Hydrodynamic Properties of the Fischer–Tropsch Slurry Process

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The indirect coal liquefaction route to produce transportation fuels, i.e., the Fischer–Tropsch synthesis, may favorably be carried out in the slurry phase. The paper reports on measurements of gas holdup and heat and mass transfer in bubble column slurry reactors of 4.1 and 10 cm diameter. The study was done under conditions prevailing in the Fischer–Tropsch slurry reactor (Rheinpreussen–Koppers process). The results enable, at least, an estimation of the majority of the hydrodynamic properties involved in designing a slurry-phase reactor. Under the conditions of the Fischer–Tropsch synthesis the slurry reactor can be treated as a two-phase system which permits some conclusions concerning the favorable flow regimes and gas velocities.

Introduction

Owing to the scarcity of petroleum, coal utilization again has found growing interest for the production of transportation fuels and primary chemicals (Büssemeier et al., 1976; Falbe, 1977). This has also initiated a reconsideration of indirect coal liquefaction, i.e., the hydrocarbon synthesis from CO and H$_2$ which is known as Fischer–Tropsch (FT) synthesis. In recent years numerous papers have been published dealing with various aspects of this synthesis, and new experimental work was carried out (Vannice, 1976; Büssemeier et al., 1976; Mohammed, 1977; Kitzelmann et al., 1977; Schulz and Zein el Deen, 1977; Zein el Deen et al., 1978; Gaube and Hochstadt, 1978; Atwood and Bennett, 1979; Zaidi et al., 1979; Satterfield and Huff, 1980). Most of the experimental studies have been concentrated on the development and optimization of new catalysts and the modification and improvement of known catalysts, respectively (Vannice, 1976; Büssemeier et al., 1976; Kitzelmann et al., 1977; Köbel and Ackermann (1956) and recently reviewed in more detail by Köbel and Ralek (1977), the following major advantages of the slurry process can be deduced: high conversions (up to 170 g of C$_2$+/Nm$^3$ (CO $+$ H$_2$)); high olefin yield (up to 85%); exact temperature control; use of low ratio H$_2$ to CO synthesis gas; high flexibility.

A comparison of the production and operation data of the ARGE and the Syndhol reactor reported by Frohning et al. (1977) and Schulz (1977) with the slurry reactor of Rheinpreussen–Koppers also reveals that the latter gives better catalyst performance (yield per unit weight of catalyst) even at significant higher catalyst loadings while the overall reactor performance (yield per unit volume of reactor) of the three processes is of comparable magnitude. In addition, the slurry process gives high single pass conversion whereas in the ARGE and Syndhol processes the recycle to feed gas ratio is usually more than 2.

There is only the study carried out at Warren Spring Laboratory (Calderbank et al., 1963; Farley and Ray, 1964) that tends to contradict the advantageous properties of the slurry process. However, the unfavorable results of this study obviously have to be attributed to application of an unsuitable catalyst which was insufficiently active and encouraged carbon formation. This was not observed to such an extent in any other study.

In spite of the obvious advantages of the FT slurry synthesis, the Rheinpreussen–Koppers process was never realized at an industrial scale. In view of the easy availability of oil and its cheap price during the fifties, all FT

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Table I. Fischer-Tropsch Studies in Liquid Phase

<table>
<thead>
<tr>
<th>number</th>
<th>reactor diameter, cm</th>
<th>height of reactor, cm</th>
<th>range of gas velocity, cm/s</th>
<th>catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schlesinger et al. (1951)</td>
<td>2</td>
<td>150.0</td>
<td>600</td>
<td>9.5</td>
</tr>
<tr>
<td>Kolbel and Ralek (1977)</td>
<td>4</td>
<td>5.0</td>
<td>120</td>
<td>pptd. Fe catalyst, Cu-K,O promoted</td>
</tr>
<tr>
<td>Mitra and Roy (1963)</td>
<td>7</td>
<td>3.8</td>
<td>100</td>
<td>0.2-1.2</td>
</tr>
<tr>
<td>Calderbank et al. (1963)</td>
<td>5</td>
<td>5.0</td>
<td>450</td>
<td>0.6-4.5</td>
</tr>
<tr>
<td>Farley and Ray (1964)</td>
<td>6</td>
<td>24.4</td>
<td>840</td>
<td>4.5-7.0 (1.25), not S free</td>
</tr>
<tr>
<td>Mohammed (1977)</td>
<td>7</td>
<td>3.8</td>
<td>100</td>
<td>0.2-1.2</td>
</tr>
</tbody>
</table>

Figure 1. Experimental setup for measurements of heat transfer coefficient.

activities were stopped and plans for production plants were given up (for instance, the intention of the Indian government to erect an FT slurry plant with a production capacity of 250 000 t/year based on an offer from Koppers GmbH).

