Fundamentals and selection of advanced Fischer–Tropsch reactors

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Abstract

Fischer–Tropsch synthesis on a large scale is of interest as a means for conversion of remote natural gas to high-quality products, particularly liquid transportation fuels. Recent developments have resulted in reactors of advanced design having production capacities of 2500 bbl/day or higher, which is more than two orders of magnitude higher than the productivity of classical reactors operated before or during World War II. Some fundamental aspects of these reactors, which belong to the classes of gas–solid fluidized beds, multitubular trickle-beds, and slurry bubble columns are discussed to aid selection and design of reactors for a specific application. Special attention is given to scaling up of slurry bubble columns. A scaling-up strategy is proposed which might obviate the inclusion of a costly demonstration stage in the development of a novel process using bubble columns. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Fischer–Tropsch reaction that was discovered in Germany nearly three quarters of a century ago, has recently become a subject of renewed interest particularly in the context of the conversion of remote natural gas to liquid transportation fuels. The main incentives for this conversion are the increased availability of natural gas in remote locations for which no nearby markets exist, and the growing demand for middle distillate transportation fuels (gasoil and kerosene) especially in the Pacific and Asian regions. Natural gas can be converted to carbon monoxide and hydrogen (synthesis gas) via existing or newly developed processes such as steam reforming, carbon dioxide reforming, partial oxidation and catalytic partial oxidation, followed by the Fischer–Tropsch synthesis reaction

$$CO + 2H_2 \rightarrow \text{``--CH}_2\text{-''} + H_2O + 165\,kJ$$

in which "–CH$_2$" represents a product consisting mainly of paraffinic hydrocarbons of variable chain length. In most cases, the chain length distribution of the product follows an Anderson–Flory–Schulz distribution function characterised by a chain growth probability factor α.

For economic and logistic reasons, such energy conversions are best carried out in large scale projects and the capability of upscaling is, therefore, an important consideration in the selection of reactors for synthesis gas generation as well as in Fischer–Tropsch synthesis. Another important issue in Fischer–Tropsch synthesis is the strong exothermicity: e.g., compared to processes applied in the oil industry the heat released per unit weight of feed or product is an order of magnitude higher and corresponds with a theoretical adiabatic temperature rise of about 1600 K at complete conversion. Unless the product is so light

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that it is completely vaporised under reaction conditions, the reaction takes place in a three-phase system: gas (carbon monoxide, hydrogen, steam and gaseous hydrocarbon products), liquid product and solid catalyst. The amounts of syngas and product molecules that have to be transferred between the phases are quite large: i.e., an order of magnitude larger than the amount of hydrogen molecules to be transferred in hydroprocessing of oils. Therefore, great demands are placed on the effectiveness of interfacial mass transfer in Fischer–Tropsch synthesis.

The present paper discusses the selection of Fischer–Tropsch reactors against this background and compares the limitations, advantages and disadvantages of alternative reactor types on the basis of some fundamental principles.

2. Reactors for Fischer–Tropsch synthesis

2.1. Early developments

Commercial scale Fischer–Tropsch reactors have been installed and operated before and during World War II in a number of plants, mostly in Germany. In addition to these commercially applied reactors (which are very small by current standards), several other reactor types have been proposed and developed to varying degrees of commercial readiness in the period before and during World War II. These early reactor types are the following.

1. Fixed-bed reactor with internal cooling operated at high conversion in a once-through mode. The catalyst was packed in a rectangular box and water-cooled tubes fitted with cooling plates at short distances were installed in the bed to remove the reaction heat. This type of reactor was applied in the atmospheric synthesis process ('Normaldruck Synthese').
2. Multitubular reactor with sets of double concentric tubes, in which the catalyst occupied the annular space, surrounded by boiling water. This type of reactor was applied with gas at medium pressure in a once-through mode ('Mitteldruck Synthese').
3. Adiabatic fixed-bed reactor with a single bed, large recycle of hot gas which was cooled externally ('IG-Farben/Michael Verfahren').

4. Fixed-bed reactor with multiple adiabatic beds, inter-bed quenching with cold feed gas, recycle of hot gas and external cooling ('Lurgi Stufenoven').
5. Adiabatic fixed-bed reactor with large recycle of heavy condensate passing in upflow through the bed. The liquid recycle stream was cooled externally ('BASF/Duftschmid Verfahren').
6. Slurry reactor with entrained solid catalyst, large recycle of hot oil and external cooling ('BASF Schaumverfahren').

More details on these reactors can be found in the literature on the Fischer–Tropsch process, e.g., in reviews of Kölbel [1] and Roelen et al. [2]. The above reactors are mainly of historical interest since they offer limited scope for the large scale conversion of natural gas to liquid hydrocarbons. The commercially applied reactors mentioned above under 1 and 2 have very small production capacities by current standards, viz., of the order of 0.1 tonne/h or 15 bbl/day. At the low gas velocities associated with once-through operation at relatively low pressures and temperatures, heat transfer rates from the bed to the cooling surface are so low that a very large cooling area is required, which is a strong limiting factor in further upscaling.

The other reactors with external cooling need very large recycle streams to take up and transport the generated heat out of the reactor. This gives rise to high pressure drops and very high energy consumption for gas or liquids circulation, if the reactors were to be applied in Fischer–Tropsch synthesis on a very large scale. These reactor types will, therefore, not be considered further in the present context of remote natural gas conversion.

2.2. Later developments

Developments in the period shortly after World War II (in some cases based on concepts generated somewhat earlier) led to reactors with increased potential for large-scale production of synthetic fuels. The main ones are

1. A multitubular fixed-bed reactor operated with gas recycle at moderate per pass conversion, instead of once-through operation aiming at maximum conversion as in the earlier mentioned 'Mitteldruck Synthese'. This reactor, applied in the 'Arge Hochlast Synthese' developed by Lurgi

GmbH. and Ruhrchemie A.G., has a production capacity of about 50 tonnes per day (about 400 bbl/day). This substantially increased production rate as compared with the previous commercial fixed-bed reactors (by a factor of about 25) is the result of higher temperatures and pressures, a more even reaction rate profile over the reactor length and improved heat removal as a result of the higher gas velocities [3]. A commercial plant based on the Arge process was installed by the South African Coal, Oil and Gas Corporation (Sasol) at Sasolburg in South Africa [4,5].

The effect of recycling will be discussed in more detail in a later section dealing with fundamental aspects of multitubular fixed-bed Fischer–Tropsch reactors.

2. Slurry reactor in which synthesis gas is contacted in a bubble column with a slurry of fine catalyst suspended in liquid. In the process developed by Rheinpreussen AG and Koppers GmbH in the early 50 s [6–8], reaction heat is removed internally by cooling pipes immersed in the slurry. The development studies culminated in the operation of a semi-commercial reactor of $10 \, m^3$ effective volume (about 7.5 m high and of 1.3 m diameter) having a capacity of 10 tonne/day (about 80 bbl/day). For this reactor a high (about 90%) conversion of carbon monoxide has been reported when operated in a gas once-through mode at a superficial gas velocity of about 0.1 m/s [8].

