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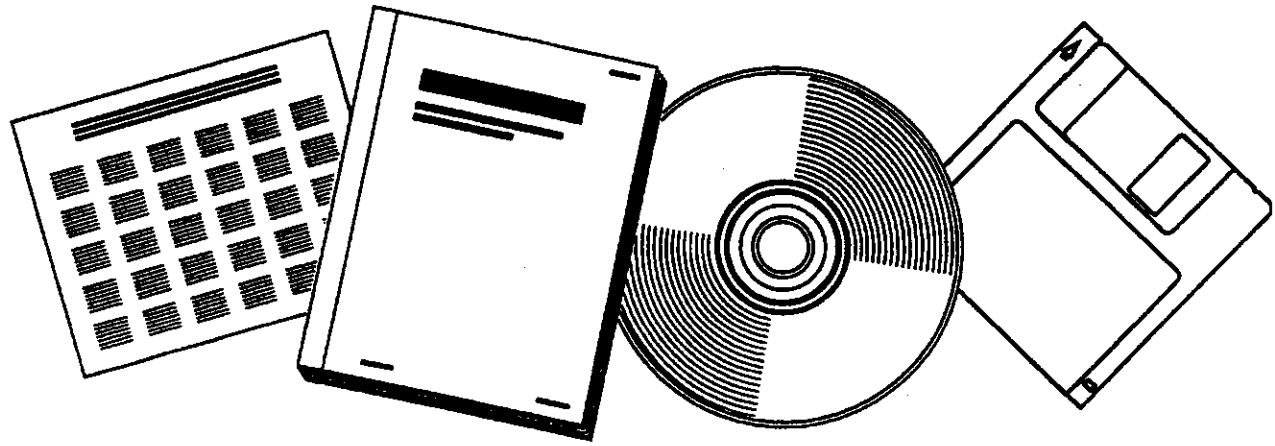
# FISCHER-TROPSCH SYNTHESIS IN SLURRY REACTORS: SUMMARY AND ANALYSIS OF THE STATE OF THE ART

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, PRETORIA (SOUTH AFRICA). CHEMICAL ENGINEERING RESEARCH GROUP

AUG 1982



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CSIR REPORT CENG 432

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**Summary and analysis of the state of the art**

**D S VAN VUUREN**

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## S Y N O P S I S

An analysis of the advantages claimed for Fischer-Tropsch slurry reactors confirms that this reactor type is preferable for high boiling point liquid products and where synthesis gas of low $H_2$:CO ratio is used. There is some evidence that it may also be the optimum reactor type for the synthesis of gaseous or low boiling point liquid products and could provide versatility in product spectrum.

Scrutiny of the available reactor design data revealed serious discrepancies and gaps in existing knowledge; recommendations are made for research to rectify this situation.

# FISCHER–TROPSCH–SINTESE IN FLODDERREAKTORS

Opsomming en analise van die bestaande kennis

## S I N O P S I S

'n Analise van die voordele van Fischer-Tropsch-sintese in die flodderproses bevestig dat hierdie proses verkieslik is vir die vervaardiging van vloeistowwe met hoë kookpunte, asook in die geval waar sintesegas met 'n lae verhouding van waterstof tot koolstofmonoksied gebruik word. Daar is ook enkele bewyse gevind dat dit die optimale reaktortipe mag wees vir die vervaardiging van gasprodukte of vloeistowwe met lae kookpunte.

'n Evaluasie van die beskikbare data wat benodig word vir die ontwerp en optimisering van sulke reaktors het daarop gewys dat daar groot leemtes bestaan. Daar is voorgestel dat navorsing gedoen moet word om die leemtes te vul.

KEYWORDS: Fischer-Tropsch, slurry reactor, literature survey, recommendations

## CONTENTS



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## 1. INTRODUCTION

The Fischer-Tropsch reaction for the manufacture of liquid fuels and other chemicals has been demonstrated on a commercial scale only in fixed bed and transported bed reactors. However, both these reactors have certain drawbacks which stem from their intrinsic characteristics.

The transported bed reactor requires relatively high operating temperatures to avoid product condensation and subsequent particle agglomeration. This results in the product spectrum being almost entirely in the gas-gasoline range.

The fixed bed reactor operates at lower temperatures to give products which cover a wide range of molecular masses. Temperature control is a problem, however, because heat transfer is poor. Tube diameters are restricted to about 0,08 m and high recycle ratios must be employed[1].

A viable alternative reactor is the slurry or bubble column reactor in which the catalyst particles are suspended in a molten wax and the synthesis gas is bubbled through the suspension. Pilot plant results obtained in an 8 m high slurry reactor were so favourable that the German company, Heinrich Koppers GmbH, made an offer to the Indian government in 1955 to erect a commercial plant based on this technology[2]. Because of the switch from coal to petroleum these plans never materialized.

The so-called "energy crisis" has made it important to re-evaluate all possibilities of coal to liquid fuel conversion. The purpose of this report is to highlight the relevance of slurry reactor technology and to pinpoint areas where further research needs to be done.

## 2. ADVANTAGES OF FISCHER–TROPSCH SLURRY REACTORS

i. *Thermal conduction and temperature control.*

Owing to the high heat capacity and the thorough mixing of the slurry, excellent temperature control is possible. Kölbel and Ralek[2] reported a temperature difference of less than 1 $^{o}$C over the total length of an 8 m pilot scale reactor. The cooling surface area necessary to remove the reaction heat is also reduced. Koppers[3] gave the following comparative data for the cooling surface area required per 1000 $m^3$ of feed gas per unit time:

| | |
|---|---|
| slurry reactor | 50 $m^2$ |
| fixed bed reactor | 240 $m^2$ |
| fluidized bed reactor | 15 - 30 $m^2$ |

Lastly, catalyst destruction owing to local "hot-spots" is prevented.

ii. *Methane formation.*

It is claimed that of all the reactors the slurry reactor gives the highest selectivity for desired products, or the lowest undesirable methane yields[3]. Since the cost of synthesis gas amounts to about 80% of the production costs of the products[2], this is of considerable economic importance. Koppers[3] stated that depending on operating conditions, a yield between 166 g and 185 g of saleable (or $C_3^+$) hydrocarbons per $m^3$ of feed gas is achieved in the slurry process, whereas it is only 155 g in the case of a fixed bed reactor using a cobalt catalyst. The fluidized bed system gives a considerably lower yield with a maximum of 165 g. However, it is also stated that a fixed bed reactor using an iron catalyst gives similar values to the slurry process. This contradicts the claim of highest selectivity for the slurry process.

