APPENDIX B

SLURRY REACTOR DESIGN STUDIES

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Contents

Summary of Literature on Design for Liquid-Phase Fischer-Tropsch Processes

This review is not a complete survey of all aspects of liquid-phase (slurry) Fischer-Tropsch (FT) processes. Instead, the intent is a critical analysis of available procedures for design of bubble-column type slurry reactors for processing syngas ($CO + H_2$). The desired results from a model are the conversion and productivity [(product produced) / (amount of catalyst) (time)] as a function of reactor length and include the influence of pressure, temperature, superficial gas velocity, reactor diameter, and catalyst loading (mass of catalyst/volume of liquid). The effects of these operating and design conditions are important for scaleup and economic optimization.

More complete reviews of the literature on F-T processing have been published (1-3).

I. Available Models

The three recent models that include mass transfer and kinetics and the known essential characteristics of bubble reactors are those of Deckwer et al (4), Kuo (5) and Stern et al (6). These models are more complete developments of the early work of Calderbank et al (7,8). Other models (9-11) do not include axial mixing (dispersion) in the slurry phase. Such mixing depends on the reactor diameter. Therefore, if the effects of diameter on performance is to be accounted for, axial dispersion is a necessary part of successful modeling.

The remainder of this review refers to the Deckwer, Kuo and Stern models. They seem to be the only published design procedures that can be used to establish the influence on performance of all the stated operating and design conditions. Kuo (5) reported experimental data and applied model

predictions only for a small (5.0 m) diameter reactor. However, his model would predict the same effect of diameter as the other two models.

II. Mass Transfer, Heat Transfer and Mixing Effects

All three models neglect mass transfer resistance between the bulk liquid and outer surface of the catalyst particles and intraparticle diffusion resistance. These transport processes are rapid with respect to other steps in the overall reactions since the catalyst particles are small (~50μm). Deckwer et al (4) included both these effects through an overall effectiveness factor η_s but in applying the equations η_s is taken equal to 1.0. This leaves gas bubble-to-liquid mass transfer, intrinsic kinetics and axial dispersion to be considered. These concepts about modeling bubble reactors are reasonable and the three significant rate steps are accounted for in all three models. However, the Kuo (6) model only includes axial dispersion in the liquid phase. The plug-flow assumption for the gas probably would not introduce much error because the solubilities of CO and H_2 in the waxy-oil liquid are relatively low (6,12) and the gas velocity would be high (~10-15cm/s) in commercial scale reactors. All three models account for the change in gas velocity, due to reaction,as the gas moves up the reactor.

Due to good mixing in the liquid and the heat capacity of the catalyst particles, F-T reactors can be operating nearly isothermally if there is internal heat transfer surface. Without heat removal, a temperature increase of 10-20°C might be expected in large reactors operated at high conversions. The Deckwer (4) and Stern (6) models include an energy balance so that the temperature rise can be evaluated. These two models also account for the effects of temperature on the intrinsic rate of reaction. The Kuo (5) model assumes isothermal operation.

A distribution of catalyst concentration along the reactor length is allowed in all three models. The distribution is due to gravitational settling and upward movement of catalyst particles due to the gas bubbles. The equations for evaluating catalyst distribution are given in either the Deckwer (4) or Stern (6) papers. However, these authors as well as Kuo (5) show that for particles of about 40μm or less the variation of catalyst concentration is negligible.

III. Difference Between Models

The Kuo model except for its isothermal restriction is based upon the same concepts as the Deckwer and Stern models. The Kuo single-component model is like that of Deckwer while the multicomponent model is similar to the Stern approach. Hence, it is sufficient to analyze the differences between the Deckwer and Stern models.

A. Stoichiometry and CO/H_2 Feed Ratio

The Deckwer model does not consider variations in hydrocarbon product chain length (the chain growth probability, α) or product composition (fraction of product that is paraffinic, γ). Rather, a constant value throughout the reactor is chosen for the ratio of CO to H_2 consumed by the reaction (the usage factor, U). Also, the feed ratio (I) of CO to H_2 is restricted to a narrow range of about 1.5 to 1.8 so that it is safe to assume a rate equation first order in hydrogen and zero order in CO. Thirdly, the water-gas-shift (WGS) reaction is assumed to be fast and irreversible so that water is not a final product. These three restrictions mean that the design model requires only mass balances for hydrogen, one for the gas phase and one for the liquid phase. However, these second-order ordinary differential equations are coupled so that they must be solved simultaneously, and with an energy balance if a temperature distribution is be be calculated.