3. Three-phase fluidized bed (ebulliated bed, also called ebullating bed) reactor in which a packing of larger catalyst particles (e.g., 8–16 mesh) is expanded by cocurrent upflow of oil and gas. The process studied by the US Bureau of Mines features circulation of oil for attaining sufficiently high liquid velocities and has therefore been referred to as the oil circulation process. Process development studies were carried out in a 3 gallon-per-day pilot reactor of 3.2 m length and 7.5 cm diameter, and also in a 1 barrel-per-day reactor of 20 cm diameter with a bed height of 2.4 m [9–11]. The process has not been commercialised.

4. Fluidized-bed reactor operated in the bubbling regime, as used in the Hydrocol process for producing gasoline from natural gas [12]. Reaction heat is removed by vertical bundles of cooling tubes submersed in the bed. A commercial plant has been erected in Brownsville, TX by Carthage Hydrocol featuring a reactor of 18 m height and 4 m diameter with a nominal capacity of 180,000 tonne per year. Due to technical as well as economic problems, the plant has been in operation for a short period only before being shut down in 1956.

5. Circulating fluid-bed system in which fine catalyst (between 40 and 150 micron diameter) is entrained by a high velocity (1–2 m/s) gas stream through a riser reactor. Catalyst separated from the effluent by cyclones is returned to the reactor inlet. Two cooling zones in the riser remove reaction heat. The process originally developed by the Kellogg Company as the Synthol process [13] has been commercialised and further improved by Sasol. In the first commercial plant that began operation in 1955 at Sasolburg in South Africa, Synthol reactors of 2.3 m diameter and a total height of 46 m with a capacity of 1500 bbl/day were installed. Considerably scaled-up reactors with a capacity of 6500 bbl/day were later installed in Sasol II and III located in Secunda in the Witwatersrand area and began operation in 1980 and 1982.

2.3. More recent developments

In the last 20 years, revived interest in the Fischer–Tropsch process in the context of conversion of remote natural gas gave rise to several developments of more advanced reactors with (potentially) large capacities that have been commercialised or can be considered to be ready for commercialisation. These reactors are mentioned below.

1. Multitubular reactor as applied in the Shell Middle Distillate Synthesis (SMDS) process for the conversion of synthesis gas in a heavy, waxy Fischer–Tropsch product [14,15]. Reactors of this type have been installed in the first SMDS plant at Bintulu, Malaysia for the production of some 470,000 tonnes per annum of synthetic hydrocarbons from natural gas starting from 1993. With a specially developed catalyst and specific reactor design, a capacity of about 3000 bbl/day per reactor is attained, which is an order of magnitude larger than the capacity of the multitubular reactor of the Arge design.

2. A fixed fluidized bed version of the Synthol process has been developed by Sasol and a first commercial scale reactor has started operation in Sasolburg in 1989 [16]. This reactor, which like the previously discussed Hydrocol reactor operates in the bubbling regime and is internally cooled by cooling tubes, has considerable advantages over the original circulating fluid-bed version of the Synthol process. Claimed advantages include a more compact reactor for the same capacity (in particular reduced height), less energy required for gas circulation, less catalyst attrition and easier operation and maintenance, resulting in substantial reductions in capital and operating cost.

   The size advantage of the fixed fluidized version of the Synthol process stands to reason, because the Fischer–Tropsch reaction is a relatively slow one, even at the high temperatures applied in the Synthol process. From a theoretical reactor engineering point of view, a riser is therefore not the optimal type of reactor due to the low catalyst density in the reactor space.

3. An internally cooled slurry reactor has been developed by Exxon as part of their Advanced Gas Conversion technology. A demonstration reactor with a diameter of 1.2 m in a 21 m high structure has been erected in 1990 at Exxon's R&D laboratory at Baton Rouge, LA [17,18]. Based on operating experience with this unit that achieved a production rate approaching 200 bbl/day, Exxon feel confident that a commercial-scale unit can be designed and constructed.

4. Sasol has also developed an internally cooled slurry reactor as an alternative to the multi-tubular fixed-bed reactors of the Arge process [19,20]. A commercial reactor of 5 m diameter and 22 m height designed for a capacity of about 2500 bbl/day was commissioned in 1993. The Sasol Slurry Bed Reactor (SSBR) technology is now considered by Sasol to be commercially proven and the design of a 10,000 bbl/day plant is being considered.

Very recently, it has been announced that Sasol and Phillips Petroleum have signed a memorandum of understanding with Qatar General Petroleum Corporation for a feasibility study on a 20,000 bbl/day plant for production of distillates and naphtha from Qatar's natural gas reserves, scheduled for start-up in 2002. This plant is to make use of the SSBR technology [21].

From the more recent developments of Fischer–Tropsch reactors discussed above, it can be inferred that the more advanced reactors with potential for large-scale conversion of natural gas to liquid hydrocarbons belong to the classes of fluidized bed, multitubular fixed-bed, and slurry reactors. Fundamental aspects of these reactor types, which have a bearing on the selection of a reactor for a specific application, will be discussed in the following sections.

3. Fluidized-bed reactors for Fischer–Tropsch synthesis

As mentioned before, the Fischer–Tropsch reaction is a highly exothermic one and therefore gas–solid fluidized beds with their excellent heat transfer and temperature equalisation characteristics are very attractive. As will be discussed later in the section on fixed beds, intraparticle diffusion limitation plays a role with particles larger than about 1 mm diameter and the possibility to use small catalyst particles, e.g., of about $100\,\mu m$ diameter, free from diffusion limitation is another advantage of fluidized beds. However, a serious issue is the possibility that heavy product deposits on the catalyst, causing particles to agglomerate and thus hampering fluidization.

The latter problem has been analysed for a Fischer–Tropsch reaction that produces mainly normal paraffins following Anderson–Flory–Schulz kinetics with a growth chance α [22]. To operate above the hydrocarbon dew point, i.e., the point where hydrocarbon molecules start to condense on the outer surface of the catalyst particles, the following condition has to be fulfilled

$$\sum_{n=1}^{\infty} x_n = \frac{(\chi/3)\,(1-\alpha)^2}{(1-(\chi/3)\,(1+\alpha))}\,\frac{P\beta^{n_{\mathrm{ref}}}}{P_{\mathrm{ref}}^0}\sum_{n=1}^{\infty}\left(\frac{\alpha}{\beta}\right)^n < 1 \tag{1}$$

in which x is the mole fraction of a paraffin in the liquid phase in equilibrium with gas, n the carbon number of the paraffin molecule, χ the synthesis gas conversion, P the total pressure and P^0 the vapour pressure of C_n at the operating temperature. n_{ref} is a carbon number chosen as reference, while β is a constant in

Table 1
Commercially applied Fischer–Tropsch processes operated in the gas–solid fluidized bed model ($\beta = 0.71$)

Process	Hydrocol	Synthol
$T/[^\circ C]$	300–350	300–350
$P/[bar]$	18–30	20–30
Conversion per pass (c)	0.38	0.28
Growth chance (a)	0.68	0.67
$\beta - \alpha$	+ 0.03	+ 0.04
$\frac{P^0_{ref}}{P\beta^{n_{ref}}}$	11–37	11–33
$\frac{(\chi/3)(1-\alpha)^2}{(1-(\chi/3)(1+\alpha))(\beta-\alpha)}$	0.55	0.26

the following equation describing the vapour pressure of paraffins as a function of chain length

$$P^0_n = P^0_{n_{ref}} \beta^{(n-n_{ref})} \qquad (2)$$

At 280°C, β (which is related to the incremental energy of vaporisation per segment of the paraffin chain) has the value of 0.71.

