase bubble column indicates that bubbles grow rapidly as a function of the height, the bubble diameter close to the porous plate will be of the order of 0.7 mm. The $k_L$ value of such small bubbles is significantly lower (± 50%) than that of bubbles with a diameter larger than 2.5 mm, according to the well-known correlation of Calderbank and Moo-Young [26]. This lower $k_L$ value decreases the effect of both the larger gas holdup and (initially) smaller bubbles formed by the porous plate.

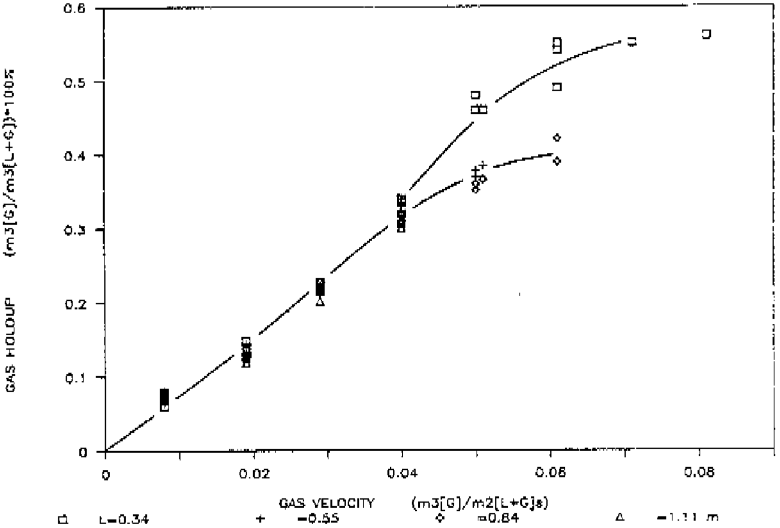

*Fig. 4.9 The gas holdup as a function of the gas velocity for various pore sizes of a porous plate distributor in the absence of solids*

### 4.7.2 Effect of the liquid/suspension level

The degree of coalescence determines the influence of the liquid/ suspension level on the mass transfer in a bubble column. In this section the influence of this level on the gas holdup will be considered first and thereafter on the volumetric mass transfer, for various catalyst concentrations.

In the two phase system squalane/nitrogen or squalane/ethene, the liquid level does not affect the gas holdup in the bubble flow regime for both types of gas distributors as shown in Figure 4.9. This indicates that coalescence is rather unimportant in this flow regime. Increasing the gas velocity up to 9 cm/s does not change this situation with a sieve plate. With a porous plate, however, the liquid level does reduce the gas holdup when the gas velocity is larger than 4 cm/s as shown in Figure 4.9. In this case thus coalescence cannot be neglected . Nevertheless, squalane without solids can be considered as a "non-coalescending medium".

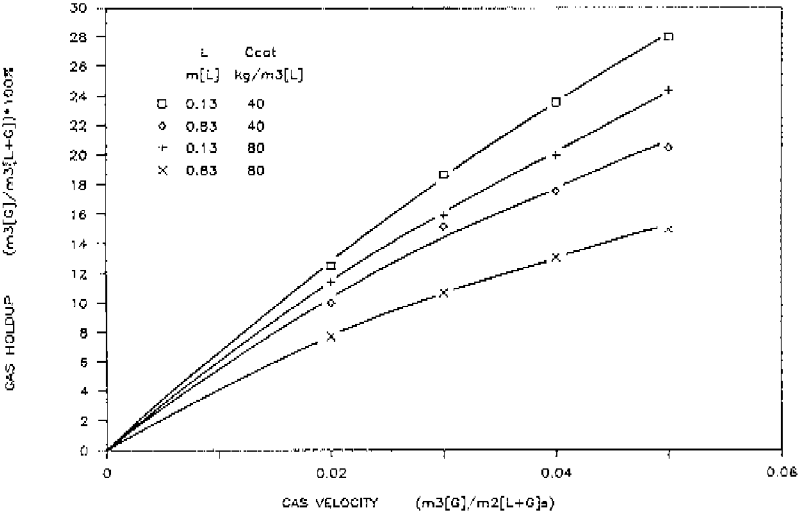

*Fig. 4.10 Effect of the suspension level on the gas holdup. The gas distributor is the porous plate. The diameter of the catalyst particles is 45 μm*

Due to the addition of catalyst particles the influence of the suspension level on the gas holdup is considerably different compared with the situation in the absence of solids. Contrary to the two phase system the gas holdup now decreases considerably with increasing suspension column height. This decrease already occurs at low gas velocities as shown in Figure 4.10. The effect of the height of the suspension column is more pronounced at a higher particle concentration (see Figure 4.8). This concentration effect will be discussed further in the following section.The lower gas holdup at a higher liquid level can be attributed to a larger mean bubble diameter, and hence a higher bubble rising velocity [25]. It can be expected that the volumetric mass transfer decreases with increasing suspension column height as a consequence of both a lower gas holdup and a larger mean bubble diameter.

The value of $k_La$ decreases indeed as a function of the suspension column height in the three phase system as shown in Figure 4.11. If the

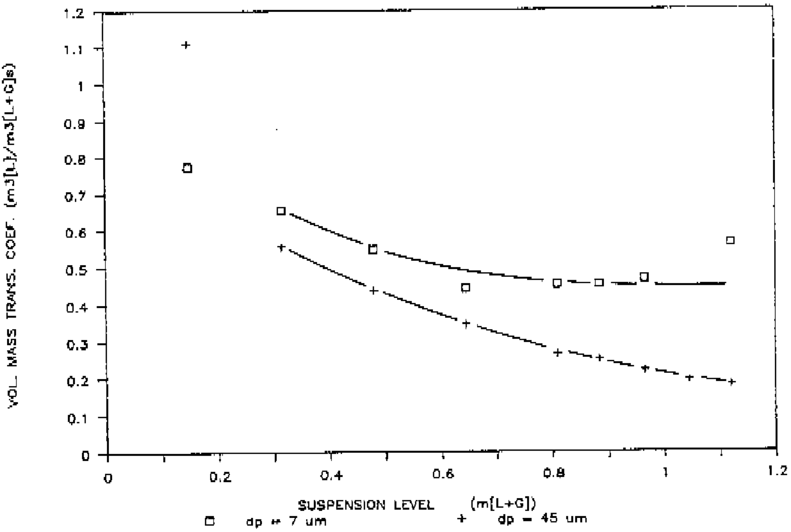

*Fig. 4.11 The value of $k_La$ as a function of the suspension level. The catalyst concentration is 73 $kg/m^3{}_L$ (10 wt%)*