The results of Hall et al.[4] confirm this claim. They performed experiments in laboratory fixed bed slurry and fluidized bed reactors using the same catalysts and operating conditions. The lowest yields of methane were found in almost all the runs in the slurry reactor, thus giving the highest selectivity for useful chemicals (see Table 1).

TABLE 1 Selected results of Hall et al.[4]

| Reaction system | Fixed bed | | | Liquid phase | | | Fluidized bed | |
|---|---|---|---|---|---|---|---|---|
| Catalyst concentration (g/ℓ reaction space) | 2 073 | 2 073 | 2 075 | 470 | 310 | 220 | ca 1000 | ca 1000 |
| Pressure (psig) | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 |
| Temperature (°C) | 265 | 300 | 265 | 265 | 265 | 300 | 305 | 305 |
| Space velocity ($hr^{-1}$) | 427 | 1 087 | 1 235 | 110 | 98 | 196 | 500 | 2 200 |
| Recycle ratio | 2 | 2 | 2,8 | 2 | 2,5 | 2 | 5,0 | 10,5 |
| $H_2$:CO ratio (reactor feed) | 3,03 | 3,0 | 3,15 | 3,54 | 3,68 | 3,43 | 3,0 | 2,94 |
| CO conversion (%) | 94,3 | 95,3 | 93,5 | 94,2 | 92,4 | 94,1 | 98,1 | 95,3 |
| CO + $H_2$ conversion (%) | 89,2 | 89,2 | 88,0 | 84,1 | 79,8 | 84,2 | 96,0 | 93,0 |
| $H_2$:CO usage ratio | 1,86 | 1,81 | 1,90 | 1,72 | 1,62 | 1,72 | 1,94 | 1,89 |
| Yields ($g/m^3$ synthesis gas) | | | | | | | | |
| $C_1$ | 33,0 | 37,5 | 37,3 | 18,1 | 14,6 | 22,6 | 48,9 | 35,0 |
| $C_2 - C_4$ | 48,1 | 56,9 | 57,9 | 59,4 | 57,9 | 63,3 | 64,0 | 64,0 |
| $C_5^+$ | 80,3 | 75,0 | 72,6 | 78,9 | 80,0 | 78,8 | 66,4 | 69,4 |
| Aqueous alcohols | 3,2 | 2,1 | 1,8 | 12,4 | 13,8 | 9,5 | 4,2 | 5,7 |
| Aqueous acids | 1,3 | 1,9 | 1,6 | 2,9 | 2,3 | 1,6 | 0,9 | 1,6 |

(An ammonia-synthesis catalyst was used in all the quoted experiments.)

Results of Deckwer et al.[5] again contradict the claim of highest selectivity for the slurry process. For all practical purposes the same product spectrum was obtained in both their slurry and fixed bed reactors. Dry[6] also reported similar methane yields in fixed bed and slurry reactors (7% in fixed bed and 5% in slurry reactor based on the carbon atoms converted).

In the case of the slurry reactor the small catalyst particle size and good temperature control eliminate almost all the temperature and concentration gradients in the catalyst particles. Theo= retically this maximizes selectivity although the high degree of back-mixing in a slurry reactor reduces the selectivity for intermediate products in a series reaction chain (eg, for olefins which may react further).

From the available data it can therefore be concluded that the methane yield in the slurry reactor is either lower or the same as that in the fixed bed reactor, but definitely not higher. In both these reactors lower methane yields than those in the transported bed system are obtained.

iii. *Flexibility.*

The slurry process has the highest flexibility in different operating conditions and conse= quently a wider product spectrum allowing changes in market demands to be met. Kölbel and Ralek[2] illustrated this point with numerous examples.

iv. *Yield.*

It is generally accepted that the transported bed reactor gives the highest yield per unit mass of catalyst and per unit reactor volume (4000 to 12000 kg/m$^3$day)[7]. It is also agreed that the slurry reactor gives a higher yield per unit mass of catalyst used than the fixed bed reactor. There is, however, a controversy about the claims made concerning the space-time yields of slurry against fixed bed reactors.

Koppers[3] of Rheinpreussen claims that they obtained a maximum space-time yield of 2800 kg/m$^3$day in a laboratory reactor, but in all the other studies published by them, considerably lower values are given (eg, 940 kg/m$^3$day in a pilot reactor and 740 kg/m$^3$ day in a laboratory reactor). Dry[6] reported a conversion of 49% in a slurry reactor, compared to 46% in a fixed bed when both reactors operated at similar operating conditions (not enough data were given to calculate space-time yields). Hall et al.[4] obtained space-time yields of $C_2^+$ hydrocarbons of 1312 kg/m$^3$day and 475 kg/m$^3$day in fixed bed and slurry reactors respectively, when both reactors were operated at 21,7 bars and 265 $^{o}$C and the same catalysts were used. The best value for the space-time yield calculated from the results of Mitra and Roy[8] is 585 kg/m$^3$day for a slurry reactor operating at a space velocity of 150 hr$^{-1}$, a pressure of 11,3 bars and a temperature of 260 $^{o}$C. Schlesinger et al.[9] obtained yields of $C_3^+$ hydrocarbons plus oxygenates of 382 kg/m$^3$day at operating conditions of a space velocity of 200 hr$^{-1}$, a pressure of 21,7 bars and a temperature of 258 $^{o}$C. In the review of Kölbel and Ralek[2] a yield of condensate 1 and condensate 2 (presumably all the $C_2^+$ product) of 433 kg/m$^3$day in a slurry reactor was quoted from the results of Konugi and Sakai[10]. In contrast to these values a CO + $H_2$ conversion of 60 to 66% for a fixed bed reactor operating at 25,8 bars, 220 to 255 $^{o}$C and a space velocity of 500 hr$^{-1}$ is quoted for the SASOL results[11]. Assuming a low yield of 0,15 kg of saleable hydrocarbons per m$^3$ synthesis gas converted, this is equivalent to a space-time yield of about 1150 kg/m$^3$day.