Since n can have very large values and the factor in front of the summation sign in Eq. (1) is positive, this condition can only be satisfied if α is smaller than β. In that case the summation represents the sum of a convergent, rather than divergent series and yields the following additional condition for dry operation

$$\frac{P^0_{ref}}{P\beta^{n_{ref}}} > \frac{(\chi/3)(1-\alpha)^2}{(1-(\chi/3)(1+\alpha))(\beta-\alpha)} \qquad (3)$$

It follows that this additional condition is best met at high temperature (high value of P^0_{ref}), low operating pressure P and low conversion χ. It is plausible, therefore, that the commercial gas–solid fluidized Fischer–Tropsch processes operate at relatively high temperature and moderate pressure, producing a relatively light product of low α value. The data in Table 1 demonstrate that for these processes the conditions represented by Eqs. (1) and (3) are indeed both met.

The condition that α must be less that 0.71 rules out the possibility of applying gas–solid fluidized beds for Fischer–Tropsch processes that produce much heavier products than gasoline. Even when low operating pressures and relatively high temperatures are adopted, the heavier tail of a high α product will inevitably condense on the catalyst particles, as is illustrated in Fig. 1. Therefore, only reactors in which a liquid phase is present besides the gas and solid catalyst phases
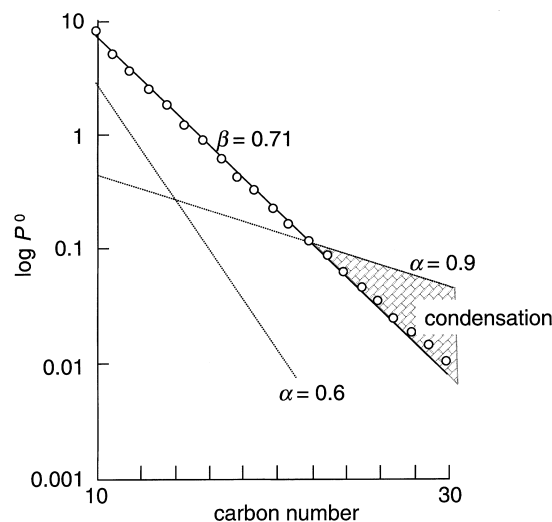

Fig. 1. Vapour pressures of normal paraffins at 280°C and partial pressures of synthetic hydrocarbons as a function of chain length.

are eligible for producing such products, and the most prominent representatives among these three phase reactors will be discussed below.

4. Fixed-bed reactors for Fischer–Tropsch synthesis

4.1. Pore diffusion limitation

Due to pressure drop constraints, catalysts in fixed-bed processes generally have diameters larger than about 1 mm. For particles of this size, intraparticle diffusion can be a limiting factor for the overall reaction rate. Studies with porous iron and cobalt catalysts under conditions which ruled out external mass transfer effects have confirmed the occurrence of diffusion limitation and made it plausible that diffusion of reactants and product molecules through liquid-filled pores is the determining factor in intraparticle transport of mass. This is demonstrated by the Thiele–Wheeler plot of Fig. 2, which correlates data obtained with different catalysts under different operating conditions. It can be seen that the experimental data correspond quite well with the theoretical curve based on an estimated diffusivity of hydrogen in a heavy paraffinic liquid, corrected for pore volume and tortuosity.
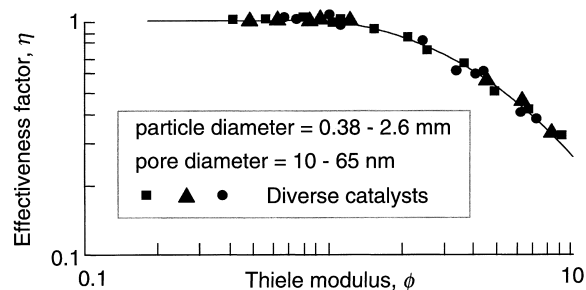
Fig. 2. Catalyst effectiveness η as a function of the Thiele modulus Φ for various cobalt and iron catalysts. Hydrogen/ carbon monoxide molar ratio 2, $P = 2.1$ MPa, $T = 473$–513 K. Adapted from Post et al. [23].

From Fig. 2 it follows that catalyst effectiveness starts to drop significantly below 1 when the Thiele modulus φ becomes greater than about 1. For Fischer–Tropsch catalysts with the usual chemical activities this means that intraparticle diffusion starts to play a role for particle diameters greater than about 0.5 mm. Intraparticle diffusion is therefore an important factor to be taken into account in choosing catalyst particle size and shape for a fixed-bed Fischer–Tropsch process, in addition to pressure drop and heat transfer considerations.

4.2. Heat transfer

A multitubular reactor in which the catalyst-filled tubes are surrounded by a cooling medium such as boiling water the reactor is, at least conceptually, an isothermal reactor and the heat of the reaction should therefore be removed by radial transport. The relatively poor heat conductivity and heat transfer to the tube wall as compared with fluidized beds easily give rise to radial temperature profiles. In an extreme case, the reactor can become unstable and temperature may run away. However, even in the stable operating region unduly large temperature peaks in the bed are to be avoided as they may give rise to an undesired reduction of selectivity or accelerated catalyst activity decline.

Aside from the choice of tube diameter, which is governed by constructional and cost considerations, catalyst particle size and gas velocity determine the effectiveness of radial heat transport and the homogeneity of temperature in the bed. Fig. 3 shows the

radial thermal conductivity and wall heat transfer coefficient as a function of the particle Reynolds number ($Re_p = d_p.u/v$, where d_p is the particle size, u the superficial velocity and v the kinematic viscosity of the fluid). It can be seen that the heat conductivity as well as the transfer coefficient become higher with increasing Reynolds number, hence heat removal becomes more effective with larger particles and at higher velocities. Limiting factors to an increase of particle size and velocity are the effectiveness of the catalyst and pressure drop.

4.3. Effect of recycle

Since axial mixing and axial heat transport in the long tubes of a multitubular reactor are relatively low, profound axial concentrations and temperature profiles can be present, particularly when one targets for a high conversion in once-through operation as in the classical fixed-bed processes. This is illustrated by Fig. 4, which shows concentration and temperature profiles pertaining to the multitubular reactor applied in the 'Mitteldruck' process [1].