assumption is made that the $k_L$ value does not vary significantly, the parameter $k_La/\varepsilon_G$ is inversely proportional to the mean bubble diameter. This $k_La/\varepsilon_G$ ratio appears to decrease sharply as shown in Figure 4.12, indicating that the mean bubble diameter increases. After comparing Figures 4.9 and 4.10 the conclusion is that the bubble diameter is the dominating factor with respect to the dependence of the volumetric mass transfer coefficient on the suspension level for 45 μm catalyst particles.

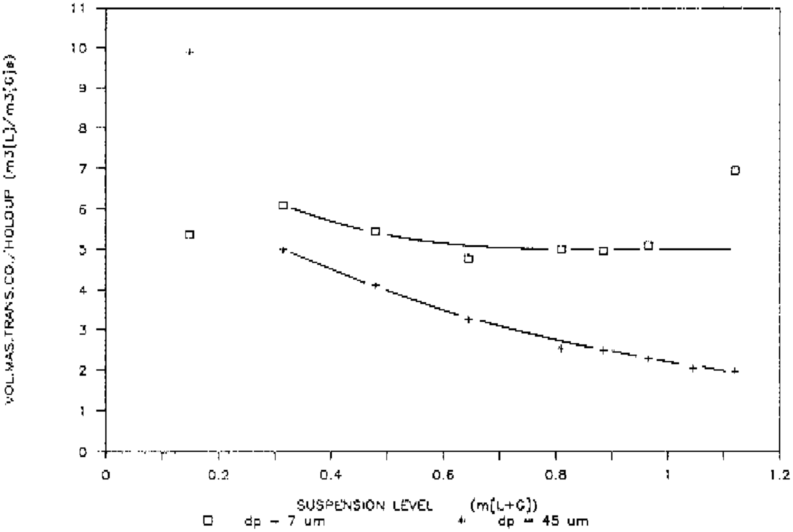

*Fig. 4.12 The $k_La/\varepsilon_G$ ratio as a function of the suspension level. The catalyst concentration is 73 $kg/m^3{}_L$ (10 wt%)*

### 4.7.3 The effect of solids on the gas holdup and volumetric mass transfer

This section deals with the influence of solid particles on the gas holdup and the volumetric gas/liquid mass transfer in a 5 cm bubble column at 250°C with squalane as the liquid phase.

The addition of 45 μm particles results in a decrease of the gas holdup in all circumstances. The conditions only determine the degree of the gas holdup decline. These conclusions can be drawn from Figure 4.13 which demonstrates the gas holdup as a function of the solid concentration at various conditions. The largest gas holdup decrease is obtained with the porous plate, a low liquid level and a high gas velocity. This means that in the presence of small particles (45 μm mean), in contrast to the two phase system, small bubbles coalesce easily, causing a lower gas holdup. Relatively large bubbles produced by a perforated plate do not coalesce significantly as is indicated by the small decline of the gas holdup compared with that observed with a porous plate (see Figure 4.13).

Addition of 45 μm catalyst particles, thus, results in a lower gas holdup. Consequently, the volumetric mass transfer will decrease as well. The effect of the solid concentration together with that of the type of the gas distributor and the suspension column height are shown in Figure 4.14 and 4.15. The value of $k_La$ is very high when the catalyst concentration is lower than 1 wt% and the initial bubbles are small which can be achieved by using a porous plate. However, the value of $k_La$ observed with this gas distributor drops sharply with increasing solid concentration. When also the suspension level is increased to 1 m the value of $k_La$ obtained is even lower with a porous plate than that with the perforated plate in a bubble column with an equal concentration of solids but with a lower suspension level. Thus the influence of the suspension column height dominates the influence of the gas distributor for moderate solid concentrations. This indicates that the mean bubble diameter at a high suspension level is lower than the initial bubble diameter formed by the perforated plate. Obviously, the lowest mass transfer is obtained in the column equipped with the perforated plate at a 1 m suspension column height. It is interesting to note that this $k_La$ value is about 10 times lower than that observed with a porous plate at a low suspension level and a low solid concentration.

It is important to know whether an equilibrium bubble diameter is reached or not by the addition of solids.In any case the $k_La$ value, which is an average value over the whole suspension volume, will decrease with increasing suspension column height. Only the course of the $k_La$ decline