Purpose

Owing to the new interest in indirect liquefaction and the favorable features of the slurry reactor, we decided to look in more detail at the hydrodynamic properties (i.e., gas holdup and heat and mass transfer) of this reactor under conditions which prevail in the FT slurry process. These conditions include: use of molten paraffin as liquid phase, temperatures of about 250 to 300 °C, pressures in the range of 1 MPa, and catalyst concentrations up to 16 wt%. The hydrodynamic aspects have received only little attention until now (Calderbank et al., 1963; Hammer, 1968); however, such data are required for a reliable design and scale-up of an FT slurry reactor. In a previous paper (Zaidi et al., 1979), we already reported some results on CO mass transfer coefficients which were obtained by means of a chemical method using the well-defined water gas shift reaction as a model system. However, these measurements were carried out in a 4.1 cm diameter column only. It is therefore questionable whether the results are also representative for larger units. This paper presents measurements of gas holdup and heat transfer in two different bubble column slurry reactors. It is shown that on the basis of these data and our previous data, the more important hydrodynamic properties of the FT slurry process can be estimated.

Experimental Section

The experiments were carried out in two bubble columns having diameters of 4.1 cm (BC I) and 10 cm (BC II). The suspension height was between 60 and 100 cm. The gas was sparged in both columns by metal sintered plates having a mean pore diameter of 75 μm. Usually nitrogen was used as the gas phase and its flow was measured and controlled by mass flow meters. The columns could be maintained at temperatures up to 300 °C by heating wires wound round the outer wall of the columns (see Figure 1). The gas holdup was measured by means of constant-temperature anemometry. The construction of the hot
wire probe is shown in Figure 2. It is screwed on a steel tube which could be introduced from the top plate of the column and was sealed by a stuffing box. However, the tube with the probe could be moved through the stuffing box. After the necessary calibrations and adjustments of the probe in the gas and slurry phase were done the probe was moved slowly down from the gas space to the suspension. When the hot wire just touches the slurry phase the heat removal and hence the electric current increases sharply. Thus the height of the gas–liquid–solid dispersion could be determined accurately. The reproducibility was usually better than 2 mm. Further details of this measuring technique are given by Louisi (1979). With this method the gas holdup was measured with molten paraffin (melting point 80 to 110 °C) as liquid phase containing various amounts of suspended solids (up to 16 wt%). Powdered Al₂O₃ (d₅ₐ ≤ 5 μm) was applied to simulate hydrodynamically the suspended catalyst of the FT process. The temperature was varied between 143 and 270 °C, and pressures between 400 and 1100 kPa were applied.

Heat transfer measurements were carried only in BC II (diameter 10 cm). The experimental arrangement is shown schematically in Figure 1. The general setup and particularly the construction of the heat source (2.1 cm outer diameter) are similar to that of Kolbel et al. (1958, 1960). Additional details can be found in the thesis of Louisi (1979). At the outer wall of the heat source two thermocouples were mounted at different positions which gave always same temperatures. Therefore the surface of the heat source has a uniform temperature. After steady-state conditions were established, the temperature difference ΔT between the thermocouples at the wall of the heated rod and that thermocouple located in the slurry (TC 2) was measured. The heat transfer coefficient was calculated from

\[ h = \frac{iU}{AΔT} \]

The surface of the heat source was 39.56 cm². For the majority of the measurements the electrical energy (iU) supplied was about 17 J/s, giving a temperature difference of less than 5 °C.

As heat transfer coefficients presented in the literature were only measured in the low temperature range, i.e., usually room temperature, some measurements were carried out at 143 °C with xylene, decalin, kogasin, and paraffin. Most measurements were done with a paraffin/Al₂O₃ suspension under variation of several parameters (gas flow rate, temperature, pressure, suspension height, temperature difference, gas composition). Thus a range of operating variables was covered which is relevant for the FT slurry process. Owing to the formation of foam, the measurements were carried out at linear gas velocities less than 4 cm/s. The linear gas velocity (volume flow rate per cross-sectional area of reactor) refers in all cases to the operation conditions of the reactor.

Results on Gas Holdup

The slurry phase was batch-wise in our study. Therefore the fractional gas holdup is calculated from the measured height of expanded gas–liquid–solid system (Hₘₐₐ) and the height of gas free suspension (H₀ₐ) by

\[ ε₇ₐ = \frac{Hₘₐₐ}{Hₘₐₐ} \]

Figure 3 shows the measured gas holdup in BC I for three gas velocities as a function of the temperature. A remarkable decrease of ε₇ₐ is found as temperatures increase from 180 to 240 °C. At higher temperatures the holdup is obviously constant in this column.

In BC II (larger diameter column) such a dependency of ε₇ₐ on T is not observed although the temperature range studied was even larger. As shown in Figure 4 for the same solid concentration, all ε₇ₐ data for temperatures between 143 and 285 °C can be described by the drawn curve. No significant differences can be discerned for ε₇ₐ values obtained at different temperatures. With regard to the liquid-phase properties it is only the viscosity which varies considerably with temperature. However, if there is a pronounced viscosity effect on ε₇ₐ it should be observable in both columns. The increased gas holdup in the smaller column may therefore be attributed to that which is commonly called a “wall” effect, but this is not clearly understood as in both columns dₕ/d₀ > 40.