It can be seen that there is a strong radial temperature profile in the region near the inlet, since in this region the reaction rates are high because of the high partial pressure of the reactants. Further down the reactor tubes, rates are much lower as the reactants are being depleted, and as a consequence radial temperatures are more even. Since the tube and catalyst dimensions have to be designed to cope with the strongest temperature peaks, it follows that the larger part of the tube is overdesigned, or in other words, does not fully utilise the potential within the existing constraints.

More even axial profiles of reactant concentration, local reaction rates and temperature in the axis of the tube are obtained when the conversion is restricted to, for instance, 20–30% per pass instead of more than 70%. As a result of recycling of the unconverted gas, linear velocities are increased and this has a beneficial effect on the effectiveness of heat removal (see above). The Arge process mentioned earlier, derives its advantages over the classical multitubular fixed-bed process from the application of gas recycle in combination with higher temperature and pressures: an enhancement of reactor capacity by a factor of 25, a reduction of the cooling area by a factor 12, and a lowering of
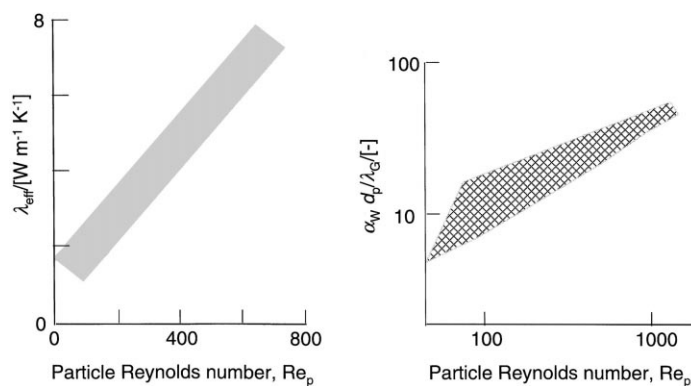
Fig. 3. Effective radial thermal conductivity λ_{eff} and wall heat transfer coefficient α_w as functions of the particle Reynolds number Re_p. d_p is the particle diameter; λ_G is the thermal conductivity of the gas.
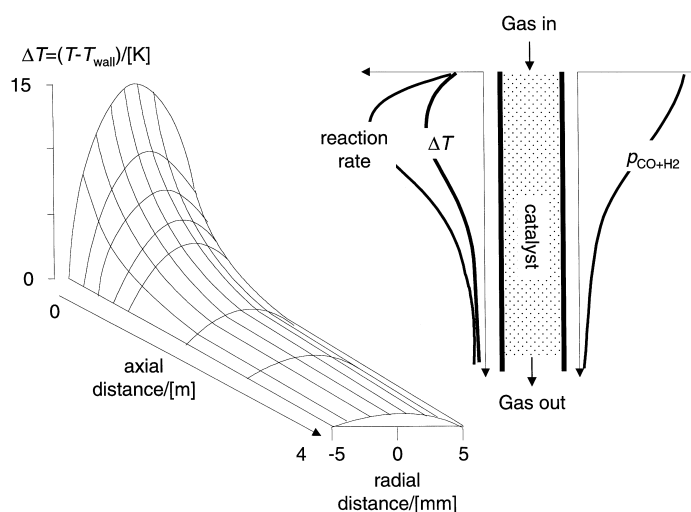

Fig. 4. Concentration and temperature profiles in a reactor of the 'Mitteldruck' Fischer–Tropsch process. Adapted from Kölbel [1].

the amount of catalyst and steel by a factor of about 7 [3].

An improvement of radial heat conductivity and heat transfer to the wall can not only be obtained by increasing the linear gas velocity in a gas–solid fixed-bed multitubular reactor, but also by operating in the presence of liquid [23,24]. In the case of a Fischer–Tropsch reaction producing a relatively heavy product, the reactant stream is initially a gas that changes to a gas/liquid mixture in the flow direction as condensable product is being produced. In this situation, the effectiveness of heat removal will be lowest in the inlet region where the reaction rates are highest. By adding liquid, one can ensure that the

whole tube including the most critical part operates in a trickle-flow mode, instead of just the bottom part.

5. Slurry bubble column reactors in Fischer–Tropsch synthesis

5.1. Hydrodynamic regimes

Two main regimes can be distinguished, viz., the homogeneous or bubbly flow regime and the heterogeneous or churn turbulent regime, see Fig. 5. The homogeneous regime, in which the bubble population consists of very small (millimetre size) bubbles pro-
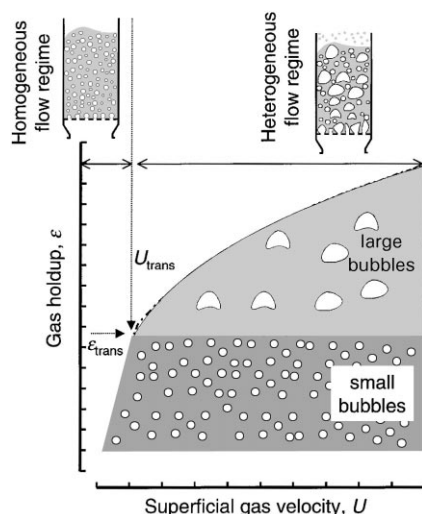
Fig. 5. Homogeneous and churn-turbulent regimes in a slurry bubble column.

duced by the inlet distributor device can only be sustained at relatively low linear gas velocities. Because of the relatively low rise velocity of these small bubbles (of the order of a few cm/s), the gas throughput is limited and with increasing gas throughput above a certain threshold bubble coalescence sets in to form much larger bubbles, ranging in diameter from about 1 to 10 cm or more. This class of large bubbles present in the heterogeneous regime has much higher rise velocities (up to 1.5 m/s) and is mainly responsible for the throughput of gas at high velocities.

Most laboratory studies on Fischer–Tropsch synthesis in slurry reactors have been carried out in the homogeneous regime, since at higher velocities slugging problems are experienced in small-diameter laboratory columns. The development studies on the Rheinpreussen–Koppers process mentioned earlier were carried out at low linear gas velocities (3.5–9.5 cm/s) and with relatively low concentration of catalyst in the slurry phase (0.07–0.09 kg/l) [8] and the operating regime was presumably also homogeneous. However, for high reactor productivity, the Fischer–Tropsch reactor needs to be operated at high superficial syngas velocity (up to 0.4 m/s) and high catalyst concentrations (up to 40 vol%), i.e., well in the heterogeneous regime. Increased catalyst concentrations tend to promote bubble coalescence, as can be seen in Fig. 6. It follows from this figure that the small bubble population is virtually destroyed as the

slurry concentration approaches 30 vol% [25]. As a result, the total gas holdup decreases significantly with increasing catalyst concentration [26,27]; see Fig. 7.

5.2. Heat transfer in bubble columns

The effective heat transfer and the good temperature equalisation in a slurry bubble column, particularly when operated in the heterogeneous regime, are important advantages of this type of reactor. Heat transfer coefficients up to 1000 W/m^2/K can be obtained, see Fig. 8. It can be seen that the heat transfer coefficient increases with increasing gas velocity and with increasing solids concentration, i.e., with factors which favour the heterogeneous regime.