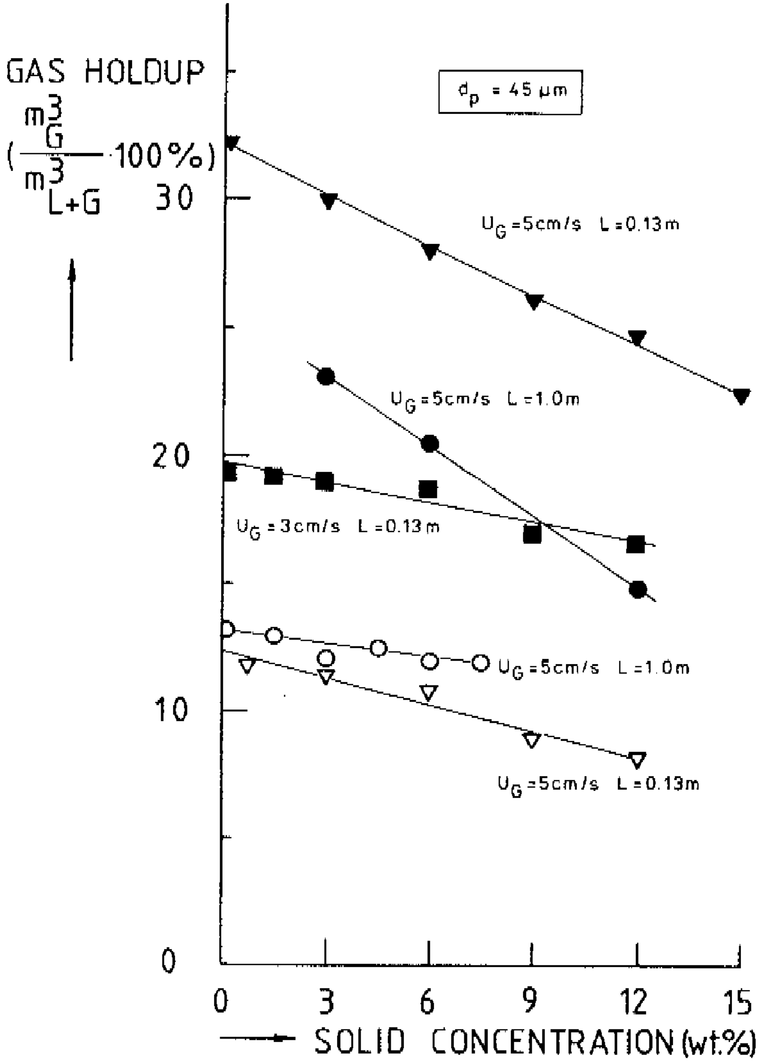

*Fig. 4.13 The effect of the solid concentration on the gas holdup. Legends: open symbols, perforated plate: filled symbols, porous plate*

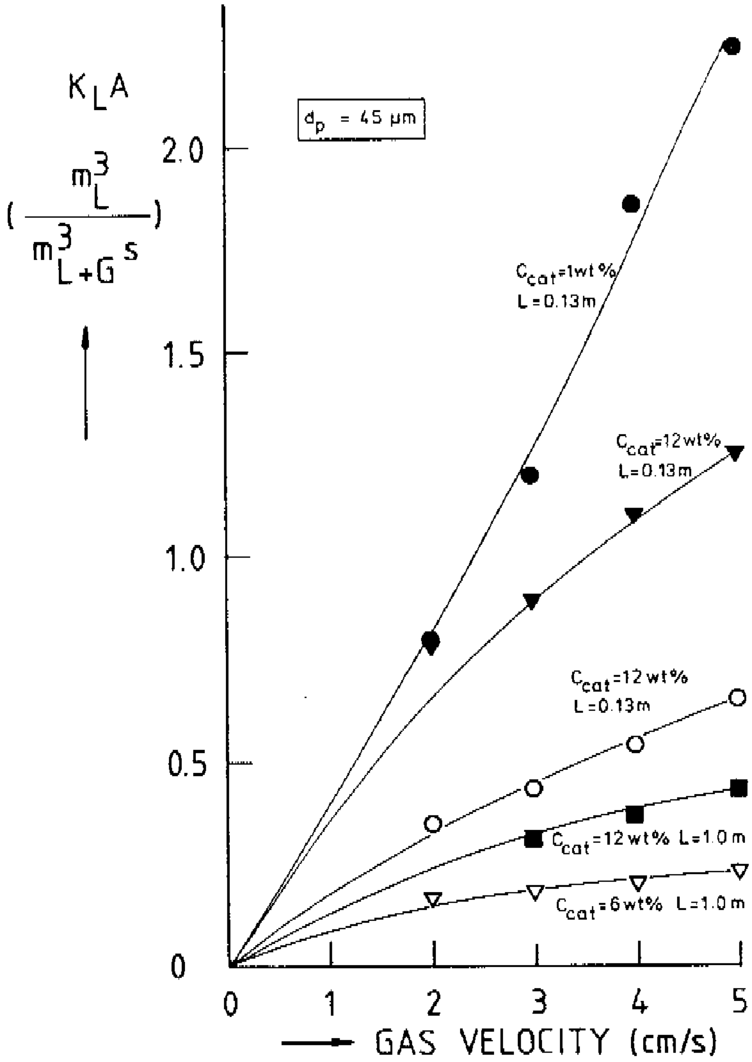

*Fig. 4.14 The value of $k_La$ as a function of the gas velocity under various conditions. Legends: open symbols, perforated plate; filled symbols, porous plate*