In contrast, the Stern, et al (6) model develops the stoichiometry (U) from α and γ. Also, the WGS reaction is assumed to be reversible with a finite rate. Hence, the kinetics of two reactions are involved,

$$x\,CO + (\tfrac{1}{2}y + x)H_2 \rightarrow C_xH_y + x\,H_2O$$

$$H_2O + CO \leftrightarrow H_2 + CO_2\ ,$$

and water is a product. With this more general treatment of stoichiometry and WGS reaction, the model includes coupled, mass-balance equations for CO, H_2, H_2O and CO_2 and C_xH_y in both gas and liquid phases. Because finite kinetics of the WGS reaction are included, the usage factor U can vary along the reactor length.

The complex stoichiometry evaluation of Stern turns out to be close to the simpler approach of Deckwer when the WGS shift reaction is irreversible and fast. For example, Stern chooses $\alpha = 0.69$ and $\gamma = 0.25$ and $\beta = 0$ [β = water/CO_2 in the product] to compare with the Deckwer et al (13) experimental data in a 3.8cm reactor. For this case the Stern equations for the stoichiometry lead to the overall reaction

$$0.64\,CO + 0.37\,H_2 \rightarrow 0.10\,C_{3.2}\,H_{7.4} + 0.32\,CO_2$$

This corresponds to a usage, U = 1.7, and the product is close to C_nH_{2n}. These results are in agreement with the values proposed by Deckwer (4). We can conclude that when an active WGS catalyst is used, and the feed CO/H_2 ratio is 1.5 to 1.8, the simpler approach of Deckwer (4) is adequate. As mentioned, the calculations are then much simpler since mass balance equations are needed only for hydrogen and the relations between α, γ, β and the stoichiometry are not involved.

On the other hand, the Stern (6) model has the flexibility to handle other feed ratios and finite WGS kinetics.

B. Contraction of Gas Velocity

Since the volume of gas decreases with reactor length due to reaction, the superficial gas velocity also decreases. This decrease depends upon the conversion of CO + H_2, and hence upon the stoichiometry and feed ratio. For the simple case of Deckwer (4) where a constant usage factor is used, the contraction of gas velocity is linearly related to the conversion of hydrogen. This relation and the relation between velocity and gas-phase mol fraction of H_2 are derived by Deckwer (4).

In the Stern model the linear relation between velocity and conversion of hydrogen does not apply, in general. However, for rapid irreversible WGS reaction the stoichiometry (and U) do not change, and the simpler contraction expression for gas velocity [Eq. (17) of Deckwer (4)] is suitable.

IV. Gas Holdup

Gas holdup is a key factor in determining both catalyst loading and bubble-liquid interfacial area, and, therefore, the importance of mass transfer in F-T process design. The holdup is a function of gas velocity. For constant bubble size increasing the gas flow rate and superficial-velocity simply increases the number of bubbles. Hence, the holdup and interfacial area are linearly proportional to the gas velocity. Over a range of flow rates and sparger sizes Deckwer et al (14) and Quicker and Deckwer (15) found bubble sizes in a wax-type liquid to be in a narrow range around a value of 0.7mm. In both the Deckwer (4) and Stern (6) models the gas holdup is calculated from the equation

$$\varepsilon_g \text{ (holdup)} = 0.053 u_g^{1.1} \qquad (1)$$

where u_g is the superficial gas velocity. This slightly greater than linear proportionality was obtained from experimental measurements at 250°C in waxy liquid (14).