The influence of the solid contents on the gas holdup in BC II can be seen from Figure 5. The addition of solids decreases the gas holdup slightly, i.e., Δε₇ₐ ≈ 0.01 to 0.02. However, a dependency on the solid concentration cannot
be recognized since solid concentrations from 5.5 to 16 wt% yield the same gas holdup. We also studied the influence of pressure on the gas holdup in the three-phase system. In agreement with Kolbel et al. (1961), no effect could be found; see Figure 6. The same result was found in BC I. In another series of runs the suspension height (without solids) was varied from 60 to 95 cm. As the gas velocities used were only small, i.e., lower than 3.4 cm/s, no pronounced influence could be observed.

From the experimental data of the Al₂O₃/paraffin/N₂ system one can give the following conclusion. For a given gas velocity (less than 4 cm/s) the gas holdup is not influenced by temperature, pressure, and solid contents provided the temperature is above 250 °C. This conclusion is strictly valid from our measurements only for solid concentrations higher than 5 wt% and lower than 16 wt%. Fischer–Tropsch studies in the slurry phase have been carried out usually between this range of catalyst concentrations. It can be expected that even somewhat higher solid concentrations do not strongly influence the holdup, but it is known that above a certain solid concentration the holdup drops down (Kato et al., 1973; Joosten et al., 1977). The holdup values under the above conditions are shown in Figure 7 for both columns. It can be seen that the data of the two columns do not differ significantly. The εₒ values of BC I lie within the range of scatter of the data obtained from BC II in which more measurements were carried out. All data points can be represented by a regression line of the form

\[ \varepsilon_o = 0.053u_{G0}^{1.1} \pm 0.015 \]  

Empirical equations for gas holdup in bubble column reactors are given by several authors. Predictions of some correlations (Akita and Yoshida, 1973; Gestrich and Rähse, 1975; Bach and Pilhofer, 1978) proposed recently on the basis of comprehensive experimental data are also given in Figure 7. It can be seen, however, that these correlations fail completely for the system studied here at gas velocities above 1 cm/s. If molten paraffin without solid would be used the discrepancy would be even larger. The discrepancies between correlations and measured data are not explainable by the use of different gas spargers alone as will be discussed below.

It was shown by Deckwer et al. (1979) that the measured holdup data of this study can also be described successfully by the concept of ideal bubble flow (Lapidus and Elgin, 1957) if the slip velocity is expressed by a Richardson–Zaki relation (1954). This treatment leads, however, to an expression which cannot explicitly be solved for εₒ. Therefore, the empirical description according to eq 3 is preferred.

From the FT studies carried out in slurry phase and summarized in Table I there are few holdup data available. Calderbank et al. (1963) reported εₒ values in wax for a 5-cm column and a temperature of 265 °C. These data are lower than those of this study, which may be attributed to the ball and cone gas distributor used by Calderbank et al. In contrast to these authors, Farley and Ray (1964) reported considerably higher gas holdup although the same kind of gas sparger was applied. Unfortunately, Farley and Ray (1964) give only one value of the gas holdup (their run 14). For a gas velocity of 7 cm/s they found in a column of 24.4 cm diameter a gas holdup of 0.45 (at low carbon content in the slurry). This value agrees exactly with that predicted from eq 3. Though this is the only value re-
ported by Farley and Ray it may be allowed to conclude that eq 3 is not only applicable to larger diameter columns but is also valid at higher gas velocities, at least to gas velocities up to 7 cm/s, and probably to somewhat higher values too.

**Gas/Liquid Interfacial Area**

Knowledge of the gas holdup permits calculation of the gas/liquid interfacial area from

\[ a = \frac{6\bar{e}_G}{d_s^*} \]  

if an estimate of the mean surface-to-volume bubble diameter (Sauter diameter) is available. Therefore, bubble diameters were measured photographically in a 5-cm glass column at temperatures between 250 and 270 °C, atmospheric pressure, and gas velocities of 1 to 3 cm/s, and without the presence of solids. A mean value of \( d_s^* \) of 0.7 mm was found which is approximately independent on gas velocity and temperature. As the bubble diameter does not depend on pressure (Kolbel et al., 1961) and assuming that the presence of solids does not considerably change the bubble diameter, this value may be used as a reasonable estimate. With \( d_s^* = 0.7 \) mm it follows from eq 3 and 4 that

\[ a = 4.5u_G^{1.1} \]  

where \( a \) is in \( \text{cm}^{-1} \) and \( u_G \) in cm/s. Hammer (1968) measured bubble diameters in paraffin under similar conditions and found even considerably lower values for \( d_s^* \). On the other hand, Calderbank et al. (1963) measured the interfacial area by a light-transmission method in wax at 265 °C. Their values of \( a \) are only about one-third of those calculated from eq 5. It is known that the photographic method overestimates the small bubbles near the wall. However, the error introduced by this method is less than 30% (Schumpe and Deckwer, 1980) and does not explain the discrepancy with the data of Calderbank et al. It seems reasonable to assume that the differences are caused, at least, partly by the different gas spargers, i.e., ball and cone in the investigations of Calderbank et al. and sintered plate distributors in this study.