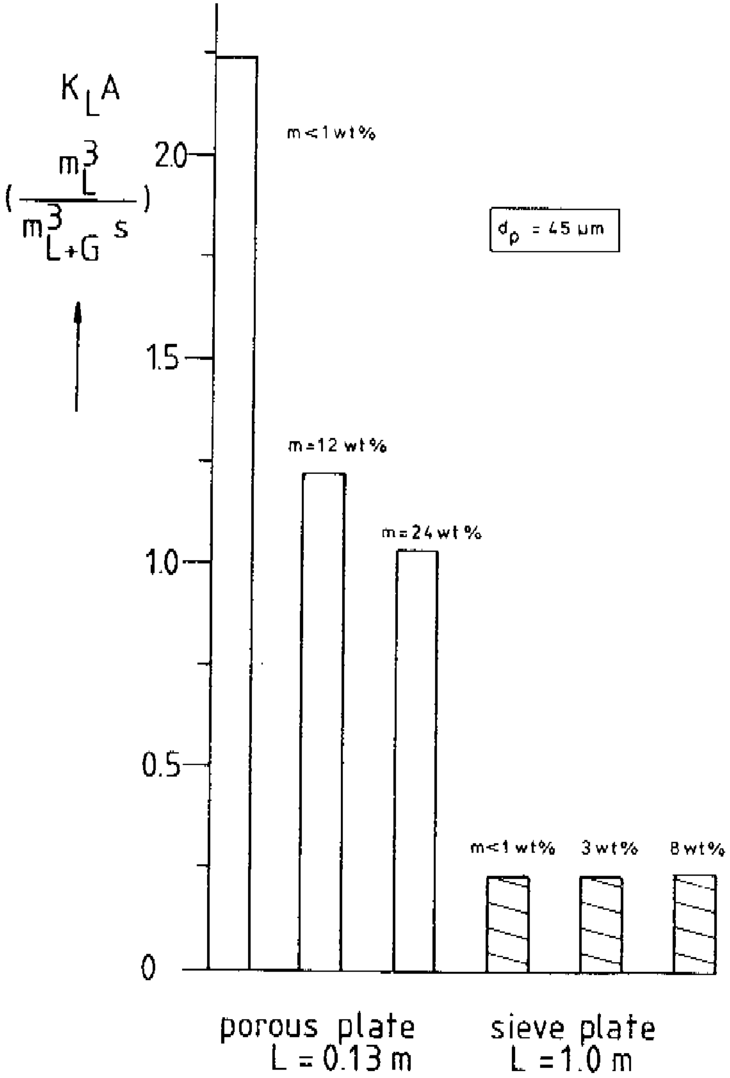

*Fig. 4.15 The effect of the solid concentration on the value of* $k_La$

differs. In case an equilibrium bubble diameter is reached rapidly (just above the gas distributor) $k_La$ will approach rapidly a minimum value with increasing suspension column height. If bubbles even at the top of the column have not reached an equilibrium diameter, the $k_La$ value will continue to decline with increasing suspension column height. The influence of the suspension column height on the hydrogen conversion for two different particle sizes is shown in Figure 4.16. The conversion with 7 µm diameter particles increases continuously but surprisingly the conversion with 45 µm particles reach a maximum value at approximately 0.7 m and appears even to decrease slightly with increasing suspension column height. This can only be explained by a decrease of the $k_La$-value in the lower part of the column. As $k_La$ decreases with increasing solid concentration (see Figure 4.14), apparently the increase of the

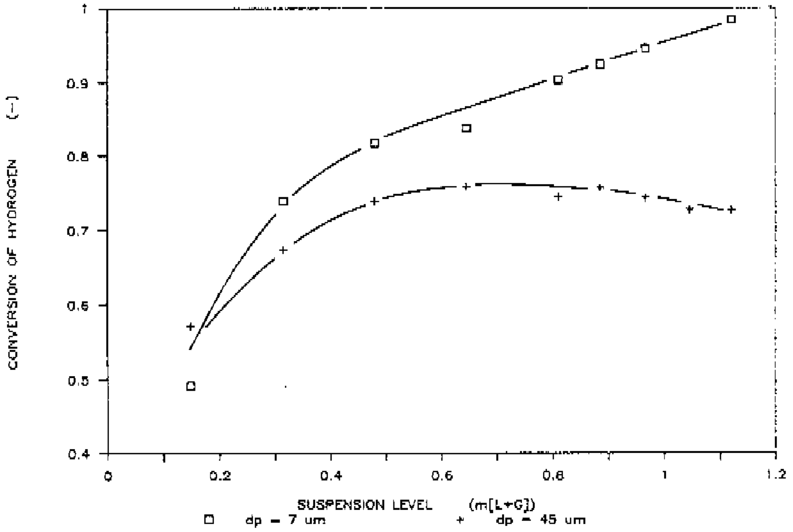

*Fig. 4.16 The conversion of hydrogen as a function of the suspension level for the perforated plate. The catalyst concentration is 73 kg/m$^3_L$ (10 wt%). The gas velocity is 3 cm/s*

suspension column height leads to an increase of the solid concentration in the lower part of the column. In order to verify the presence of a concentration profile, the solid concentration was measured at the top of the column for 3 and 45 µm diameter particles (suspension level and superficial gas velocity were 1.12 m and 3 cm/s respectively). It appeared that 3 µm particles were completely homogeneously suspended (5 wt % suspension) whereas with 45 µm particles the solid concentration at the top was only 35% of the mean concentration (10wt%).

In order to confirm that the influence exerted by the solid concentration on $k_La$ depends strongly on the particle diameter, the following experiments were carried out. The column was filled with 10 wt% 7 µm diameter catalyst particles. After that carrier particles (these

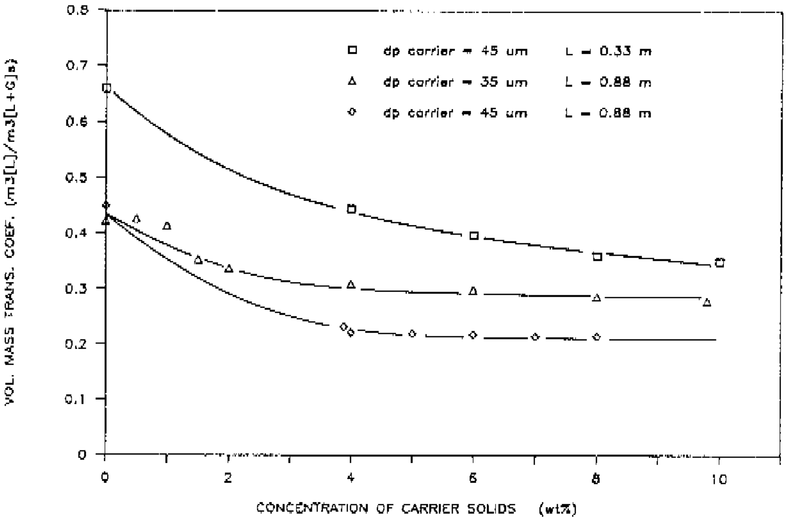

*Fig. 4.17 The effect of the addition of 35 and 45 µm diameter carrier particles to a 10 wt% suspension of 7 µm diameter catalyst particles on the value $k_La$. The gas velocity is 3 cm/s. The gas distributor is the perforated plate*

particles are indentical to the catalyst particles only palladium is lacking) with a diameter of 35 or 45 µm were added to the column. The effect of these carrier particles is shown in Figure 4.17. This figure shows that the presence of just a few percent of carrier particles causes a strong decrease of the $k_La$ value. This decline of $k_La$ depends both on the suspension level and the particle diameter. As these factors affect especially the concentration profile in the column [27], it may be concluded that this profile is a main cause of the strong $k_La$ decline observed with 45 µm solids in Figure 4.17 and the conversion decrease in Figure 4.16. This points to a sharp decrease of $k_La$ as well, as shown in Figure 4.11. Thus both as a result of the suspension column height increase (Figure 4.16) and carrier addition (Figure 4.17), the solid concentration in the vicinity of the distributor increases, resulting in a lower specific area in this region. The decrease of the gas-liquid area is caused by an increased coalescence resulting both in a lower gas holdup and in a larger mean bubble diameter as indicated by Figure 4.18. Here the $k_La/\varepsilon_G$ decline represents the increase of the mean bubble diameter, provided the $k_L$ value is not significantly changed.