Equation (1) represents experimental data at low and moderate gas velocities, but at high velocities bubble hydrodynamics may change. Bubbles coalesce and ultimately form large slugs, even void columns through which the gas moves. Important studies have been reported recently by Bukur and colleagues (16-18) who measured gas holdup in waxy liquid at F-T reaction conditions and over a wide range of gas velocities. They concluded that foaming was relatively unimportant in large-diameter reactors, and suggested that the data of Deckwer et al (14,15) was in the foaming regime. The effect of bubble coalescence and slug formation is to cause holdup to become constant, independent of gas velocity. At high velocities (~15cm/s) Eq. (1) could over-estimate holdup very significantly. Also, the interfacial area would cease to increase with velocity so that bubble-to-liquid mass transfer has a greater effect on conversion and productivity.

The increase in ε_g with u_g suggests a maximum in the curve of productivity vs. gas velocity, first suggested by Schumpe et al (19) and confirmed by the Deckwer model (4).

Bukur and Daly (16) could well represent holdup data up to ~15cm/s by the correlation developed by Bach and Pilhofer (20):

$$\left(\frac{\varepsilon_g}{1-\varepsilon_g}\right) = 0.115\left[\frac{u_g^3\,\rho_L}{g\,(u/\rho)_L\,(\rho_L-\rho_g)}\right]^{0.23} \qquad (2)$$

where ρ = density, μ = viscosity and subscripts L and g designated liquid and gas and all units are cgs.

There remains (it seems to me) some uncertainties in the gas holdup at F-T reaction conditions and this affects interfacial area and, ultimately, the importance of gas-to-liquid mass transfer. In view of this uncertainty it does

not seem warranted to try to account for variation in holdup with reactor length. This variation is involved in the Stern model as a result of the stoichiometry treatment. Note, however, that ϵ_g and k_L do not vary with gas velocity as much if the Bukur and Daly (16), rather than Deckwer's (4), correlation is used. If a uniform ϵ_g is used, any correlation may be chosen [Eq. (1), (2), etc.] for use in either the Deckwer (4) or Stern (6) model without complicating the methods of solution of the model equations.

V. Kinetics

Rate equations for the F-T reaction are given by Dry (21) and Huff and Satterfield (22). The equation for the rate of the overall reaction

$$x\,CO + (\tfrac{1}{2}y + x)H_2 \rightarrow C_xH_y + x\,H_2O$$

proposed in reference (22) is

$$r_{H_2+CO} = \frac{k_F C^2_{H_2} C_{CO}}{aC_{CO} C_{H_2} + C_{H_2O}} \qquad (3)$$

For conversions of CO up to 60%, this expression can be replaced with a simple, first-order-in-hydrogen expression with an error of less than 10% (22).

Moe (23) suggests a stoichiometric-type equation for the rate of the WGS reaction,

$$r_s = k_s \left[C_{CO} C_{H_2O} - \tfrac{1}{K} C_{CO_2} C_{H_2} \right] \qquad (4)$$

The equilibrium constant K for this reaction is large (~50) at 250°C. This lends confidence to the assumption of irreversibility used in the Deckwer model.

Values for the constants in the rate equations are reported in references (21-23) and in (4). For example, Deckwer (4) suggests the following first-order

expression for the rate of combined H_2 + CO consumption for a feed and usage ratio of 1.5

$$r_{H_2 + CO} = A W_{Fe} C_H \exp\left(-\frac{E}{RT}\right) \varepsilon_L \quad (5)$$

where r = moles/(cm^3 reactor volume) (s)

A = [(s) (wt. % catalyst in slurry)]$^{-1}$ = 1.12×10^5

W_{Fe} = wt. % catalyst in slurry

C_H = liquid phase H_2 concentration, moles/cm^3

ε_L = liquid holdup

E = 70,000 kJ/mol

U = usage ratio

Kuo (5) also gives numerical values for the rate constants in Equation (3) and for the WGS reaction written as Equation (4).

It should be noted that Deckwer, apparently but not clearly, defines the intrinsic rate per unit volume of reactor while Stern defines the rate per unit mass of catalyst.

VI. Solution of Model Equations

A. Deckwer Model (4)

There are three second-order ordinary differential equations (mass balances of hydrogen in the gas and liquid phases and an energy balance) and appropriate boundary conditions. The solution gives concentration profiles (C vs. reactor length) in the gas and liquid phases and conversion vs. reactor length. These results can be obtained for various values of gas velocity, reactor diameter and catalyst loading and for different pressures and feed temperature.