5.3. Mass transfer in bubble columns

Due to the small size of catalyst particles in slurry reactors (particle diameter typically of the order of 50 μm), intraparticle diffusion is not a limiting factor. With catalysts of relatively low activity present in low concentration in bubble columns operated in the homogeneous regime, gas–liquid mass transfer is unlikely to be a limiting factor either in view of the large surface area of the small bubbles and their long residence time in the liquid. However, for reactors of increased productivity as a result of the use of more active catalysts in high concentrations and operation in the heterogeneous regime, gas–liquid mass transfer becomes a factor that needs serious consideration. Conventional calculation of mass transfer rates based on the application of the surface renewal theory with the hold-up and size of the large bubbles (which represent the major part of the gas throughput) as input yields relatively low rates which would considerably detract from the attractiveness of bubble columns as Fischer–Tropsch reactors. Experimental data obtained on model systems would seem to suggest that the situation is not as bleak, however, since actual rates are found to be higher than calculated ones by a factor of 5–10. Experimental gas–liquid mass transfer rates for turpentine-nitrogen in the heterogeneous regime were found to be an order of magnitude higher than estimated on the basis of correlations that have been established for small bubbles mainly [29].
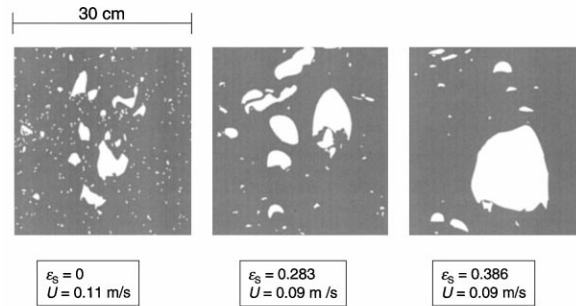
Fig. 6. Influence of increased solids concentration on the gas holdup structure for air/paraffin oil slurries. Measurements were made at a height of 0.65 m in a 2D column. From de Swart et al. [25].
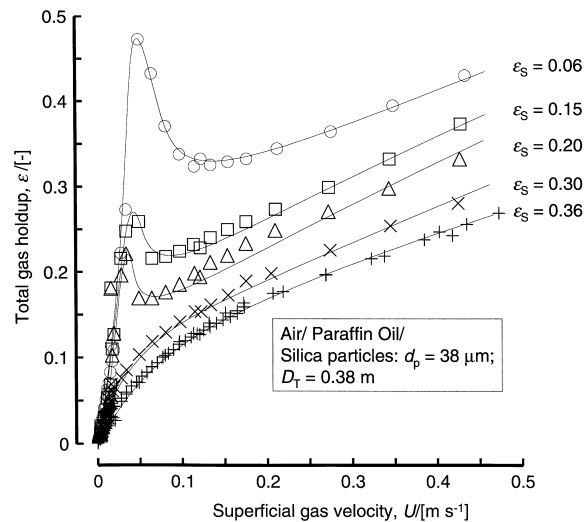

Fig. 7. Influence of solids concentration and superficial gas velocity on the gas holdup. Measurements in a 0.38 m diameter column. From Krishna et al. [27].

Fig. 8. Effect of solids concentration and gas velocity on the heat transfer coefficient in bubble columns. Adapted from Deckwer et al. [28].

An explanation for this paradox was obtained in recent work of de Swart et al., using high speed video imaging techniques to study the dynamics of large bubbles in concentrated slurries [25,26]. In these studies it was observed that within the class of large bubbles, bubbles of a given size do not lead an isolated life, but are continually disappearing and reappearing as a result of break-up and coalescence. Fig. 9 shows eight sequential pictures (frames) taken from an experimental run in a 2D column of 30 cm width operating with a 28.3 vol% paraffin oil slurry at a superficial gas velocity of 0.09 m/s. The time interval
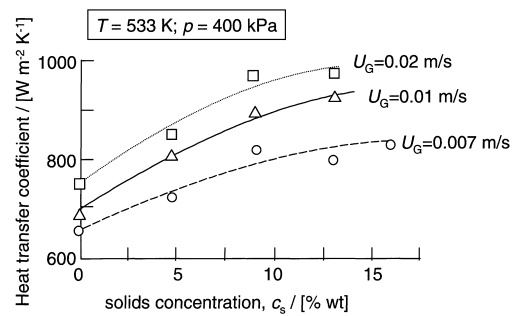
between the individual frames is 40 milliseconds and the 'small' bubbles, smaller than 10 mm, have been filtered out. Two bubbles A and B are followed as they rise through the column. It can be seen from frames 1 to 4 that bubble B rises faster than bubble A. In frame 5 bubble B reaches the wake of bubble A and coalescence follows; in frame 6, A and B are coalesced and bubble AB is formed. Bubbles D and E in frame 7 coalesce to form DE in frame 8. Tracking the history of bubble C in frames 1, 2, 3 and 4, it is noted that in frame 4 bubble C breaks up into bubbles C1 and C2. De Swart et al. [25,26] determined that the exchange of gas between various bubble classes occurs at a very high rate, at least 4/s, which is higher than the characteristic renewal rate for mass transfer. Put another way, during the characteristic time for mass transfer from the gas to the liquid phase, a bubble loses its identity because of frequent exchange with gas in other bubble size classes. Thus, whereas the gas throughput is
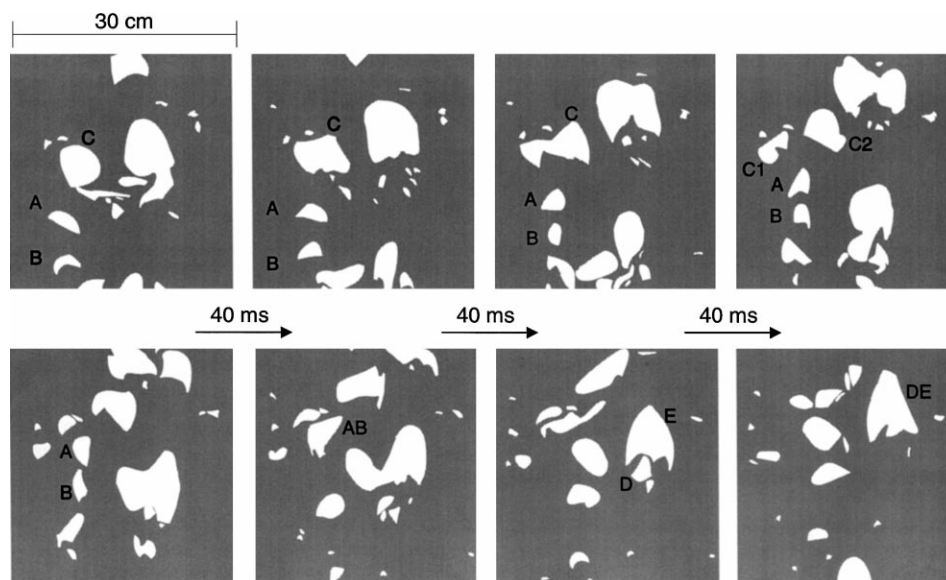
Fig. 9. Bubble coalescence and bubble breakup as followed by high speed video recording in a 2D bubble column. From de Swart et al. [25,26].

mainly represented by the largest bubbles, gas–liquid mass transfer is to a large extent determined by the interfacial area of the smaller bubbles. In other words, the equivalent bubble size as regards mass transfer is relatively small and small enough for mass transfer not to be a limiting factor in Fischer–Tropsch synthesis in most cases.