It is interesting to note that the $k_La$ value reaches a constant value when 4 wt% 45 µm carrier particles are added for the case of the suspension level being 0.88 m (see Figure 4.17). This indicates that the suspension level at which bubbles reach their equilibrium diameter is not affected anymore by further increasing the carrier particle concentration. In contrast to a high suspension level, at 0.33 m the $k_La$ value continues to decline with increasing carrier concentration to a value of 0.35 $m^3_L/m^3_{L+G}.s$ at 10 wt% carrier particles. This value is much lower than with 10 wt% 45 µm catalyst particles alone (0.52 $m^3_L/m^3_{L+G}.s$). Apparently, the 7 µm carrier particles strengthen the affect of the 45 µm particles on the coalesence. This implies that the level at which the equilibrium bubble diameter is reached in the 0,33 m column is lower when both 7 and 45 µm particles are present. This situation, however, is different at a high suspension level. The $k_La$ value with 10 wt% 45 µm alone and with the combination of 10 wt% 7 µm and 4-8 wt% 45 µm carrier particles are 0.24 and 0.22 $m^3_L/m^3_{L+G}$ s respectively at 0.88 m suspension column height. As these values are so close together it can be concluded that the $k_La$ value is not affected by the coexistence of 7 and 45 µm

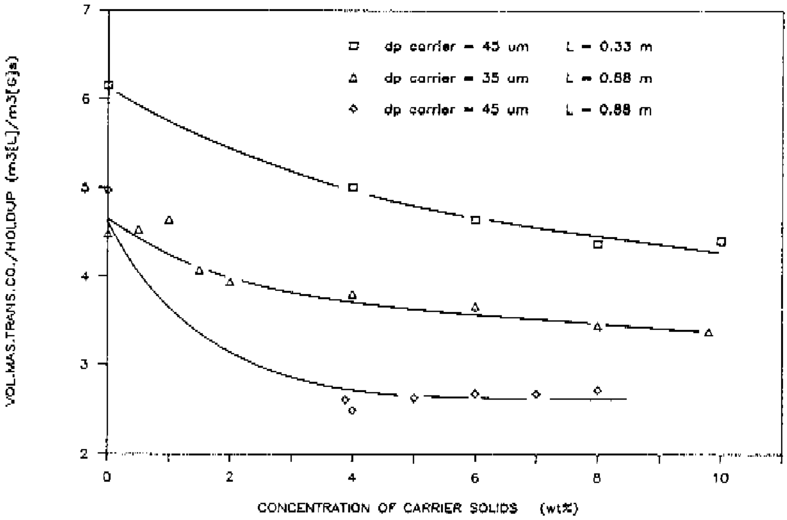

*Fig. 4.18 The effect of the addition of 35 and 45 µm diameter carrier particles to 10 wt% suspension of 7 µm diameter catalyst particles on the $k_La/e_G$ ratio. The gas velocity is 3 cm/s. The gas distributor is the perforated plate*

particles compared with 45 µm particles alone. Probably, the mass transfer coefficient has already reached the minimum value when exclusively 45 µm particles are present. Therefore, it is likely that the equilibrium bubble diameter with these particles is already reached at a small distance from the gas distributor.

It may be noted that the viscosity of the suspension plays no role as the viscosity hardly changes by the small addition of 45 µm diameter particles. Thus, the influence of particles on the volumetric mass transfer differs considerably from that in a stirred reactor with kerosine as the liquid phase, since the $k_La$ decline in this type of reactor correlated with the apparent viscosity [28].

The strong influence of only a few percent of 45 µm particles and the higher $k_La$ value observed when 35 µm particles are used, denotes that the promotion of coalescence by particles decreases with decreasing particle diameter. This may result in an increase of the suspension level at which bubbles reach the equilibrium diameter. This equilibrium diameter is of the order of 2-3 mm which is much larger than that reported by Quicker and Deckwer [5], Zaidi et al.[9] and Deckwer et al. [16].

*Finally*, it can be concluded from the results of section 4.7.1-4.7.3 that in a gassed two phase bubble column with squalane as the liquid, coalescence is of little importance allowing a high gas holdup and a high volumetric gas-liquid mass transfer coefficient to be obtained by the application of a gas distributor with small pores. However, in the presence of 7-45 µm diameter solids, bubbles coalesce rapidly to the equilibrium diameter. Hence, the formation of initially small bubbles hardly increases the gas-liquid mass transfer in this three phase system. The promotion of coalescence by solids appears to increase with the diameter of the solids.

## 4.8 The relevance of gas-liquid mass transfer limitations to the Fischer-Tropsch slurry process

As written in the introduction of this chapter it is uncertain whether gas-liquid mass transfer exerts an influence on the conversion of synthesis gas in a bubble column. Although in many models [1-4,14,33] the Fischer-Tropsch reaction is assumed to be first order in hydrogen, no experimental data of the volumetric gas-liquid mass transfer coefficient is available. Therefore, this data is calculated and used for the prediction of the importance of gas-liquid mass transfer of hydrogen. In this section, these calculated $k_La$ values are compared with the experimental results obtained in this study and the first order reaction rate constants of various iron catalysts.