Since the equations constitute a boundary value problem, either a shooting method or polynomial approximation (to convert the differential to algebraic equations) is needed. Finlayson (23) describes the shooting and orthogonal-collocation form of polynominal approximation while Denison, et al (24) formulates a spline-collocation form of polynominal approximation and suggests using COLSYS software for the solution. The COLSYS computer code is described by Ascher, et al (25) and Denison, et al, and the former paper gives programs for solution of two examples of equations. Deckwer (4) solved his model equations with orthogonal collocation.

B. Stern Model

Stern, et al (6) used COLSYS software to solve the differential equations in their model. Since this model is set up to include both F-T and WGS kinetics, five mass balances equations (for H_2, CO, H_2O, CO_2, C_xH_y) are required for each phase. No energy balance is needed because isothermal operation is assumed. The Deckwer (4) model could be adapted to include the kinetics of both F-T and WGS reactions by adding mass balances and the Stern (6) model could be applied to non-isothermal operation by adding an energy balance. The essential difference between the two models is in the treatment of reaction stoichiometry as mentioned in Section IIIA. The Stern model can be used for different feed ratios, and different usage ratios could result for difference choices of the chain growth probability and product composition. Stern, et al (6) found, however, that the simple, first-order kinetic model had to be modified with a water retardation effect to fit data at higher H_2/CO ratios where water is a byproduct.

VII. Design Quantities

Examination of the model equations shows that both Deckwer and Stern models require numerical values for the following quantities: kinetic

constants for the rate expressions, gas and liquid holdups, mass transfer coefficient k_La from gas bubble-to-liquid, and axial dispersion coefficients for both gas and liquid phases. For non-isothermal operation (Deckwer model) additional quantities are needed. These are the axial thermal dispersion coefficient, heat of reaction, and heat transfer coefficient from the slurry to the cooling surface.

Deckwer (4) in an Appendix gives recommended correlations and values for the mentioned quantities as well as values of the properties (viscosities, densities, diffusivities, heat capacities, thermal conductivities) needed in the correlations. Due to the simplified stoichiometry, the Deckwer model also requires a specified usage ratio and a constant contraction ratio (also given the symbol α by Deckwer, et al). In Deckwer's examples the usage ratio is taken equal to the feed ratio (1.5 to 1.8) and $\alpha = -0.5$.

Knowing these quantities the models can be solved for the effect of reactor diameter, gas velocity and catalyst loading on conversion and productivity. Instead of a specified usage ratio the Stern model develops the stoichiometry from the chain growth probability and product composition.

The kinetic constants for the rate equations will vary with catalyst formulations, with age[1] and even between different batches of the same formulations. These constants, along with the mass transfer coefficient k_La, determine the influence of mass transfer. Since k_La varies with gas velocity, the effect of gas velocity on performance depends indirectly on the particular values chosen for the kinetic constants. This is because the kinetic constants affect the relative importance of mass transfer on the overall reaction rate.

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[1] The treatment of deactivation given in the Air Products report (27) for methanol synthesis is believed to be fundamentally sound when loss of activity is due to structural changes in the catalyst (for example, sintering). The equations on p. III-42 and III-45 would need to include a poison concentration if deactivation is due to a contaminant in the liquid or gas feed.

Similarly, the effect of diameter on performance will depend upon the values chosen for the axial dispersion coefficients, particularly for the liquid. The value of the models for predicting effects of reactor diameter, gas velocity and catalyst loading will be determined by the accuracy of the required reaction rate constants and transport coefficients. For example, Deckwer (4) recommends the Calderbank and Moo Young (8) correlation for k_L and an expression similar to Eq. (1) for $\underline{a}$, but the more recent data and correlation of Akita and Yoshida (26) may be preferable. Also, there is a very limited amount of data for axial dispersion coefficients in bubble columns [The Deckwer (4), Stern (6) and Kuo (5) publications include the available references]. The uncertainties in the necessary kinetics and transport coefficients suggest that it would be best to obtain conversion and productivity results for a range of values of these coefficients. These uncertainties also suggest that the design models may be best used for scaleup and interpolation of actual pilot-plant measurements.