From the above data it appears that the space time yields in the slurry and fixed bed reactors are similar. Because the fixed bed reactor can be operated at higher velocities without any detrimental effects on the hydrodynamic properties of the bed as in the case of the slurry reactor, it appears that higher space-time yields can be obtained in the fixed bed reactor at the expense of increased recycle cost.

v. *Synthesis gas composition.*

As mentioned before, the cost of synthesis gas amounts to about 80% of the total cost of the process. Synthesis gas costs can be reduced by reducing the hydrogen to carbon monoxide ratio in the gas[3,12]. The ratio is, however, limited by the increasing rate of carbon deposition with increasing carbon monoxide concentration[13] and the subsequent deterioration of the Fischer-Tropsch catalyst.

Quoted values for the hydrogen to carbon monoxide ratios in the feed gas to the SASOL reactors are 1,8 and 2,4 respectively for the fixed bed[14] and fluidized bed reactors[15]. In contrast to these values, the Rheinpreussen pilot scale slurry reactor operated at a ratio of 0,67 without any apparent excessive carbon formation. This advantage has not been confirmed in any of the earlier studies, but recently Satterfield and Huff[13] proposed a mechanism to explain why lower ratios can be tolerated in the slurry as opposed to the fixed or transported bed reactors. According to their theory high conversions (above about 90%) and thorough mixing of the liquid phase in the reactor must be sustained to allow the watergas shift reaction to increase the $H_2$:CO ratio throughout the whole reactor in the liquid phase.

iv. *Construction.*

Because the construction of the slurry reactor is the simplest of the three reactors considered, its capital cost per unit volume reactor space is also the lowest. Since the catalyst particles are in continuous movement, continuous replacement of spent catalyst is a simple matter (as with the transported bed, but not the fixed bed reactor).

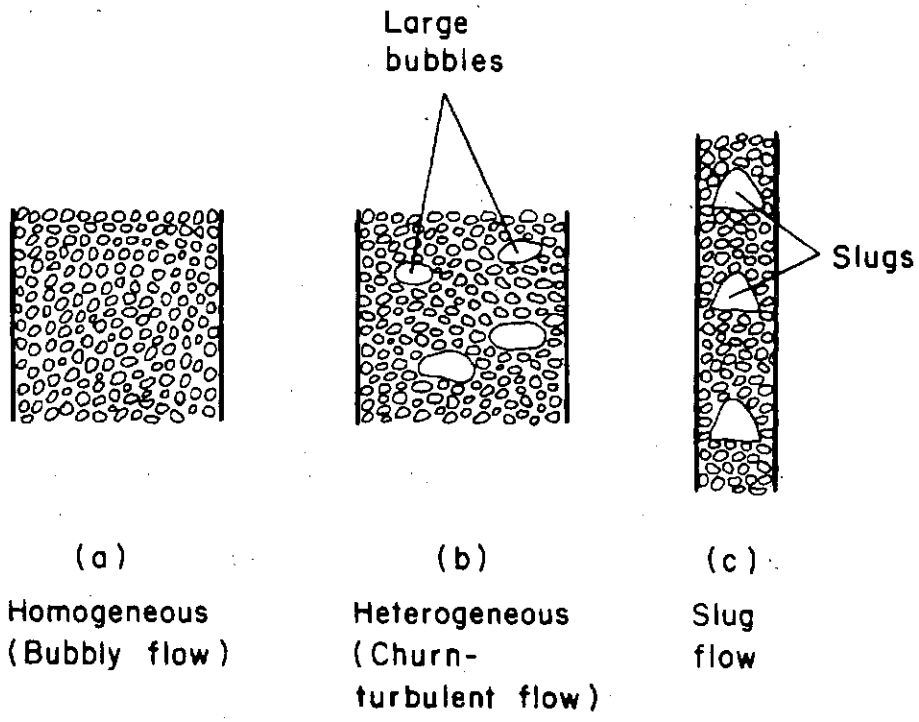
## 3. IMPORTANT DESIGN PARAMETERS FOR SLURRY REACTORS

The classification of design parameters used by Shah[16] has been used in this report with some minor additions.

### 3.1 Flow regime

Three flow regimes are of practical interest in laboratory bubble flow columns, viz, the homogeneous, the heterogeneous and the slug flow regimes (see Figure 1). The slug flow pattern is not found in large diameter reactors.

FIGURE 1 Flow regimes in bubble columns [Deckwer et al.[17]]




An attempt by Deckwer et al.[17] to characterize the various flow regimes is given in Figure 2. According to them the transitions are not sharp and depend on the dispersion height, the gas distributor, the liquid velocity and the physico-chemical properties of the slurry. An additional factor which is unaccounted for is the solids loading.

Kölbel and Ralek[2] gave a flow regime map in their review which shows the effect of solids loading (Figure 3). Figures 2 and 3 are not complementary because of the difference in the terminology used. If the design recommendations of Schumpe et al.[18] or Kölbel and Ralek[2] are accepted, two different operating conditions will be specified, viz, either a superficial velocity of about 0,05 m/s or one of about 0,09 m/s. Clarification of this point is necessary before reliable design or optimization of slurry reactors for Fischer-Tropsch synthesis can be made because a difference of 80% in the space velocity results.