The calculation of $k_La$ is divided into two or three parts: $k_L$ and a or $k_L$, $\varepsilon_G$ and $d_b$. The value of $k_L$ is often calculated by means of the correlation of Calderbank and Moo-Young [26], although this correlation is derived for a two phase system.

$$k_L = 0.31 \left( \frac{D^2{}_L \, \rho_L \, g}{\mu_L} \right)^{1/3} \qquad d_b < 2.5 \text{ mm} \qquad (4.40)$$

$$k_L = 0.42 \left( \frac{D^3{}_L \, \rho_L \, g^2}{\mu_L} \right)^{1/6} \qquad d_b > 2.5 \text{ mm} \qquad (4.41)$$

*Table 4.2*

*Experimental and calculated values of the diffusion and mass transfer coefficient in "Fischer-Tropsch liquids" at 250°C.*

| $D_{L,H_2}$ $[m^4{}_L/m^2{}_{L+G}\ s]$ | $k_{L,H_2}$ [6] $[m^3{}_L/m^2{}_{G-L}\ s]$ | Ref. |
|---|---|---|
| $10.0 \times 10^{-8}$ [1] | $15.0 - 28.9 \times 10^{-4}$ | 30 |
| $7.0 \times 10^{-8}$ [2] | $13.0 - 24.0 \times 10^{-4}$ | 31 |
| $2.3 \times 10^{-8}$ [3] | $5.5 - 14.1 \times 10^{-4}$ | - |
| $0.9 \times 10^{-8}$ [4] | $3.0 - 8.8 \times 10^{-4}$ | 3 |
| $0.9 \times 10^{-8}$ [5] | $2.9 - 8.6 \times 10^{-4}$ | - |

1) measured in Krupp wax

2) measured in squalane

3) calculated for squalane according to the relation of Wilke-Chang [42]:

$$D_{L,H_2} = 7.4 \times 10^{-8} \, \frac{T \, (X \, MW)^{0.5}}{\mu_L \, V_b{}^{0.6}}$$

wherein the association parameter X is equal to 1, the molecular weight MW=422.83 g/mol and the molar volume of $H_2$, $V_b = 14.3$ $cm^3/mol$.

4) calculated for n-triacontane $CH_3\,(CH_2)_{28}\,CH_3$ according to Wilke-Chang

5) calculated for squalane according to the correlation of Sovova [32]:

$$D_{L,H_2} = \frac{3.374 \times 10^{-4}}{\mu_{L,H_2}{}^{0.5} \, V_{B,H_2}{}^{0.6}}$$

wherein D is in $cm^2/s$, $\mu_L$ in cP, and $V_{B,H_2}$ is the molar volume of hydrogen (14,3 $cm^3/mol$)

6) calculated according to Calderbank and Moo-Young [26]:

$$k_{L,H_2} = 0.31 \, (D_{L,H_2}{}^2 \, \rho_L \, g/\mu_L)^{0.33} \qquad d_b < 2.5 \text{ mm and}$$

$$k_{L,H_2} = 0.42 \, (D_{L,H_2}{}^3 \, \rho_L \, g^2/\mu_L)^{0.17} \qquad d_b > 2.5 \text{ mm}$$

In these correlations the value of the diffusion coefficient is a matter of dispute and the predicted values vary considerably (a few examples are given in Table 4.2). Therefore, the diffusion of hydrogen in squalane is measured experimentally. This value agrees well with the diffusion of hydrogen in Krupp wax as shown in Table 4.2. It is interesting to note that both experimental values are much larger than values predicted according to Wilke-Chang or Sovova. Furthermore the reported values of the viscosity of wax (paraffin) differ substantially. The values reported in literature for the density of wax (paraffin) agree closely (see Table 4.3). In view of the foregoing it can be concluded that an accurate prediction of $k_L$ is difficult. As the specific area (gas holdup and bubble diameter) is in dispute as well (see section 4.1) the predicted values of $k_La$ vary appreciably as shown in Figure 4.19, in which values determined experimentally in this study are shown as well. As a result of the high diffusion coefficient observed in Krupp wax Calderbank [14] predicts a high $k_La$ value (0.53 $m^3_L/m^3_{L+G}$ s) despite the low specific area in comparison with Deckwer. The $k_La$ value predicted by the latter agrees well with that of this study, although the values of $k_L$ and a seem to be too low and too high respectively, with respect to the results obtained in squalane. The $k_La$ value reported by Satterfield [3] seems to be

*Table 4.3*

*Viscosity and density of various "Fischer-Tropsch liquids"*

| Type of wax | $\mu_L$ [Ns/m$^2$] | $\rho_L$ [kg/m$^3$] | Ref. |
|---|---|---|---|
| Paraffin | $2.80 \times 10^{-3}$ | 675 | 1 |
| Krupp | $1.80 \times 10^{-3}$ | 680 | 14 |
| Squalane | $0.61 \times 10^{-3}$ | 660 | – 1) |
| Paraffin | $0.33 \times 10^{-3}$ | – | 29 2) |

1) this work

2) used by Stern et al. [2]

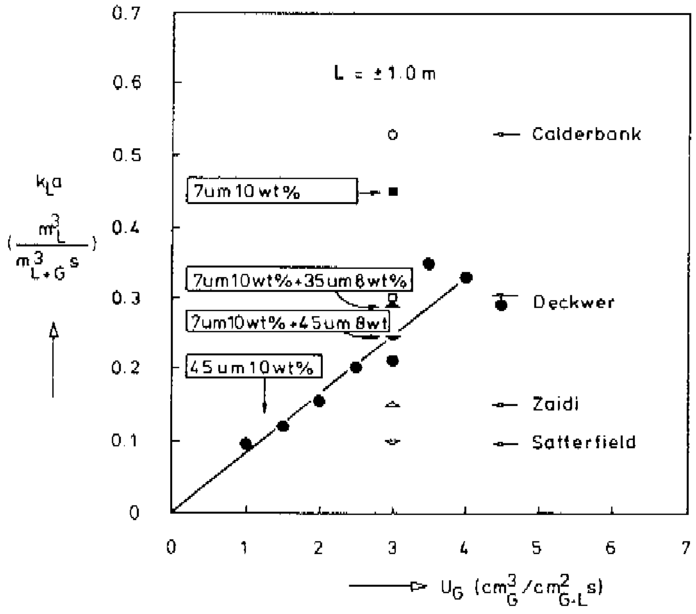

*Fig. 4.19 Values of the volumetric mass transfer in a bubble column at 250°C. The filled symbols are experimental values of $k_La$ obtained in this study with the perforated plate and a suspension column height of 1 m. The open symbols are predicted values of $k_La$ reported in literature. For each data point of the mass transfer coefficient, specific area and bubble diameter are given below. The value of Zaidi is an exception because this value is measured for CO*

| | $k_L$ $[m^3{}_L/m_{G-L}\ s]$ | $a$ $[m^2{}_{G-L}/m^3{}_{L+G}]$ | $d_b$ [mm] |
|---|---|---|---|
| Calderbank [14] | $15x10^{-4}$ | 350 | 2.1 |
| Deckwer [16] | $2x10^{-4}$ | 1500 | 0.7 |
| Zaidi [9] 1) | $1x10^{-4}$ | 1500 | 0.7 |
| Satterfield [3] | $3x10^{-4}$ | 350 | 2.1 |