The influence of bubble–bubble exchanges are illustrated by simulations carried out for conditions relevant for the Fischer–Tropsch synthesis [25,26]. Hydrogen absorption from synthesis gas into paraffin oil at a pressure of 40 bar and a temperature of 513 K is considered. Hydrogen and carbon monoxide are present in the syngas feed at a ratio of 2. The superficial gas velocity through the total large bubble population of 0.079 m/s, is assumed to be constant over the reactor height of 30 m. Fig. 10 shows the dimensionless hydrogen concentration ($C_{g,H2}/C_{g0,H2}$) profile along the column height obtained for each of three bubble size classes: 0.01, 0.04 and 0.1 m in diameter. The three profiles coincide with one another because of very frequent exchange rates between the bubble class and the conversion at the reactor outlet is 68%. The conversion behaviour of the three bubble class system, with 0.01, 0.04 and 0.1 m diameter bubbles is found to be equivalent to that of a single bubble class system of
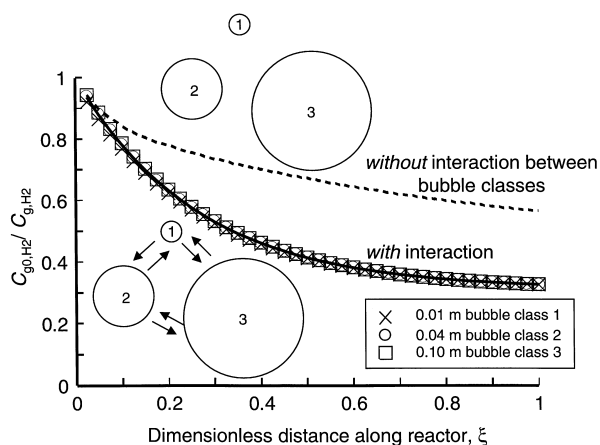

Fig. 10. Effect of bubble–bubble interaction on axial concentration profiles of hydrogen concentration in the bubbles as determined by computer modelling. From de Swart et al. [25]. The dashed line represents the profile obtained when the interaction between the three assumed bubble classes is negligible.

diameter 0.021 m. Put another way, due to frequent bubble-bubble interchange the effective bubble diameters for the 0.04 and 0.1 m diameter classes are reduced to about 0.02. This implies an enhancement for the 0.1 m bubble class of five.

In order to further demonstrate the significance of the bubble-bubble interchange, simulations were also carried out assuming no exchanges between the three bubble classes. The results of this model are shown as dashed line in Fig. 10. The overall conversion achieved by the non-exchanging bubble ensemble is only 43%, significantly lower than that obtained taking interactions into account.

6. Other factors determining reactor choice

In addition to the principal differences between the various reactor types as discussed above, there are other factors which affect reactor selection. These include factors that relate to operability and ease of scaling-up, as will be discussed below.

6.1. Some factors related to operation

6.1.1. Loading and unloading of catalyst; catalyst replenishment

The large number of catalyst-filled tubes in a large-capacity multitubular reactor makes catalyst loading and unloading a rather tedious affair. The multitubular reactor is, therefore, less attractive if catalyst life is short, e.g.,if catalyst has to be changed-out more frequently than once a year. By contrast, catalyst loading and unloading in fluid-bed and slurry reactors is much easier and can be accomplished in a shorter time. Moreover, the activity of the catalyst inventory in the reactor can be upheld by withdrawal of catalyst and replacement with fresh catalyst during a run.

Easy unloading of catalyst from a multitubular reactor requires that the catalyst flows freely after completion of an operating cycle; cementing of catalyst particles should therefore not occur.

6.1.2. Need of gas–solid or liquid–solid separation

The multitubular fixed-bed reactor does not need facilities for solids separation, in contrast to fluid-bed and slurry reactors. Particularly in the case of the synthesis of heavy Fischer–Tropsch products, separation of solids from the liquid may not be a trivial problem. Distilling-off the product is not possible with heavy liquids, and filtering may prove necessary. The separation problem is aggravated if fines are produced by catalyst attrition (either mechanical or chemical attrition).

6.1.3. Gas–liquid separation

Foam formation is obviously a problem to be avoided in a bubble column Fischer–Tropsch reactor.

6.1.4. Distribution of reactants

Even distribution of reactants over the reactor cross section is more critical for multitubular reactors than in the case of fluid-bed or slurry reactors where lateral mixing takes place.

6.1.5. Catalyst settling or agglomeration

At too low velocities, a concentration gradient may develop in a slurry reactor and this may limit the turn-down ratio. Deposition of insoluble, sticky material onto the catalyst particles may hamper proper suspension of the catalyst.

6.2. Scaling-up aspects

Scaling-up of the multitubular reactor from a pilot plant to a commercial size reactor is a relatively straightforward affair. Since all tubes in a multitubular reactor are in principle identical, experiments in a pilot plant reactor with one or more tubes of the actual commercial dimensions can yield data that are fully representative for the commercial reactor.

Scaling-up of fluid-bed or slurry reactors is much less easy and requires a carefully planned scale-up strategy to avoid the risk of making errors in the commercial design. For successful commercial reactor scale-up one needs to predict at least the gas holdup, interphase mass transfer and dense (liquid) phase phase backmixing. Because in general physical/chemical properties as well as hydrodynamics play a role, the direct use of process data from pilot-plant reactors (where the hydrodynamics may deviate considerably from those in an industrial reactor) for a commercial design is in general not possible without taking unduly large risks. Therefore, a demonstration stage involving the operation of a reactor of say, 1 m diameter and 10–20 m height under actual process conditions is generally included in the commercialisation of novel fluid-bed and slurry processes. Such a 'hot' demonstration unit, which was also an impor-
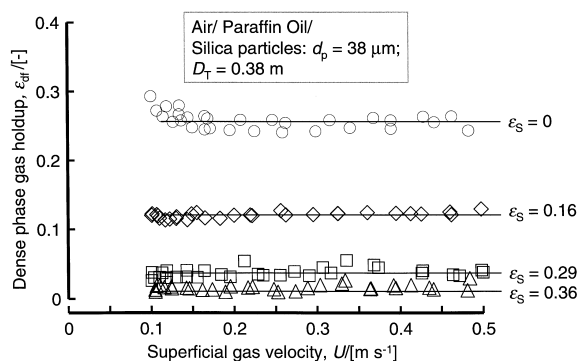
Fig. 11. Dense phase gas holdup as a function of the superficial gas velocity. Experimental data from de Swart [26] and Krishna et al. [33].
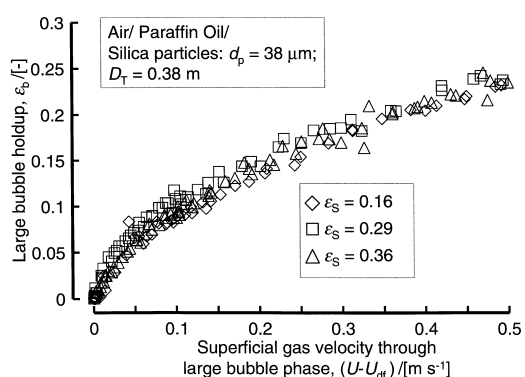