FIGURE 2 Approximate flow regimes [Deckwer et al.[17]]

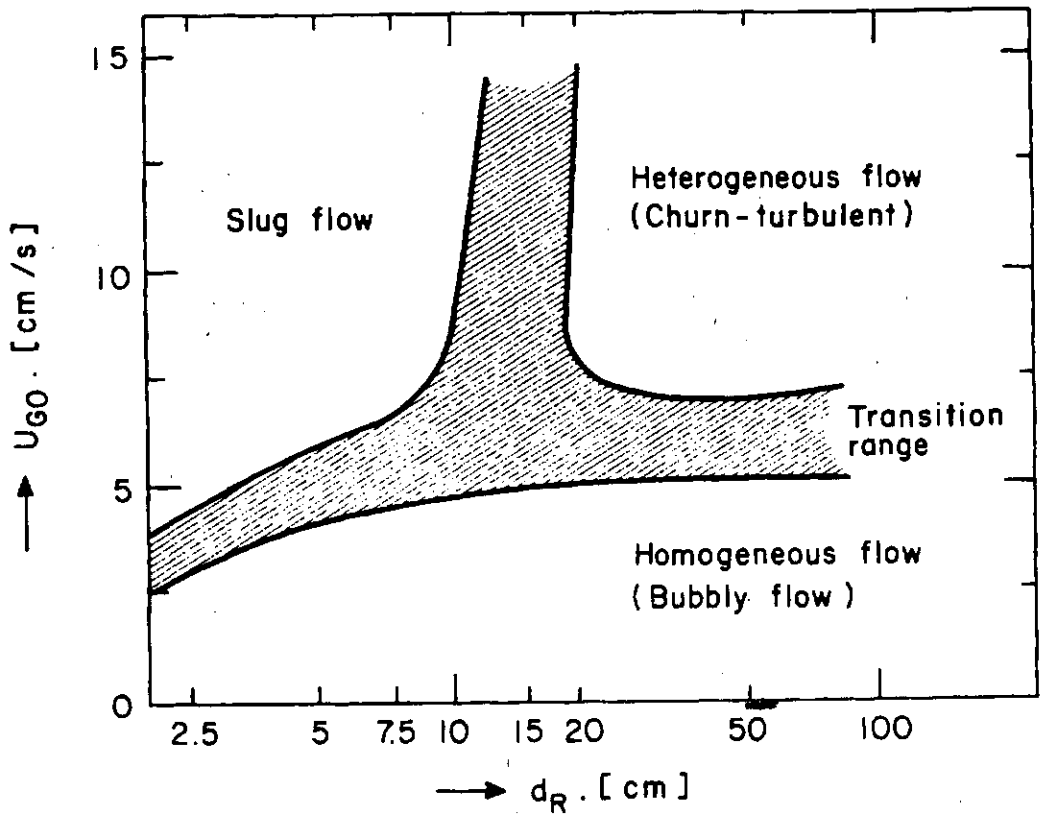
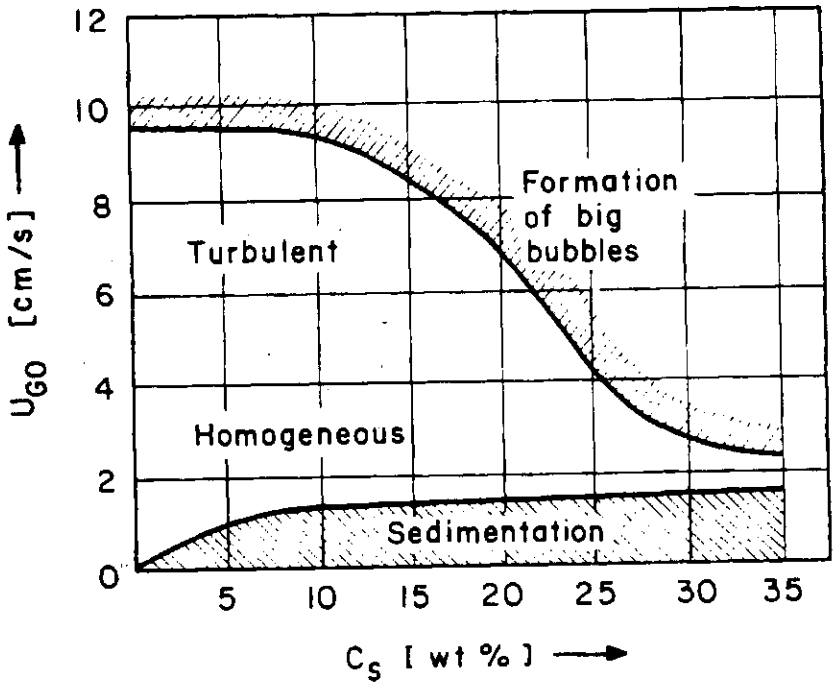



FIGURE 3 Operational range diagram for a bubble column reactor with suspended solid matter (particle size : 30 µm) [Kölbel and Ralek[2]]



## 3.2 Pressure drop

Fischer-Tropsch slurry reactors are normally operated at pressures above 11 bars. The hydrostatic head of a slurry of 3 m in height and a density of 800 kg/m$^3$ is only 0,24 bar. It can therefore be approximated that the reactor operates at isobaric conditions.

Since pressure has a minor effect on liquid physical properties, the effect of pressure on the hydrodynamic behaviour of slurry reactors is small, as shown by Deckwer et al.[17].

## 3.3 Hold-ups

The gas hold-up is an important factor since it determines the effective reactor volume available for the catalyst suspension.