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Summary of Literature on Methanol Production from Synthesis Gas

I. Background on Methanol Processes

Prior to about 1960 methanol from hydrogen and carbon monoxide was produced in high pressure (>10 MPa) fixed-bed reactors using metals and oxides of Cu, Zn, and Cr_2O_3 (1-4). In the 1960 decade new, extremely selective $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ catalysts were developed by Imperial Chemical Industries (ICI) and Lurgi. These catalysts gave high rates of production at lower pressures (5-10 MPa) and at 220° to 280°C. A detailed history of methanol production is available including a description of new processes in the development stage (5).

The maximum conversion of CO or CO_2 to methanol is limited by equilibrium. Since the reactions are exothermic, higher maximum conversions are obtained at lower temperatures. In fixed-bed reactors it is difficult to prevent some temperature rise so that much of the effort in reactor design has been directed toward efficient removal of the heat of reaction. The temperature control problem also is partially responsible for the development work on the liquid-phase process. Fine catalyst particles are suspended in an inert liquid and the synthesis gas flows upward through the slurry. The relatively good mixing and heat capacity of the slurry prevents large temperature gradients. The reaction heat is removed either by internal heat transfer surface or by circulating the slurry through an external exchanger.

As with the prior literature survey on the slurry Fischer-Tropsch process, this review is a limited one. The emphasis is not on modeling but on a comparison of the fixed-bed and slurry processes. More complete

reviews of the technological aspects of methanol production have been published (6, 7).

II. Reaction Kinetics

As noted by Bart and Sneeden (6), methanol synthesis involves five reactants and products, H_2, CO, H_2O, CO_2 and CH_3OH. Usually carbon dioxide and often steam are present in the gas feed. Hence, the water-gas-shift (WGS) reaction

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (1)$$

provides either H_2 or CO to react along with the feed CO or H_2 to produce more CH_3OH by the base reaction

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (2)$$

Adding reactions (1) and (2) gives the overall reaction for producing methanol from CO_2

$$CO_2 + 3H_2 \leftrightarrow H_2O + CH_3OH \quad (3)$$

Both reactions (2) and (3) are exothermic (ΔH_2 is about -100kJ/mol and ΔH_3 about -61 kJ/mol) at process temperatures. When synthesis gas is produced either by reforming of natural gas or by coal gasification H_2O and CO_2 are present unless efficient upstream separation is installed.

Because of the interaction of the five species, the kinetics of methanol production via reactions (2) and (3) is complex. Therefore, many different rate equations have been proposed. For the $Cu/ZnO/Al_2O_3$ catalysts, Bart and

Sneeden (6) list seven separate rate expressions written in terms of partial pressures in the gas phase. These expressions would be applicable for slurry processes only if gas and liquid compositions are in equilibrium and solubilities (Henry's law constants) are introduced. Reference (6) provides an abbreviated assembly of all the studies on methanol kinetics for the Al_2O_3-based catalysts. Graaf (8, 9) has proposed somewhat different but equally complex rate equations that are applicable for the Al_2O_3-based catalysts (employed in the ICI process).

Separate expressions are proposed for the fixed-bed (8) and for the slurry (9) processes. Presumably, these rate equations are all based upon experimental data. While complex, all formulations have the general Langmuir-Hinshelwood form of a reversible driving force and a denominator term representing adsorption. For example, the rate for methanol production by reaction (2) for the fixed bed (gaseous system) is

$$r = \frac{k\left[f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / f_{H_2}^{1/2}\right]}{\left(1 + K_1 f_{CO} + K_2 f_{CO_2}\right)\left(f_{H_2}^{1/2} + K_3 f_{H_2O}\right)} \qquad (4)$$

where f represents fugacity and k, K_1, K_2, K_3 are rate and adsorption equilibrium constants.

Simpler rate expressions have been proposed. For example Andrew (10) suggested from data on the commercial (ICI) $Cu/ZnO/Al_2O_3$ catalyst:

$$r \text{ (for } CH_3OH) = k\, p_{H_2}^{0.7}\, p_{CO}^{0.4}\, \phi(CO_2) \qquad (5)$$

where $\phi(CO_2)$ is an unspecified function of CO_2 pressure.