Fig. 12. Large bubble holdup as a function of the superficial gas velocity through the large bubble phase. Experimental data from de Swart [26] and Krishna et al. [33].
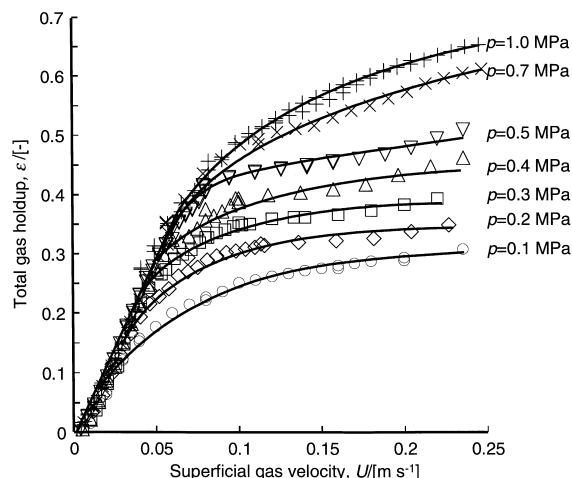

Fig. 13. Total gas holdup in a bubble column ϵ as a function of the superficial gas velocity u at different pressures. Measurements in a bubble column of 0.15 m diameter with the system nitrogen water, by Letzel et al. [32].

The latter point is illustrated in Figs. 11 and 12 with respect to the concentration of solids in the slurry as a system parameter. It can be seen that in the region of interest the small bubble holdup is very much dependent upon the solids concentration, but hardly dependent on velocity. By contrast, the large bubble holdup depends strongly upon gas velocity, but is practically independent of concentration.

Fig. 13 shows the total holdup as a function of gas velocity and pressure, which is an important process variable in Fischer–Tropsch synthesis. It can be seen that pressure does significantly affect the total holdup. The effect of pressure is two-fold. Firstly, the regime transition point is delayed. Secondly, increased system pressure promotes the break-up of large bubbles [32].

The above distinction between system-dependent/ scale-independent and scale-dependent/system-independent factors has important implications in the scale-up of slurry bubble columns in that a more rational scale-up strategy may be followed instead of the empirical one involving a costly demonstration stage. The chemistry and physics of the process may be studied as a function of the system-dependent variables under actual conditions in 'hot' pilot plants and even smaller units. These plants can be small as the scale has no effect. Hydrodynamic aspects which are scale dependent but which do not depend on the nature of the system, may be conveniently studied in

tant part in the development of the earlier mentioned fluid-bed and slurry processes of Exxon and Sasol, generally takes quite some time and money to build and its operation is also very costly in terms of manpower and materials usage.

An important conclusion, derived from numerous measurements on the gas holdup structure in slurry bubble columns at the University of Amsterdam, is that the division of the total bubble population into two distinct classes allows a clear discrimination between system and scale-dependent effects: the behaviour of the small bubble class proved to be dependent on the nature of the system, but not on scale and velocities whereas the behaviour of the large bubbles proved to be dependent on velocities and scale only, see e.g. [30,31,34].
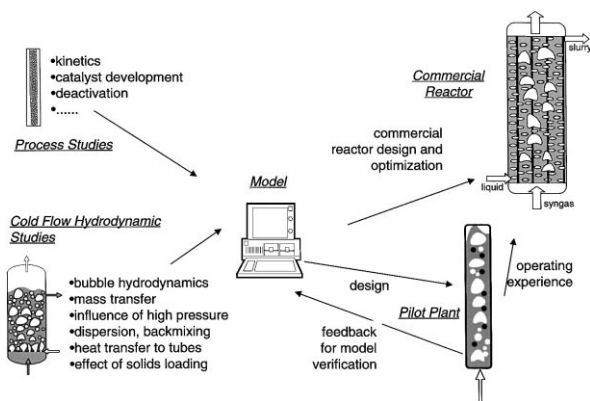
Fig. 14. Scale-up strategy for the Fischer–Tropsch slurry reactor. Adapted from Krishna et al. [34].

Fig. 16. Influence of column diameter D_T on the axial dispersion coefficient D_{ax} of the 'dense' phase in fluid beds and bubble columns. The curve represents the estimation of the axial dispersion coefficient in a slurry bubble column reactor operating at a superficial gas velocity of 0.3 m/s.
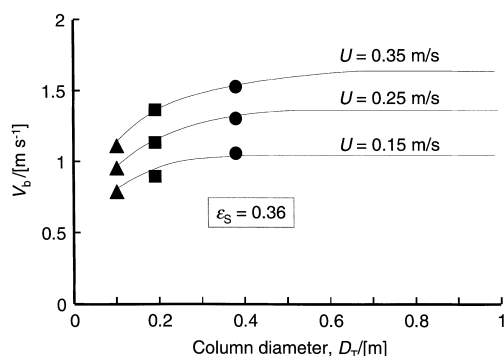

Fig. 15. Influence of column diameter D_T on the rise velocities V_b of large bubbles. Experimental data obtained in columns of 0.1, 0.19 and 0.38 m diameter by Krishna et al. [33].

'cold-flow test rigs' of representative size [34]. This scale-up strategy is depicted in Fig. 14.

Even with convenient model systems, experiments on an actual industrial scale are generally too costly and difficult. Therefore, extrapolation from cold-flow studies in columns of, say 0.4 m diameter to commercial reactors of, say 7 m diameter is still required and an understanding of the nature of the scale effect is desirable as it opens a way to a rational upscaling approach instead of one which relies on empiricism. The large bubbles portrayed in Figs. 6 and 9 can have sizes approaching 0.1 m, and therefore, wall effects in small diameter columns will have a significant effect on their rise velocity. The scale effect on the rise velocity of large bubbles as measured by Krishna et al. [33] is shown in Fig. 15. The rise velocity is expected
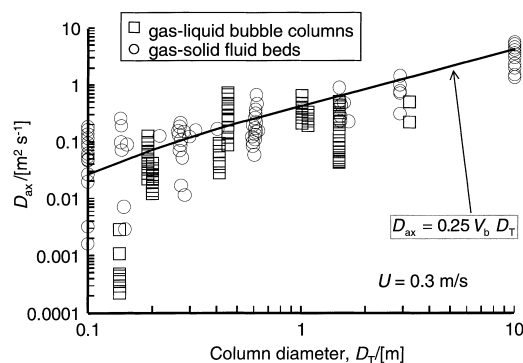
to reach a plateau at a column diameter of about 1 m, where the wall effect ceases to be important.