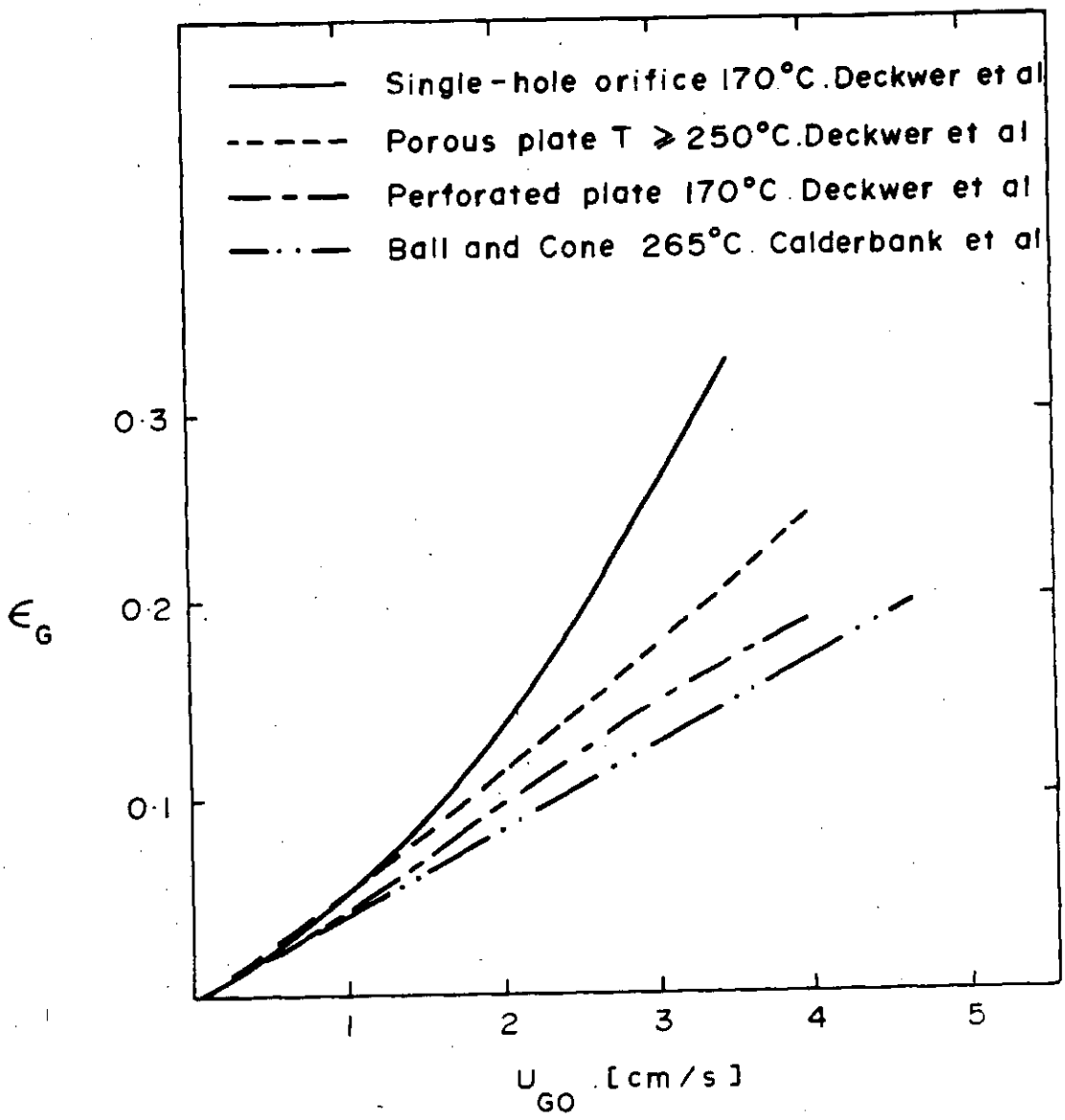
Despite the importance of the hold-up no reliable method exists to predict its magnitude numerically. The available experimental data for slurry reactors similar to the Fischer-Tropsch slurry reactor are contradictory and more data and understanding are necessary for reliable design procedures.

Calderbank et al.[19] measured the gas hold-up in a reactor containing molten Fischer-Tropsch wax at 265 $^{o}$C using an open-ended pipe with a steel ball as gas distributor. Deckwer et al.[17] measured the gas hold-up in a molten paraffin (melting point 80 to 110 $^{o}$C) in two sizes of columns over a range of temperatures. They found a temperature-dependence in the smaller column (ID 0,0414 m) at temperatures below 240 $^{o}$C. In the bigger column (ID 0,1 m) this dependence was not observed. They used a sintered plate with pores of a mean diameter of 75 µm as gas distributor. In a later study Quicker and Deckwer[20] measured the gas hold-up in a 0,095 m diameter column containing Vestowax, a hard paraffin wax with a melting point of 105 to 122 $^{o}$C, at 130 and 170 $^{o}$C. A perforated plate and a single hole nozzle were used as gas distributors. The results of the various studies are summarized in Figure 4.

It can be seen that the various relationships differ considerably, eg, at 0,03 m/s the highest value is almost double the lowest value. Quicker and Deckwer[20] compared their data with available empirical correlations and found that their data could not be represented by any of the correlations. They concluded that the macroscopic physico-chemical properties such as density, viscosity and surface tension are not sufficient to describe the fluid dynamic behaviour of gas/liquid dispersions.

The pilot plant Fischer-Tropsch reactor at Rheinpreussen operated at superficial gas velocities of about 0,09 m/s. The hold-up data in Figure 4 were measured at velocities below 0,045 m/s and can therefore not be extrapolated to velocities as high as 0,09 m/s. Farley and Ray[21] reported one value for the gas hold-up in their Fischer-Tropsch slurry reactor operating at a

FIGURE 4 Gas hold-up in Fischer-Tropsch bubble columns




superficial gas velocity of 0,07 m/s. That value agrees exactly with the extrapolated curve of Deckwer et al.[17], but since it is only one data point the correspondence could have been purely coincidental.

### 3.4 Residence-time distribution and axial mixing

The simplest reasonable assumptions concerning the axial mixing of the various phases are no mixing in the gas phase and perfect mixing in the liquid phase.

However, in large diameter columns the recirculation currents of the liquid phase can be large enough to enforce back-mixing in the gas phase. This phenomena can be expected to depend on the type of gas distributor. Very little data are available and certainly no data for Fischer-Tropsch type slurry reactors.

Sherwood and Farkas[22] found the assumption of a perfectly mixed liquid phase adequate in columns with a length to diameter ratio between 12 and 35. However, Govindarao[23], in a numerical model study in which the length to diameter ratio was varied between 3 and 10 and the various parameters were calculated from literature correlations, found that this assumption could not be made. Since the accuracy of the approximation that the liquid phase is perfectly mixed must increase with decreasing length to diameter ratios, the two findings are contradictory.