Apparently, the activity of the catalyst depends significantly in its oxidation states and this in turn depends on the H_2, CO, and CO_2 content of the gas. This complex situation means that catalyst activity of the same catalyst can vary within a reactor as the gas composition changes.

Berty and colleagues (11) have proposed for the $Cu/ZnO/Cr_2O_3$ catalyst rate equations that follow stoichiometry. Their expressions for reactions (2) and (1) are

$$r_{CH_3OH} = r_2 = k_2 \left[C_{H_2} - \frac{C_{CH_3OH}}{K_2 C_{H_2} C_{CO}} \right] \tag{6}$$

$$r_1 = k_1 \left[C_{H_2} = \frac{C_{CO} C_{H_2O}}{K_1 C_{CO_2}} \right] \tag{7}$$

where K_2 and K_1 are equilibrium constants for reaction (2) and the reverse of reaction of reaction (1).

Still another power-law type rate equation has been used in evaluating the performance of the Laporte Process-Development-Unit (PDU) for the liquid-phase process (12). This equation is (for methanol rate)

$$r = k\, p_{CO}^{1/3}\, p_{H_2}^{2/3} \left[1 - \frac{p_{CH_3OH}}{K\, p_{CO}\, p_{H_2}^2} \right] \tag{8}$$

Since no terms for CO_2 or H_2O are included, this expression should be applicable only when neither of these two species are present. Then K is proportional to the equilibrium constant for reaction (2). Also, gas and liquid phase concentrations are apparently assumed to be in equilibrium since the equation is expressed in partial pressures for the liquid-phase processes, Henry's law constants are incorporated in k and K.

In their detailed discussion of the kinetics for methanol synthesis, Bart and Sneedon (6) conclude that neither the mechanism of reactions (1-3), the rate controlling steps or the nature of the active adsorbed species are well understood. For example, the role of the copper site and its interaction with ZnO adsorption is still uncertain. However, completely reduced copper alone is now known to catalyze methanol synthesis. Reference (6) discusses the voluminous literature on mechanistic, adsorption, and surface phenomena with respect to catalytic activity.

III. Reactor Design

A. Fixed Bed

The ICI and Lurgi reactor designs appear to be well tested with numerous operating commerical-size plants (5,13). The chief difference is in the design for removing the heat of reaction. In the ICI reactor (5,7) the single, large diameter catalyst bed is divided into sections with provision to introduce cold, quench gas between each action. The Lurgi reactor (5,7) consists of a manifold of small-diameter tubes filled with catalyst. Reaction heat is transferred to pressurized boiling water in the jacket surrounding the assembly of tubes.

An important retardant to the reaction rate in the fixed bed is intraparticle diffusion. Hence, in a design model the effectiveness factor must be considered. In cases where there is a moderate heat of reaction, the general

rule is that external mass transfer resistance is negligible with respect to intraparticle diffusion, while the external (bulk fluid-to-particle) temperature difference is more important than the intraparticle temperature gradient. Öztürk, et al (14) in their modeling of the fixed-bed process, include both external and intraparticle temperature and concentration gradients. Of these four transport effects only intraparticle mass transfer was significant at the conditions studied. The Öztürk approach (which utilized Equations (6) and (7) for the intrinsic rate) is a general one for representing mass and energy transport effects in a non-isothermal, adiabatic, fixed-bed reactor. Their model is for a catalyst bed without intercooling (Lurgi type) except that the bed is considered to be adiabatic rather than exposed to a constant surroundings temperature. Alternately, the model could be applied to an individual segment of an ICI reactor which operates close to adiabatically. While the Öztürk, et al results are given for a $Cu/ZnO/Cr_2O_3$ catalyst, the same procedure could be applied to any catalyst with appropriate changes in the rate equations.