**Liquid Side Mass Transfer Coefficients**

By application of the concepts of resistances in series, Zaidi et al. (1979) measured the volumetric mass transfer coefficients \( k_L \) in the 4.1-cm column of this study. As a model system, the CO conversion reaction was used which is part of the FT synthesis itself if carried out on Fe catalysts. In that study (Zaidi et al., 1979) the reaction resistance was varied by using different amounts of catalyst, and the \( k_L a \) values were obtained from plots of the overall resistance vs. the reaction resistance. The determined \( k_L a \) values increase from about 0.1 s\(^{-1}\) at \( u_G = 1 \) cm/s to about 0.2 s\(^{-1}\) at \( u_G = 3.6 \) cm/s. These values are higher by a factor of about 2 than the predictions of the correlation of Akita and Yoshida (1973) but they agree fairly well with the value reported by Hammer (1968) for the CO methanation on Ni suspended in paraffin.

As the interfacial areas for the two columns used in this study agree within the range of scatter, it is justified to expect that the \( k_L a \) values found in the 4.1-cm column should also apply to larger diameter reactors as the liquid side mass transfer coefficient \( k_L \) can be assumed to be independent of the reactor diameter. The \( k_L \) values calculated from the \( k_L a \) data and eq 4 are plotted in Figure 8 as function of the gas velocity. The \( k_L \) values seemingly run through a minimum. However, in view of the scatter, it is more appropriate to assume that the \( k_L \) data are not very dependent on gas velocity and temperature. Applying the correlation of Sovova (1976) to estimate the CO diffusivities in paraffins, the experimental \( k_L \) values can be compared with predictions of empirical correlations. The relation of Sovova has the advantage that the molecular weight of the solvent must not be known, and is as follows

\[ D = 3.374 \times 10^{-4} \mu_L^{0.5}V_G^{0.6} \]

where \( D \) is in \( \text{cm}^2/\text{s}, \mu_L \) in cP, and \( V_G \) is molar volume of the gas \( (V_G = 29.3 \text{ cm}^3/\text{mol}) \). For small diameter bubbles \( (d_B < 2.5 \text{ mm}) \) Calderbank and Moo-Young (1961) proposed the subsequent empirical correlation

\[ k_L Sc^{1/3} = 0.31 \left( \frac{\mu D \rho_L \varepsilon}{\rho_L G^2} \right)^{1/3} \]

which, in approximate accordance with the data presented in Figure 8, does not contain a dependency of \( k_L \) on \( u_G \). The predictions of eq 7 and the experimental findings are compared in Figure 9. If one considers the experimental conditions under which the \( k_L \) values were determined and the errors involved to estimate the diffusivity, the agreement is sufficient. The correlation of Hughmark also gives predictions which are in sufficient agreement with the experimental data (Zaidi et al., 1979), while the correlation of Akita and Yoshida (1973) gives values which are considerably lower. From Figures 8 and 9 it can be deduced that \( k_L \) for CO in \( \text{Al}_2\text{O}_3/\text{paraffin suspension} \) is about 0.01 cm/s which is a reasonable guideline for practical purpose.
the heat transfer coefficients in gas-liquid dispersions are obtained with slopes between
water at temperatures measured with water at 25 °C. As pointed out by Kast (1962), the heat transfer coefficients in gas-liquid dispersions are at least 10 times larger than in one-phase flow taking a liquid velocity which is equal to the gas velocity applied in the two-phase system, as shown by the lowest curve in Figure 10.

Heat transfer from walls and inserted coils was analyzed theoretically by Deckwer (1980). By application of Higbie's unsteady-state mass transfer theory to heat transfer, Deckwer obtained

\[ h \propto \frac{k \rho c_p}{\theta}^{0.5} \] (8)

The contact time \( \theta \) can be interpreted as the mean lifetime of macroscale eddies which are generated by macroscale eddies resulting from the rising bubbles; \( \theta \) can be formulated in terms of Kolmogoroff's theory of isotropic turbulence which finally leads to the equation

\[ h \propto k^{0.5} \rho^{0.25} c_p^{0.5} \mu^{0.25} g^{0.25} \frac{\rho}{\kappa} \] (9)

which can be rearranged to give

\[ \frac{h}{\rho c_p \mu G} \propto \left( \frac{\rho G}{\kappa} \right)^{-1/4} \left( \frac{\rho c_p}{g} \right)^{-1/2} \] (10)

or in dimensionless numbers

\[ St = \beta (Re Fr Pr^2)^{-1/4} \] (11)

where \( \beta \) is a constant.

Results on Heat Transfer
The coefficients of heat transfer from the inserted heat source to the gas-liquid dispersion for xylene, kogasin, decalin, and paraffin at 143 °C are plotted as a function of \( \rho G \) in Figure 10. In this log-log plot, straight lines are obtained with slopes between 0.2 and 0.27. For comparison, Figure 10 also gives the data of Burkel (1974) measured with water at 25 °C. As pointed out by Kast (1962), the heat transfer coefficients in gas-liquid dispersions are at least 10 times larger than in one-phase flow taking a liquid velocity which is equal to the gas velocity applied in the two-phase system, as shown by the lowest curve in Figure 10.

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which can be rearranged to give

\[ \frac{h}{\rho c_p \mu G} \propto \left( \frac{\rho G}{\kappa} \right)^{-1/4} \left( \frac{\rho c_p}{g} \right)^{-1/2} \] (10)

or in dimensionless numbers

\[ St = \beta (Re Fr Pr^2)^{-1/4} \] (11)

where \( \beta \) is a constant.