1) data obtained for CO

too low as this value is even lower than the $k_La$ observed for CO by Zaidi et al. [12]. From Figure 4.19 it may be concluded that the value of $k_La$ for hydrogen in a Fischer-Tropsch bubble column under industrial conditions will be at least 0.2 $m^3_L/m^3_{L+G}$ s at a superficial gas velocity of 3 cm/s or higher. It is assumed that the influence of the pressure can be neglected [41].

*Table 4.4*

*First order reaction rate constants of hydrogen for various iron catalysts. The rate constant is based on a 20 wt% suspension and calculated with help of the data reported by Deckwer [4].*

| Authors | Catalyst | Temperature [°C] | $k_H$ [1/s] |
|---|---|---|---|
| Kölbel, Ackerman[34] | Pptd. Fe | 268 | 0.15 |
| Kölbel, Ralek[35] | Pptd. Fe | 266 | 0.18 |
| Schlesinger et al.[36] | Fused Fe | 258 | 0.032 |
| Mitra, Roy[37] | Pptd. Fe | 260 | 0.077 |
| Kunugi et al.[38] | Pptd. Fe | 260 | 0.37 |
| Mohammed[39] | Red mud | 280 | 0.36 |
| Mohammed[39] | Pptd. MnFe | 327 | 0.054 |
| Schmidt et al.[40] | Pptd. MnFe | 303 | 0.29 |

Pptd. Fe = precipitated Fe

Finally, when this $k_La$ value is compared with the first order reaction rate constants of the hydrogen conversion over iron catalysts, based on a 20 wt% suspension (see Table 4.4), it can be concluded that the gas-liquid mass transfer will certainly limit the conversion of synthesis gas over active iron catalysts in a Fischer-Tropsch bubble column. Consequently, the olefin selectivity will be lower than obtained in the kinetic regime (see Chapter 2, section 2.9.4) due to an increased olefin/carbon monoxide concentration ratio in the liquid phase.

## Symbols

| | | |
|---|---|---|
| $a$ | gas bubble interfacial area | $m^2_{G-L}/m^3_{L+G}$ |
| $a_S$ | external catalyst surface area per liquid or suspension volume | $m^2_{L-S}/m^3_L$ |
| $C_{cat}$ | catalyst concentration | $kg\ cat/m^3_L$ |
| $C_L$ | concentration of hydrogen in the liquid phase | $mol/m^3_L$ |
| $C^*_L$ | hydrogen concentration in the liquid phase at equilibrium with the gas phase | $mol/m^3_L$ |
| $C_S$ | hydrogen concentration at the catalyst surface | $mol/m^3_L$ |
| $d_b$ | bubble diameter | $m_G$ |
| $D_L$ | diffusion coefficient in the liquid phase | $m^4_L/m^2_{L+G}\ s$ |
| $D_G$ | dispersion coefficient in the gas phase | $m^2_G/s$ |
| $d_p$ | particle diameter | m or µm |
| $D_r$ | reactor diameter | $m_L$ or $m_{L+G}$ |
| $f$ | fraction hydrogen in the feed gas | - |
| $F$ | gas flow | $m^3_G/s$ |
| $g$ | gravity | $m/s^2$ |
| $H$ | Henry coefficient | $dm^3\ atm/mol$ |
| $k$ | reaction rate constant | $m^3_L/kg\ cat.s$ |
| $k_L$ | liquid film mass transfer coefficient | $m^3_L/m^2_{G-L}\ s$ |
| $k_La$ | volumetric gas-liquid mass transfer coefficient | $m^3_L/m^3_{L+G}\ s$ |
| $k_o$ | apparent reaction rate constant | $m^3_L/kg\ cat\ s$ |
| $k_{ov}$ | reciproke of the overall resistance | $m^3_L/m^3_{L+G}\ s$ |
| $k_S$ | liquid-particle mass transfer coefficient | $m^3_L/m^2_{L-S}\ s$ |
| $L$ | liquid or suspension column height without gas bubbles | $m_L$ |
| $L_{L+G}$ | expanded liquid or suspension column height | $m_{L+G}$ |
| $m$ | solubility coefficient (H/RT) | $m^3_L/m^3_G$ |
| $n_G$ | number of mixed cells | - |
| $r$ | reaction rate | $mol/m^3_{L+G}s$ |
| $t_m$ | mixing time of the liquid phase | s |
| $t_r$ | charateristic reaction time ($k_om$) | s |
| $U_G$ | superficial gas velocity | $m^3_G/m^2_{L+G}\ s$ |
| $V_L$ | volume of expanded liquid or suspension | $m^3_L$ |
| $V_{L+G}$ | liquid or suspension | $m^3_{L+G}$ |
| $X$ | conversion of hydrogen | vol % |

| | | |
|---|---|---|
| $z$ | vertical coordinate | $m_L$ or $m_{L+G}$ |
| $\delta$ | liquid film thickness | $m_L$ |
| $\epsilon_G$ | gas fraction | $m^3{}_G/m^3{}_{L+G}$ |
| $\eta$ | effectiveness factor | – |
| $u$ | dynamic viscosity | $Ns/m^2{}_L$ |
| $\rho_L$ | density of the liquid phase | $kg/m^3{}_L$ |