If the liquid phase is perfectly mixed and if the mass transfer resistance between the gas and liquid phases is negligible the behaviour of the slurry reactor reduces to that of a continuous flow stirred tank reactor. Therefore, any device that reduces the mixing of the liquid phase without causing bubble coalescence or solids settling will be advantageous.

## 3.5 Heat and mass transfer

Owing to the high exothermicity of the Fischer-Tropsch reaction heat removal is essential. Deckwer et al.[17] measured heat transfer coefficients in a Fischer-Tropsch type slurry reactor and proposed a correlation which they derived from Kolmogorof's theory of isotropic turbulence and by treating the slurry as a homogeneous phase. They found that there was good agreement between the theory and their own data as well as data published by others.

Interphase heat exchange is not important because the inlet gas is normally preheated by the outlet gas to temperatures close to the reactor temperature.

Interphase mass transport occurs between the gas and liquid and the liquid and solid phases (it is assumed that the suspended solids are not in contact with the gas phase). Owing to the high surface area of the suspended particles, the resistance to mass transfer between the solid and liquid phases can be neglected[17].

The mass transfer resistance between the gas and liquid phases has been a subject of dispute. Satterfield and Huff[24] elaborated on the importance of this resistance whereas Deckwer et al.[25] maintained that it is relatively unimportant. The main source of the disagreement was shown to be the difference in the predictions of the interfacial area by the two groups of researchers[26]. Satterfield and Huff used the data published by Calderbank et al.[19], whereas Deckwer et al. used the data of Deckwer et al.[17]. In the paper of Quicker and Deckwer[20] more data were given but as with gas hold-up data the discrepancy between the various studies is so large that no conclusion can be made without further investigation.

The mass transfer resistance is also dependent on the mass transfer coefficient. Since the catalyst particles are very small they can penetrate the boundary layer between the gas bubbles and the liquid. Mass transport enhancement can therefore result and correlations for mass transport coefficients such as that of Calderbank and Moo-Young[27], where this effect was irrelevant, can therefore not be accepted without further verification.

Considerations of intraphase mass transport inside the catalyst particles are irrelevant because the particles break down to sub-micron sizes where diffusional restrictions are unimportant.

### 3.6 Physical properties

Important liquid physical properties affecting the gas dispersion and the interphase mass transfer rates are density, viscosity and surface tension. Published data of these properties for heavy paraffin waxes differ to varying degrees. Table 2 is a comparison between the density and viscosity data cited by Deckwer et al.[17] for molten paraffin wax (melting point 80 to 110 °C) and Calderbank et al.[19] for Krupp wax (melting point not specified). Deckwer et al. also gave surface tension data.

TABLE 2 Comparison between published physical properties

| Temperature | Deckwer et al.[17] | | Calderbank et al.[19] | |
|---|---|---|---|---|
| | Density | Viscosity | Density | Viscosity |
| °C | ($kg/m^3$) | ($10^{-3}$ kg/ms) | ($kg/m^3$) | ($10^{-3}$ kg/ms) |
| 143 | 730 | 13,0 | 757 | 6,4 |
| 220 | 690 | 4,0 | 711 | 2,5 |
| 260 | 670 | 2,0 | 687 | 1,7 |

According to the correlation of Calderbank and Moo-Young[27] for small gas bubbles, the mass transfer coefficient (in cgs units) is:

$$k_L = 3{,}08 \left( \frac{D^2 \rho}{\mu} \right)^{\frac{1}{3}} \qquad (1)$$

At 220 °C mass transfer coefficients which differ by 18% result when the sets of data in Table 1 are used.

The diffusivity also affects the mass transfer coefficient. Zaidi et al.[28] recommended the Sovova equation to predict the diffusivity whereas Satterfield and Huff[24] used the Wilke-Chang correlation for triacontane as model liquid. At 250 °C the two correlations give diffusivities of hydrogen in the liquid of $4{,}1 \times 10^{-9}$ and $9{,}2 \times 10^{-9}$ $m^2/s$ respectively. From Equation (1) mass transfer coefficients differing by 73% are obtained.

Another important physical factor is the solubilities of the reactant gases in the liquid phase. Calderbank et al.[19] measured the solubility of hydrogen in Krupp wax whereas Peter and Weinert[29] measured the solubilities of hydrogen, carbon monoxide, carbon dioxide and water in molten paraffin. Calderbank et al.[19] compared their data with that of Peter and Weinert and found that there was good agreement at temperatures between about 180 and 300 °C. At lower temperatures the disagreement became large.

### 3.7 Intrinsic kinetics

Although several reaction models exist for the Fischer-Tropsch reaction[30], the reaction rate constants are still unknown and must be determined experimentally. These models can be extremely complex and the experimentally determined constants apply only to the catalyst used.

An important simplification that can be made is that the reaction products do not influence the rate of synthesis gas conversion. Insight into reactor performance can thus be obtained without considering a multitude of products. For economic optimization where a specific market for all the various products exists, the whole product spectrum must be considered.

## 4. DISCUSSION

### 4.1 Comparison of reactors

Table 3 is a summarized comparison of the three reactors considered in this report.

The slurry reactor has the following advantages when compared with the transported bed reactor: lower methane formation, higher flexibility, formation of higher molecular weight products, lower $H_2$:CO ratios and the simplest construction. On the other hand the following disadvantages are revealed: slightly higher heat transfer surface areas are required, lower space-time yields and lower catalyst activity. Although it is impossible to judge from these characteristics alone which reactor is the most economical, it can be seen that when mainly high boiling point liquid products are desired or when low $H_2$:CO ratio feed gas must be used, the slurry reactor is preferred. When the required products are gaseous under reaction conditions (eg, gasoline, low molecular weight olefins) a detailed economic analysis is necessary.