![Figure 10. Heat transfer coefficients of some hydrocarbons at 143 °C.](image)

Table II. Physicochemical Properties of Liquid Media Applied in Heat Transfer Measurements (Values Given in Brackets Are Estimated from Data at Lower Temperatures)

<table>
<thead>
<tr>
<th>liquid media</th>
<th>T, °C</th>
<th>( \rho ), g/cm³</th>
<th>( \mu ), mPa s</th>
<th>( k ), cm/s</th>
<th>( c_p ), J/kg K</th>
<th>( \sigma ), dyn/cm</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>xylene</td>
<td>143</td>
<td>(0.75)</td>
<td>0.21</td>
<td>0.116</td>
<td>2218</td>
<td>(19)</td>
<td>Kern (1950)</td>
</tr>
<tr>
<td>kogasin</td>
<td>143</td>
<td>0.68</td>
<td>0.41</td>
<td>0.144</td>
<td>2135</td>
<td>18.0</td>
<td>Orlicek and Poll (1951)</td>
</tr>
<tr>
<td>decalin</td>
<td>143</td>
<td>0.78</td>
<td>0.49</td>
<td>0.101</td>
<td>2092</td>
<td>22.0</td>
<td>Beilstein (1960)</td>
</tr>
<tr>
<td>paraffin</td>
<td>143</td>
<td>0.73</td>
<td>13.0</td>
<td>0.169</td>
<td>2927</td>
<td>29.1</td>
<td>Hammer (1968)</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>0.69</td>
<td>4.0</td>
<td>0.165</td>
<td>2927</td>
<td>24.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.67</td>
<td>2.0</td>
<td>0.162</td>
<td>2927</td>
<td>21.2</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 11. Check of eq 11 for xylene, decalin, and kogasin at 143 °C and paraffin at 143, 220, and 260 °C.](image)

Equation 11 is valid for gas velocities less than 10 cm/s. At higher gas velocities the heat transfer coefficient does not increase any more. Empirical correlations are very similar to eq 11. Heat transfer coefficients measured at low temperatures, i.e., room temperature, are described with striking agreement by this equation if \( \beta = 0.1 \) (Deckwer, 1980).

The measurements with hydrocarbon liquids (without solids) shown in Figure 10 were mainly carried out to check the validity of eq 11 at higher temperatures. Using the physical data given in Table II the required dimensionless groups can be calculated. The calculations are presented in Figure 11. Agreement between experimental data and eq 11 again using \( \beta = 0.1 \) is good. It should be pointed out here that the experimentally obtained heat transfer coefficients depend slightly on the temperature difference between the surface of the heat source and the bulk liquid. This is probably due to the lower viscosity at the heat source. As the heat transfer resistance is located there, the temperature at the outer wall of the heat source was used to estimate the physical properties. However, for the majority of runs carried out the temperature difference was less than 5 °C and its effect on \( h \) could be neglected.

In what follows, the measurements with the Al₂O₃/paraffin suspension will be treated. The influence of the Al₂O₃ concentration is shown in Figure 12. Increasing solid contents also increases the heat transfer coefficients. It is possible that similar to gas-solid fluidized beds, the increase of \( h \) is caused by independent motion of the particles leading to increased exchange frequency of fluid elements at the heat surface area. On the other hand, one may argue that the suspension can be regarded as a ho-
Figure 12. Influence of solid concentration on heat transfer coefficient.

Table III. Physical Data of Al₂O₃/Paraffin Suspension (Calculated from Eq 12 to 15)

<table>
<thead>
<tr>
<th>temp, °C</th>
<th>concn, wt%</th>
<th>( \rho )</th>
<th>( \mu )</th>
<th>( c_p )</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>4.8</td>
<td>0.708</td>
<td>4.30</td>
<td>2837</td>
<td>0.169</td>
</tr>
<tr>
<td>9.1</td>
<td>0.736</td>
<td>4.52</td>
<td>2756</td>
<td>0.173</td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>0.762</td>
<td>4.88</td>
<td>2662</td>
<td>0.177</td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>0.784</td>
<td>4.82</td>
<td>2626</td>
<td>0.181</td>
<td></td>
</tr>
<tr>
<td>260</td>
<td>4.8</td>
<td>0.698</td>
<td>2.08</td>
<td>2838</td>
<td>0.166</td>
</tr>
<tr>
<td>9.1</td>
<td>0.725</td>
<td>2.15</td>
<td>2758</td>
<td>0.170</td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>0.751</td>
<td>2.23</td>
<td>2686</td>
<td>0.174</td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>0.773</td>
<td>2.29</td>
<td>2690</td>
<td>0.178</td>
<td></td>
</tr>
</tbody>
</table>

mogeneous phase as the particle size is very small \( (d_s \leq 5 \mu m) \). Then the variation of \( h \) will be only the result of changing physicochemical properties.