The liquid phase axial dispersion caused by large eddies in the liquid is a strong function of reactor size and is expected to be roughly proportional to the reactor diameter. This implies that a commercial reactor of several metres in diameter will be highly back-mixed whereas a pilot plant reactor of 0.2 m diameter or less would have a high degree of staging. Using the principle of hydrodynamic analogies, Krishna et al. [34] have suggested a prediction method for the dense phase axial dispersion coefficient by taking this parameter to be proportional to the product of the large bubble rise velocity and the column diameter. The constant of proportionality is suggested as being 0.25. For a slurry bubble column with high catalyst concentrations (35 vol%), the variation of the large bubble rise velocity with column diameter is as portrayed in Fig. 15 and it is then a simple matter to estimate the axial dispersion coefficient for a given superficial gas velocity. Calculations for a superficial gas velocity of 0.3 m/s are shown in Fig. 16. Fig. 16 also shows available experimental data for the dense phase backmixing coefficient in gas–solid fluid beds and in gas–liquid bubble columns. It is interesting to note that the estimated axial dispersion coefficient for a slurry bubble column of 10 m diameter, i.e. $4 \, m^2/s$ is of the same order of magnitude as the solids dispersion coefficient as measured in a FCC regenerator of 10 m diameter. The concept of hydrodynamic analogies, developed in Krishna et al. [34], provides justification for this coin-

cidence of values. Data on backmixing in commercial scale fluid bed reactors can be used with confidence in predicting the performance of large scale slurry bubble columns for Fischer–Tropsch synthesis.

7. Maximal capacity and economy of different type reactors

The recently developed reactors of advanced design, viz., the multitubular trickle-bed, the bubbling gas–solid fluidized bed and the slurry reactor can all have substantially higher capacities (2500 bbl/day or higher) than the reactors developed before, during and shortly after World War II. The maximum feasible capacity is not fixed, however, as other factors besides the fundamental limitations discussed so far can play a role. Aside from mechanical construction aspects, the weight of the reactor can be a limiting factor if the reactor has to be transported and erected in remote areas with poorly developed infrastructure. For offshore installation on fixed and floating platforms, other limiting criteria such as floor space needed and maximum height may apply. Interest in offshore production of synthetic fuels appears to be mounting, as indicated by recently announced alliance between the Norwegian Oil Company Statoil and Sasol for developing this option [35].

For a specific case of conversion of syngas into a relatively heavy Fischer–Tropsch product, de Swart et al. have compared the multitubular trickle-bed reactor with slurry reactors operating in either the homogeneous or the heterogeneous regime [36].

With a maximum weight of 900 tonnes per reactor as limiting criterion, the number of reactors needed for a plant capacity of 5000 tonnes/day (approximately 40,000 bbl/day) were found to be 10 for the multitubular trickle bed, 17 for the slurry reactor operating in the homogeneous regime, and 4 for the heterogeneously operated slurry reactor. The 1250 tonnes/day capacity of the latter reactor is not the absolute limit, however, as this capacity is still to a large extent determined by the concentration and activity of the assumed catalyst. Fig. 17 shows simulation results for the C_{1+} productivity of a slurry reactor of 7 m diameter and 30 m height [37]. At a slurry concentration of 35 vol % and a superficial velocity of 0.35 m/s, a reactor capacity of more than 2500 tonnes/day may be
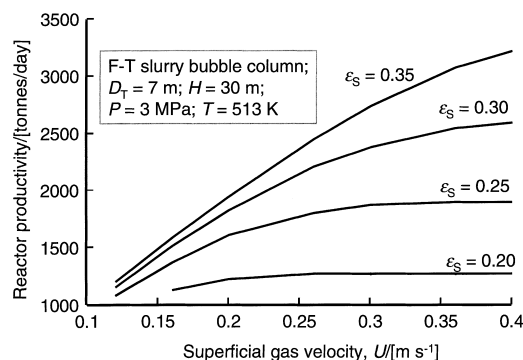

Fig. 17. Reactor productivity of C_{1+} hydrocarbons of a Fischer–Tropsch slurry reactor of 7 m diameter and 30 m height. Model calculations from Krishna and Maretto [37].

achieved. This means that a 5000 tonne/day plant may be built with only two reactor trains.

While the maximum achievable capacity in Fischer–Tropsch reactors is undoubtedly a very important factor in the economy of large-scale natural gas conversion, it is not the only one that governs reactor choice. Reactor costs may differ for different reactors of equal capacity, depending upon the complexity of construction. In this regard too, the bubbling fluid-bed and the slurry bubble column may compare favourably with alternative reactors. It should be kept in mind, however, that the cost of the Fischer–Tropsch reactors is generally only a relatively small part of the total gas conversion plant cost. Although in absolute terms the cost savings in the Fischer–Tropsch reactor section by proper choice of reactor type may be substantial, their impact on the total plant economy may be modest.

8. Conclusions

The recently developed Fischer–Tropsch reactors of the gas–solid fluidized bed, multitubular trickle-bed, and slurry bubble column type have considerably larger production capacities than the classical ones: commercial reactors of all three types have been built with capacities of 2500 bbl/day or higher, which is more than two orders of magnitude higher than that of the commercial reactors operated before and during World War II. The gas–solid fluidized reactor is restricted to the synthesis of products characterised by a growth chance parameter α of less than 0.7, and

is, therefore only applicable if gasoline is the target product. The multitubular trickle-bed and the slurry bubble column are suited for the production of heavier Fischer–Tropsch products, such as middle distillates, lubeoils and waxes. With multitubular trickle-bed reactors, intraparticle diffusion limitation plays a role and catalyst particle size and shape should therefore be carefully chosen. For large-scale production the slurry bubble column is best operated in the heterogeneous or churn turbulent regime. Notwithstanding the presence of large diameter bubbles and their short residence time in the liquid, gas–liquid mass transfer is quite fast in this regime due to the effective interaction between bubbles of various sizes.

Whereas the upscaling of the multitubular reactor from a pilot plant scale to an industrial scale is relatively straightforward and safe, this is not the case for the bubble column reactor and a costly demonstration stage is generally considered to be necessary. However, recent insights in the hydrodynamics of this reactor suggest that a rational upscaling strategy based on investigations in small 'hot' pilot plants and larger 'cold-flow' engineering test rigs may be adopted as alternative to the traditional, largely empirical development route. Based on the presently available knowledge, it can be expected that a bubble column Fischer–Tropsch reactor may achieve a productivity of 2500 tonnes a day (about 20,000 bbl/day), which is a thousand times higher than that of the classical Fischer–Tropsch reactor operated in the forties.

Besides developments in reactor technology, significant improvements have also been realised in the catalysis of the Fischer–Tropsch process in recent years. A discussion of the advances in catalysis, which is rendered difficult because most information is in the domain of proprietary company know-how, is outside the scope of the present paper. However, it will be clear that the combination of advances in catalysis and reactor technology, together with innovations in syngas production, have considerably improved the prospects of large-scale economic production of synthetic hydrocarbons from remote natural gas.

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