Such an analysis was done by UOP Inc. under contract to the Department of Energy of the USA[31]. Four reactor types were considered, namely, the entrained bed (or transported bed), the tube-wall, the slurry and the ebulliating bed (or oil circulation) reactors. Hypothetical plants operating at about 0,8 million cubic metre of synthesis gas per hour were designed and the operating conditions were manipulated to maximize the gasoline yield.

TABLE 3 Comparison between fixed bed, transported bed and slurry reactors for Fischer-Tropsch synthesis

| Feature | Fixed bed | Transported bed | Slurry phase |
|---|---|---|---|
| Temperature control | Poor | Good | Good |
| Surface required for heat exchange | 240 $m^2$ per 1000 $m^3$ feed gas | 15 - 30 $m^2$ per 1000 $m^3$ feed gas | 50 $m^2$ per 1000 $m^3$ feed gas |
| Maximum reactor diameter | ± 0,08 m | Large | Large |
| Methane formation | Low | High | As fixed bed or lower |
| Flexibility | Intermediate | Little | High |
| Products | Full range | Restricted to low molecular weight | Full range |
| Space-time yield ($C_2^+$ hydrocarbons) | > 1000 kg/$m^3$. day | 4000 - 12000 kg/$m^3$. day | ± 1000 kg/$m^3$. day |
| Catalyst effectivity | Lowest | Highest | Intermediate |
| Back-mixing | Little | Intermediate | Large |
| Minimum $H_2$:CO feed ratio | As slurry phase or higher | Highest | Lowest |
| Construction | | | Simplest |

Although many approximations were made in that study, and although it applied to economic conditions in America, the results can not be ignored. It revealed that on the basis of an index investment cost of 100 for the entrained bed reactor, the slurry reactor plant cost only 46, the ebulliating bed reactor plant 65 and the tube wall reactor system the most, namely 208.

Since the difference between the slurry and entrained bed reactor systems is so big, it seems likely that the slurry system will also be the most economical in South Africa, even if low molecular weight products are desired.

Because the only advantage of a fixed bed reactor over a slurry reactor is a slightly higher space-time yield, it appears that the slurry reactor is always a better alternative than the fixed bed reactor in Fischer-Tropsch synthesis processes.

## 4.2 Design parameters

It has been shown in Section 3 that the available data for most of the design parameters are contradictory. Before expending any further effort on these subjects, it is necessary to point out the importance of each parameter to be studied.

The optimum superficial gas velocity is bounded by the flow regime in the reactor. Since the recommendations of Schumpe et al.[18] and Kölbel and Ralek[2], which are based on two different flow regime correlations, differ by 80% and because it is not possible to discriminate at this stage between the two maps, further investigation is necessary.

The effect of pressure on the hydrodynamic behaviour appears to be minor, but its influence on the reaction kinetics must be known to determine the optimum reactor pressure. This is a function of the catalyst used and the desired products.

The gas hold-up determines the effective reactor volume available for a suspended catalyst. As an example the operating conditions of the pilot plant reactor at Rheinpreussen and the correlations of Deckwer et al.[18] and Calderbank et al.[19] are considered.

The correlations of Deckwer et al. and Calderbank et al. predict gas hold-ups of 0,63 and 0,41 respectively. This implies that, in the absence of mass transfer limitations, the two correlations lead to reactor lengths required for a given conversion which are in the ratio $\left(\frac{1,0 - 0,41}{1,0 - 0,63}\right) = 1,6$. It is therefore necessary to study the factors influencing the gas hold-up, especially at high superficial gas velocities (greater than 0,04 m/s).

Because of the inter-relationship of the various physical phenomena in a slurry reactor, it is difficult to visualize the importance of each factor. An attempt is made below to illustrate the importance of the intrinsic reaction rate, the liquid mixing and the mass transfer rate.

The data of Schlesinger et al.[9] were used as an example. The results were analysed using the following assumptions:

i. plug flow in gas phase,
ii. liquid phase completely mixed,
iii. the overall rate of the process is only limited by gas-liquid mass transfer and intrinsic kinetics,
iv. the hydrogen reaction rate is $r_H = k_R w(1 - \varepsilon_G) c_{HL}$,
v. the catalyst is uniformly distributed in the suspension,
vi. a gas volume contraction factor of 0,5 and
vii. solubility data of Peter and Weinert[29] for $H_2$ in molten paraffin.

The derivation of the model equations is given elsewhere[32].

Depending on the correlations used for the gas hold-up, the interfacial area and the liquid phase diffusivity, different reaction rate constants were obtained. Using these results the hypothetical conversions in various limiting cases were calculated to illustrate the importance of that factor. These results are given in Table 4.

TABLE 4 Analysis of the data of Schlesinger et al.[9]

| Temp. °C | $X_H$ Experimental | Assumption | $X_H$ (Predicted) "Large" D "Large" a + ε | "Large" D "Small" a + ε | "Small" D "Large" a + ε | "Small" D "Small" a + ε |
|---|---|---|---|---|---|---|
| 220 | 0,2155 | $k_H a \to \infty$ | 0,2186 | 0,2579 | 0,2224 | 0,2876 |
| | | $k_R \to \infty$ | 0,9989 | 0,7072 | 0,9898 | 0,5596 |
| | | No liquid mixing | 0,2196 | 0,2163 | 0,2184 | 0,2160 |
| 230 | 0,2810 | $k_H a \to \infty$ | 0,2845 | 0,3422 | 0,2902 | 0,3933 |
| | | $k_R \to \infty$ | 0,9996 | 0,7589 | 0,9941 | 0,5977 |
| | | No liquid mixing | 0,2893 | 0,2827 | 0,2867 | 0,2819 |
| 240 | 0,4179 | $k_H a \to \infty$ | 0,4223 | 0,5318 | 0,4327 | 0,6472 |
| | | $k_R \to \infty$ | 0,9999 | 0,7998 | 0,9966 | 0,6271 |
| | | No liquid mixing | 0,4398 | 0,4215 | 0,4322 | 0,4195 |
| 250 | 0,5624 | $k_H a \to \infty$ | 0,5658 | 0,7158 | 0,5791 | 0,8816 |
| | | $k_R \to \infty$ | 1,0 | 0,8334 | 0,9979 | 0,6514 |
| | | No liquid mixing | 0,6112 | 0,5688 | 0,5929 | 0,5640 |
| 258 | 0,6389 | $k_H a \to \infty$ | 0,6409 | 0,7897 | 0,6529 | 0,9599 |
| | | $k_R \to \infty$ | 1,0 | 0,8608 | 0,9986 | 0,6743 |
| | | No liquid mixing | 0,7106 | 0,6475 | 0,6830 | 0,6399 |