Equation 11 can be applied to discriminate among these different views. This requires the estimation of the physical properties of the suspensions from the individual data of Al₂O₃ and the paraffin. The mean densities were calculated from

\[
\overline{\rho} = \upsilon \rho_S + (1 - \upsilon) \rho_L \tag{12}
\]

where \( \upsilon \) presents the volume fraction and \( S \) and \( L \) refer to solid \( (Al₂O₃) \) and liquid \( \) (paraffin). The viscosities were obtained from Einstein's relation

\[
\overline{\mu} = \mu_L (1 + K \upsilon_S) \tag{13}
\]

The constant \( K \) was taken from Meisl (1967), who found for a suspension of a Hopcalite catalyst in paraffin a \( K \) value of 4.5. The heat capacity of aluminum oxide at temperatures between 220 and 280 °C can be calculated from the data given in Landolt-Börnstein (1961). The heat capacity of the suspension is then given by

\[
\overline{c_p} = \upsilon_S c_{PS} + (1 - \upsilon) c_{PL} \tag{14}
\]

where \( \upsilon \) presents the weight fraction. For estimating heat conductivities of suspensions, Tareef (1940) proposed the equation

\[
k = k_L \frac{2k_L + k_S - 2 \upsilon_S (k_L - k_S)}{2k_L + k_S + \upsilon_S (k_L - k_S)} \tag{15}
\]

which was used in this study. The physicochemical data of the Al₂O₃/paraffin suspensions calculated by means of eq 12 to 15 are summarized in Table III for temperatures of 220 and 260 °C where most of the heat transfer measurements were carried out.

The plot of \( St \) vs. \( (ReFrPr^2)^{-1/4} \) for the measurements with suspended Al₂O₃ is given in Figure 13. Though the majority of data points lies above the correlation line for liquids, the description by eq 11 with \( \beta = 0.1 \) is fairly good. As Figure 13 reveals no clear dependence on the solids concentration, one can assume that the Al₂O₃/paraffin slurry can be treated as a homogeneous phase with respect to heat transfer. The increase of \( h \) shown in Figure 12 is therefore mainly due to changes of the physicochemical properties.

Owing to the successful description of the heat transfer in the present slurry system with eq 11, it was challenging to check the validity of the equation for other slurry systems.

Kölbel et al. (1958, 1960) carried out comprehensive heat transfer studies with different slurry systems in bubble column reactors. Calculating the physical data of the suspensions by eq 12 to 15, the log-log plot of \( St \) vs. \( (ReFrPr^2)^{-1/4} \) can be prepared. This is shown in Figure 14 together with the data of this study. The slurry systems considered are defined in Table IV. For clearness only a selection of the large amount of data of Kölbel could be represented in that figure. However, extreme values are taken into account preferentially. As can be expected from
the result with powdered $\text{Al}_2\text{O}_3$ particles, heat transfer in suspensions of kieselguhr in various liquid media is described by eq 11 without need for any modification.

The experimental data with suspended sand particles are also represented by eq 11. However, all values of $St$ calculated for sand suspension lie at the upper limit of data field shown in Figure 14. Therefore, heat transfer in the presence of sand particles will be better described with a $\beta$ value of 0.12. This indicates that the larger sand particles contribute to heat transfer not only by alterations in physicochemical properties but also by an additional mechanism. This is probably due to collisions against the surface of the heat source giving increased transport of fluid elements and thus enhanced heat transfer. However, this extra effect is small and amounts to 20% as the value of $\beta$ indicates. On the other hand, it should be considered that calculation of the physical properties of suspensions with 20 wt% of solids from eq 12 to 15 gives only rough estimates. The deviation of the sand suspensions observable in Figure 14 may also be attributable to uncertainties in $k$ and $\mu$. Hence it may be possible to conclude from a conservative point of view that heat transfer in bubble-agitated liquid–particle suspensions with particles diameter less than 100 $\mu$m can be well represented by eq 11 using $\beta = 0.1$.

### Liquid–Solid Mass Transfer

The heat transfer measurements indicate that for the catalyst particles commonly used in the FT slurry process the suspension phase can be treated homogeneously. Hence, one can conclude as an approximation that the particles do not move independently. Therefore, their slip velocity is low; in the limiting case it will be zero. Under this condition the liquid–solid mass transfer coefficient can be obtained from

$$Sh = \frac{k_v d_s}{D} = 2$$

(16)

Of course, this relation yields only the lower limit of $k_v$, but together with the specific liquid–solid surface area $a_s$ ($$cm^2$$/$$cm^3$$ of gas–liquid–solid suspension) which is given by

$$a_s = \frac{6(1 - \varepsilon_G)}{d_R^2} \rho L s G$$

(17)

the liquid–solid mass transfer resistance ($1/k_v a_s$) can be estimated. This quantity is commonly used to compare the relative importance of transport resistances in slurry reactors. Owing to the high surface area of the suspended particles, a resistance at the liquid–solid surface can usually be neglected even for the lower limit of $k_v$.

### Dispersion

If a larger FT unit has to be designed, reactor models with distributed parameters should be applied, of course. Due to the small catalyst particles, pore diffusion resistance and liquid–solid mass transfer resistance can be neglected, and the liquid–solid suspension can be regarded as a homogeneous phase. Therefore a two-phase description will suffice provided a possible height dependency of the catalyst concentration caused by sedimentation is taken into account. Pertinent design models of two-phase reactors, i.e., bubble columns, which consider local dependencies of various parameters have been proposed by Deckwer (1976, 1979). However, application of such models leads to another group of design parameters which are mainly determined by the hydrodynamics of gas–liquid dispersions, i.e., the dispersion coefficients of the different phases.