*References*

4.1 Deckwer, W.-D.; Serpemen, Y.; Ralek, M.; Schmidt, B., I.E.C. Proc. Des.Dev., 21 (1982) 231-241

4.2 Stern,D.; Bell, A.T.; Heinemann, H., Chem.Eng.Sci., 38 (1983) 597-605

4.3 Satterfield, C.N.; Huff, G.A.Jr.; C.E.S., 35 (1980) 195-202

4.4 Deckwer W.-D.; Serpemen, Y.; Ralek, M.; Schmidt, B., Chem.Eng.Sci., 6 (1981) 765-771

4.5 Quicker, G.; Deckwer, W.-D., Chem.Eng.Sci., 36 (1981) 1577-1579

4.6 Satterfield, C.N.; Huff, G.A.Jr., Chem.Eng.Sci., 36 (1981) 790-791

4.7 Deckwer, W.-D. Sepermen, Y., Ralek, M.; Schmidt, B., Chem.Eng.Sci., 36 (1981) 791-792

4.8 Quicker, G.; Deckwer, W.-D., Chem.-Ing.-Tech., 53 (1981) 474-475

4.9 Zaidi, A.; Louisi, Y.; Ralek, M.; Deckwer, W.-D., Ger. Chem. Eng., 2 (1979) 94-102

4.10 Bell, A.T.; Albal, R.S.; Shah, Y.T.; Carr, N.L., Chem. Eng. Sci., 9 (1984) 905-907

4.11 Ledakowicz, S.; Nettelhoff, H.; Deckwer, W.-D., I.E.C. Fundam., 23 (1984) 510-512

4.12 Zaidi, A.; Louisi, Y.; Ralek, M.; Deckwer, W.-D., Chem.-Ing.-Tech., 50 (1987) 628-629

4.13 Hammer, H., Ph.D. Thesis TU Berlin (1968), reported by Zaidi et al, see ref. 4.9

4.14 Calderbank, P.H. et al., Catalysis in practice (1963) 66-74 London; Instn Chem.Engrs.)

4.15 Calderbank, P.H. Trans.Instn Chem. Engrs, 36 (1958) 443

4.16 Deckwer, W.-D.; Louisi, Y.; Zaidi, A.; Ralek, M., I.E.C. Proc. Res.Dev., 19 (1980) 699-708

4.17 Satterfield, C.N., "Mass Transfer in Hetereogenous Catalysis", R.E. Krieger Publishing CO, Matabar Florida (1981)

4.18 Beenackers, A.A.C.M.; Swaaij, W.P.M. van, Chemical Reactor Design and Technology, ed. Lasa, H.I. de, NATO ASI Series, Series E, No 110, Dordrecht, M. Nijhoff Publ. (1986) 463

4.19 Alper, E.; Wichtendahl, B.; Deckwer, W.-D., Chem. Eng. Sci., 35 (1980) 217-222

4.20 Pal, S.K.; Sharma, M.M.; Juvekar, V.A.; Chem. Eng. Sci., 37 (1982) 327-336

4.21 Lee, Y.Y.; Tsao, G.T., Chem. Eng. Sci, 27 (1972) 1601-1608

4.22 Kars, R.L.; Best, R.J.; Drinkenburg, A.A.H., Chem. Eng. J., 17 (1979) 201-210

4.23 Alper, E.; Deckwer, W.-D., published in "Mass Tranfer with Chemical Reaction in Multiphase Systems" Vol II, ed. Alper, E. NATO ASI Series E: No 73 (1983) Martinus Nijhoff Publishers, The Hague

4.24 Alper, E., Chem. Eng. Sci., 34 (1979) 1076-1077

4.25 Frijlink, J.J., Ph.D. Thesis, Technical University Delft (1987).

4.26 Calderbank, P.H.; Moo-Young, M.B., Chem. Eng. Sci., 16 (1961) 39-54

4.27 Brian, B.W.; Dyer, P.N., Chemical and Catalytic Reactor Modeling (1984) 107-124

4.28 Joosten, G.E.H.; Schilder, J.G.M. and Janssen, J.J., Chem. Eng. Sci., 32 (1977) 563-566

4.29 Bland W. and Davidson R.L., Petroleum Processing Handbook. Mc Graw-Hill, New York 1967, reported by Stern et al. see ref. 4.2

4.30 Peter, S.; Weinert, M., Z. Physik. Chem., 9 (1956) 49

4.31 Cüsters, H., Private communication

4.32 Sovova, H., Collect Czech. Chem. Commun., 41 (1976) 3715, reported by Deckwer et al. see ref. 4.16

4.33 Kuo, J.C.W., U.S. DOE Final Report No. DOE IPC/30022-10, Dec. (1983)

4.34 Kölbel, H.; Ackermann, P., Chem. Ing. Technik, 28 (1956) 381

4.35 Kölbel, H.; Ralek H., Cat. Rev. Sci. Eng., 21 (1980) 225

4.36 Schlesinger, M.D.; Benson, H.E.; Murphy, E.M.; Storck, H.H., Ind. Eng. Chem., 46 (1954) 1322

4.37 Mitra, A.K.; Roy, A.N.; Ind. Chem. Engr., (1963) 127

4.38 Kunugi, T.; Sakai, T.; Negishi, N., Sekiyu Gakkai Shi, 11 (1968) 636

4.39 Mohammed, M., Ph.D. Thesis, TU Berlin 1977

4.40 Schmidt, B.; Ralek, M.; Deckwer, W.-D., reported by Deckwer, W.-D. et al., see ref. 4.1

4.41 Kölbel, H.; Borchers, E., Langemann, H., Chem.-Ing.-Tech., 33 (1961) 668

4.42 Mangartz, K.-H.; Pilhofer, Th., VT "Verfahrenstechnik" 14(1980)40-44

4.43 Prandit, A.; Joshi,J., Chem. Eng. Sci., 38(1983) 1189-1215

4.44 Westerterp, K.R.; Swaay, W.P.M. van; Beenackers, A.A.C.M., Chemical Reactor Design and Operation, John Wiley and Sons, Chichester (1984) 183-189