"Large" D in the table is the hydrogen diffusion coefficient as calculated via the Wilke-Chang correlation used by Satterfield and Huff[24]. "Small" D refers to the diffusion coefficient as calculated by the Sovova correlation cited by Zaidi et al.[28]. "Large" a and ε were calculated using the correlations of Deckwer et al.[17] and "small" a and ε using the correlations of Calderbank et al.[19]. In all cases the density and viscosity data of Calderbank et al.[19] were used and the mass transfer coefficients were calculated using Equation (1).

From column 4 it follows that if the diffusivity, the interfacial area and the gas hold-up are "large", the mass transfer limitations are indeed negligible as concluded by Deckwer et al.[25]. The reactor then behaves as a continuous flow stirred tank reactor and the conversion can therefore be improved by reducing the liquid mixing. This improvement increases with conversion which is typical in any comparison of a first order reaction in a CFSTR or plug flow reactor.

A possible way of accomplishing this is by inserting sieve plates or perforated plates in the column. By doing this an increasing temperature gradient along the reactor length can also easily be maintained which can be beneficial under certain circumstances[2]. To the author's knowledge design data for Fischer-Tropsch slurry reactors in this mode are non-existent.

Where the correlations giving low diffusion rate, interfacial area and gas hold-up are employed (column 7) mass transfer limitation is significant. At high temperatures (above 240 $^{o}$C) it is even more important than the reaction rate resistance. It is also apparent that little improvement in the conversion is gained by reducing the liquid mixing under these conditions.

In the other cases shown in Table 4 the various effects are intermediate between those of "large" D, a and $\varepsilon$ and "small" D, a and $\varepsilon$.

From the above analysis it is clear that it is important to know the magnitude of the diffusivity, the interfacial area, the gas hold-up and the liquid mixing. If the mass transfer resistance turns out to be negligible, the obvious way of increasing the reactor yield is to increase the catalyst loading. The effect of this on all the other factors is unclear, so that it is at this stage impossible to optimize slurry reactor operation.

A possible reason for the discrepancies between the various correlations for predicting hydrodynamic properties is the effect of gas distributor type on the initial bubble size and the subsequent rates of coalescence and break-up. It is normally assumed that the rates of coalescence and break-up are fast [Akita and Yoshida[33]] so that the effect of gas distributor variations are negligible. Since the effect of gas distributor type is not negligible (see Figure 4) these assumptions are invalid. It is therefore essential to quantify these effects in Fischer-Tropsch slurry reactors to select a gas sparger on a rational basis.

Another important effect induced by the gas distributor is the so-called "doughnutting". In large columns with a central single-hole sparger or nozzle, a large upward current is enforced in the central region of the column by the incoming gas stream. At the outer regions of the column a nett down-flow results. Phenomena associated with this recirculation are back-mixing of the gas and larger gas bubble sizes in the centre. One can visualize that this effect can be so large that a fraction of the gas bypasses the reaction zone completely while another fraction is in a back-mixed mode.

To study this effect, it is essential to measure bubble sizes in the centre of the column and to experiment at different gas velocities, column diameters and column heights and with different gas distributors. Naturally the liquid physical properties are also important.

## 5. CONCLUSIONS

i. Fischer-Tropsch synthesis in slurry reactors is an attractive alternative to conventional synthesis in the fixed and entrained bed reactors.

ii. The most probable applications of Fischer-Tropsch slurry reactors are:

   a. In synthesis of mainly high boiling point liquid products (eg, diesel oil or wax);
   b. When synthesis gas with a low ratio of hydrogen to carbon monoxide (less than about 1,0) is used; and
   c. Where versatility in product range is required.

iii. If the economic analysis of UOP Inc. is correct, production of products such as gasoline or short-chain olefins is also advantageous.

iv. Hydrodynamic data required to optimize or design Fischer-Tropsch slurry reactors are insufficient.

## 6. RECOMMENDATIONS

i. Generate hydrodynamic data for Fischer-Tropsch slurry reactors (gas hold-up, interfacial area and liquid mixing) to explain the discrepancies in the existing data and to extend the range over which correlations can be applied. Of specific importance are the effects of gas distribution, bubble coalescence and break-up, high superficial gas velocities (above 0,04 m/s) and high solids loading (above 16% by mass).

ii. Measure liquid phase physical properties, density, viscosity and surface tension to enable correlation of the hydrodynamic properties.

iii. Determine the reactant diffusion rates to establish whether the Wilke-Chang or the Sovova correlations are applicable.

iv. Investigate the effect of mass transfer enhancement to establish reliable mass transfer coefficient correlations.

v. Obtain reaction kinetic data by experiment or from another source where it has been measured.

vi. Compare the performance of an experimental reactor with the theory to establish the reliability of reactor models which are required for up-scaling and optimization.

vii. Study novel effects such as reduction of liquid mixing or enforcement of a temperature gradient along the reactor length.

## 7. NOMENCLATURE

| | |
|---|---|
| $a$ | gas liquid interfacial area |
| $c_{HL}$ | liquid phase hydrogen concentration |
| $D$ | liquid phase diffusion coefficient |
| $k_H$ | mass transfer coefficient |
| $k_L$ | mass transfer coefficient |
| $k_R$ | hydrogen reaction rate constant |
| $r_H$ | hydrogen reaction rate |
| $U_G$ | superficial gas velocity |
| $w$ | catalyst concentration |

*Greek symbols*

| | |
|---|---|
| $\varepsilon_G$ | gas hold-up |
| $\rho$ | liquid density |
| $\mu$ | liquid viscosity |

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