The axial dispersion coefficient of the liquid phase can be calculated from (Deckwer et al., 1974)

$$E_L = 2.7\nu_G 0.3 d_R^{1.4}$$

(18)

($$E_L$$ in $$cm^2$$/$$s$$, $$\nu_G$$ in $$cm/s$$, and $$d_R$$ in $$cm$$) or from the dimensionless correlation proposed by Kato and Nishiwaki (1972).

Equation 18 comprehends the data of various authors and was confirmed by Subramanian and Tien (1978). In a recent review on dispersion in gas–liquid reactors, Shah et al. (1978) also recommended use of this relation though it does not include liquid phase properties. However, it may be reasonable that $$E_L$$ does not depend largely on liquid phase properties as can be suspected from experimental results (Hikita and Kikukawa, 1974; Mashelkar and Ramachandran, 1975).

Data on gas-phase dispersion in bubble columns are few. The latest results were obtained by Mangartz and Pilhofer (1980), who also critically analyzed the results of other authors. Mangartz and Pilhofer (1980) propose the relation

$$E_G = 5 \times 10^{-d_R^{1.4}}$$

(19)

where $$E_G$$ is in $$cm^2$$/$$s$$, $$d_R$$ in $$cm$$, and $$\nu_G$$ in $$cm/s$$. Particularly at high conversion levels, the performance of the slurry reactor may considerably be affected by gas-phase dispersion (Deckwer, 1976).

In general, catalyst sedimentation has to be accounted for in slurry reactors. The distribution of the catalyst along the reactor can be computed using the sedimentation–dispersion model. As to the results of Kato et al. (1972), the solid dispersion coefficients do not differ much from those of the liquid phase. From the data provided by Cova (1966), Imafuku et al. (1968), and Kato et al. (1972), the solids concentration profiles can be calculated. As in the FT process the catalyst particles are usually small, according to Kölbel and Ralek (1977) the diameter should be less than 50 $\mu$m, the catalyst profiles are not very pronounced, in accordance to the measurements of Cova (1964). In addition, numerical computations on the basis of the sedimentation–dispersion model assuming a first-order reaction on the catalyst surface indicate that an influence of the nonuniformity of the catalyst distribution...
Flow Regimes and Effective Application of Slurry Column Reactors

The majority of the results presented in this paper indicate that the slurry column reactor can be treated as a two-phase bubble column provided the particle diameters are small, say \( \leq 50 \, \mu \text{m} \), and the solids concentration does not exceed about 16 wt\%. Therefore, the flow regimes observed in two-phase bubble column reactors will also apply to the Fischer-Tropsch slurry systems. This allows some conclusions on the gas velocities which lead to an effective use of the slurry column reactor.

At low gas velocities the gas flow in a pseudo-two-phase system is characterized by bubbles rising rather undisturbed in the column, their diameter distribution is narrow, and the interaction between the bubbles is small. This hydrodynamic situation is called homogeneous or ideal bubbly flow; see Figure 15a. If the gas velocity is increased \( (u_G > 5 \, \text{cm/s}) \) and the reactor is high enough, say \( > 1 \, \text{m} \), bubble coalescence occurs. Hence, larger bubbles appear in the dispersion. However, the bubbles cannot grow indefinitely, as an equilibrium between coalescence and breakup will be established. This leads finally to a flow situation, shown in Figure 15b, which should be denoted as heterogeneous or churn-turbulent. Among the pseudo-homogeneous dispersion of small and approximately spherical bubbles, a few large bubbles are encountered which raise through the bubble in a churn-like motion. Though their number is not large, they contribute considerably to the gas flow as their rise velocity is large. A special behavior may occur in small diameter columns. Here the bubbles generated by coalescence may reach the reactor diameter. They are stabilized by the wall and form slugs; see Figure 15c.

Figure 16 presents an approach to characterize the various flow regimes in two-phase and slurry column reactors as a function of the gas velocity and the reactor diameter which are certainly the main influences. The transitions between the different flow regimes are not sharp; the exact limits depend additionally on the dispersion height, the gas sparger, the liquid velocity, and the physicochemical properties of the slurry (liquid) phase. The transition between the homogeneous and the heterogeneous flow can usually be observed at about 5 to 7 cm/s if the reactor diameter is not too small. However, for certain liquids as, for instance, higher viscous Newtonian and non-Newtonian media and if single and multinozzle spargers (with nozzle diameters \( \geq 1 \, \text{mm} \)) are applied, bubbly flow behavior may not be observable at all. The flow is churn-turbulent then even at low gas velocities (Shah and Deckwer, 1981).

Schumpe et al. (1979) have studied the performance of bubble column reactors in the various flow regimes. They showed that in the slow reaction regime of mass transfer theory bubble columns are effectively operated if the flow is homogeneous, where high space–time yields at high conversions are obtainable. Even the case of absorption enhanced by fast chemical reaction in the liquid phase operation at high gas velocities gives little advantage. Schumpe et al. (1979a,b) recommend the selection of a reactor diameter that guarantees possible operation in the homogeneous regime, particularly if the effective reactor diameter is small, say \( d_R \leq 10 \, \text{cm} \). In larger diameter columns, gas velocities considerably larger than 10 cm/s should not be applied. Above all, slug flow should be strictly avoided as the interfacial area and hence the conversion is small.

In Figure 16 the gas velocity ranges applied in the FT slurry studies summarized in Table I are given. It can be seen that most of these investigations were obviously carried out at favorable flow conditions. Owing to heat transfer tubes the effective diameter in the demonstration plant of Rheinpreussen–Koppers was assumed to be still larger than 25 cm. Though the applied inlet gas velocity was 9.5 cm/s the reactor worked very effectively, probably because the effective diameter was large enough to prevent bubble slug formation. In addition, the catalyst activity was high and high conversions could be achieved.

Summary and Conclusions

Gas holdup measured in the 4.1- and 10-cm diameter bubble columns do not differ. Hence one can conclude that the volumetric mass transfer coefficients \( k_{G1} \) of our previous study (Zaidi et al., 1979) in the 4.1-cm column are also valid for larger diameter columns. Though the present investigations were carried out at low gas velocities, this does not have to be a serious limitation as the results can be extrapolated to higher gas velocities. For instance, the proposed correlation for the gas holdup eq 3 predicts exactly the value reported by Farley and Ray (1964). In addition, the measured heat-transfer coefficients agree surprisingly well with other findings in two- and three-phase bubble columns and can be correlated uniformly on the basis of a recently proposed theoretical model (Deckwer, 1980). Since the dispersion coefficients can be calculated from correlations available from the literature and the liquid–solid mass transfer resistance can be neglected, one may therefore conclude that from the hydrodynamic point of view all relevant parameters are available which are required for designing an FT slurry reactor provided the system is not operated in the churn–turbulent flow regime. As the solubilities of CO and H\(_2\) in paraffin are also known, it is really a thorough kinetic study under relevant operational conditions which is needed for a more reliable design. It is thought that the hydrodynamic

**Figure 15.** Flow regimes in bubble column (slurry) reactors.

**Figure 16.** Assumed dependency of flow regimes on gas velocity and reactor diameter.
properties evaluated in this contribution are also valuable for coal liquefaction processes.

Nomenclature

\[ a = \text{gas-liquid interfacial area per unit volume of three-phase system}, \ cm^{-1} \]
\[ a_g = \text{liquid-solid interfacial area per unit volume of three-phase system}, \ cm^{-1} \]
\[ A = \text{heat transfer area (heat source), } \ cm^2 \]
\[ c_p = \text{specific heat capacity, } J/g \ K \]
\[ c_w = \text{concentration of solid, wt% (100 x weight of solid divided by weight of slurry)} \]
\[ D = \text{diffusion coefficient, } cm^2/s \]
\[ d_B = \text{mean bubble diameter}, \ cm \]
\[ d_R = \text{reactor diameter}, \ cm \]
\[ d_S = \text{mean diameter of solid particle}, \ cm \]
\[ d_B^* = \text{Sauter mean bubble diameter}, \ cm \]
\[ E = \text{dispersion coefficient, } cm^2/s \]
\[ F_r = \text{Froude number, } u^2_{sd}/g d_S \]
\[ g = \text{gravitational acceleration}, \ cm/g^2 \]
\[ h = \text{heat transfer coefficient, } J/m^2 s K \]
\[ H = \text{height of gas free slurry in column}, \ m \]
\[ H_{sl} = \text{height of expanded slurry in column}, \ m \]
\[ i = \text{electric current, } A \]
\[ k = \text{heat conductivity, } J/m s K \]
\[ k_L = \text{liquid side mass transfer coefficient, } cm/s \]
\[ k_g = \text{liquid-solid mass transfer coefficient, } cm/s \]
\[ P = \text{pressure, kPa} \]
\[ P_r = \text{Prandtl number, } \mu c_p/\kappa \]
\[ Re = \text{Reynolds number, } u^2_{sd}/\mu \]
\[ Sh = \text{Sherwood number, } k_L/Le \]
\[ St = \text{Stanton number, } h/(\rho c_p u) \]
\[ T = \text{temperature, } ^\circ C \]
\[ U = \text{voltage, } V \]
\[ u = \text{superficial velocity, } cm/s \]
\[ V_G = \text{molar volume of gas} \]
\[ w = \text{volume fraction} \]
\[ \omega = \text{weight fraction} \]

Greek Symbols

\[ \beta = \text{dimensionless constant in eq 11} \]
\[ \epsilon = \text{holdup, defined by eq 2} \]
\[ \mu = \text{dynamic viscosity, } Pa s \]
\[ \nu = \text{kinematic viscosity}, \ cm^2/s \]
\[ \theta = \text{mean contact time, } s \]
\[ \rho = \text{density, } g/cm^3 \]
\[ \sigma = \text{surface tension, dyn/cm} \]

Indices

\[ 0 = \text{inlet} \]
\[ G = \text{gas} \]
\[ L = \text{liquid} \]
\[ S = \text{solid} \]

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