B. Liquid-Phase Process

Detailed models for predicting the effects of kinetics and mass and energy transport on the performance of slurry reactors have been developed for Fischer-Tropsch (F-T) processing (see literature survey for Liquid-Phase Fischer-Tropsch Process). With different kinetics the same kind of models can be used for slurry reactors for methanol production. However, note that in the Deckwer, et al model* batch liquid was assumed. This probably is satisfactory when only a hydrogen mass balance is necessary. For this situation the low solubility of hydrogen in the liquid suggests that a negligible

* Deckwer, W.-D., et al, Ind. Eng. Chem. Proc. Res. Dev. 21 231 (1982).

amount of hydrogen would leave the reactor if there were an effluent liquid stream. When the kinetics are not first order in hydrogen alone, mass balances are needed for other species. Then the postulate of a batch liquid phase may not be correct. For example, a continuous exit stream or periodic liquid removal is necessary to remove the accumulating hydrocarbons produced in Fischer-Tropsch processes. This is not a problem in methanol synthesis, since the methanol product is in the gas phase. There is only a build up of byproducts in the liquid. In the Öztürk, et al (14) modeling of the methanol process non-linear kinetics are involved and the authors allow for a steady flow of liquid in and out of the reactor. The presumption is that the heat of reaction is removed in an external heat exchanger. The model of Stern, et al (15) developed for Fischer-Tropsch synthesis could be applied to a methanol reactor with external heat exchange since continuous flow of liquid is considered.

A simple model assuming plug flow of gas and well-mixed batch liquid, as presented by Bukur (16) for F-T reactors, might be applied to methanol production. This would require that the heat of reaction be removed internally and that the rate of accumulation of methanol (and CO and CO_2) in the liquid is negligible with respect to the reaction rate.

The results (12,17) obtained for the Laporte PDU demonstration-size reactor provide useful experimental data on the performance of the liquid-phase process. Data are available for the effects of catalyst loading (10-50 wt%), feed composition [55% H_2, 19 CO, 5 CO_2 and 35% H_2, 51 CO, 13 CO_2 and 1% inerts], catalyst deactivation, gas holdup, type of slurry liquid, and method of heat transfer, on methanol production rate. It was shown that internal heat transfer could be used satisfactorily so that continuous circulation of slurry through an external heat exchanger could be eliminated. With internal heat

removal, constant productivity could be achieved with periodic withdrawal (daily, for example) of a small volume of slurry, combined with addition of an equal volume of slurry with fresh catalyst. Catalyst life tests showed a deactivation rate of less than 0.2% per day. A uniform decrease of 0.2% per day at constant temperature corresponds to a drop to 11% of original activity in three years. However, the rate of decrease could diminish with time, and also the temperature could be increased to approach constant activity. Maximum space time yields above 1.0 kg CH_3 OH per kg catalyst per hour were obtained.

The authors of reference (17) conclude that the technology of the liquid-phase process is now reasonably well established. Once field tests are satisfactorily completed on removal of catalyst poisons (prime poisons are iron and nickel carbonyls, H_2 S, COS and HCl), it was proposed to go to the next step toward commercialization--a 500 ton/day methanol unit.

IV. Comparison of Fixed-Bed and Slurry Processes

Three publications compare methanol production in slurry and fixed-bed reactors. This comparison is difficult because the intrinsic rate (rate at a catalytic site) equations can be different in the liquid and gas phases (11,18). Serwin and Frank (19) compared the technology of the multi-bed quench process (ICI) with the slurry reactor process. Öztürk, et al (14) carried out model calculations for a Lurgi-type fixed-bed but assumed adiabtic operation. The Ph.D. thesis of Graaf (8) compares the multi-bed quench process with a multistage, agitated, slurry reactor. The mechanically-agitated reactor follows the original contactor design of Oldshue and Ruston (20). This type of reactor has been recommended by Joshi, et al (21) as a desirable solution when a non-agitated, single reactor operating at high pressures requires a large reactor volume.

The objective of the Öztürk et al (14) work was to compare fixed-bed and slurry reactor performance. Hence, the same intrinsic rate equations were used for both reactors. On this basis comparable space-time yields (mols per hr per kg catalyst) were predicted when the catalyst loading in the slurry reactor was 30 wt. %. Since the same intrinsic rate equations and feed conditions (composition and temperature) at the same pressure were employed, what was actually compared were the transport effects in the two reactors. For mass transport, the comparison is between the intraparticle diffusion resistance in the fixed-bed with the gas-to-liquid mass transfer resistance in the slurry reactor. Intraparticle diffusion resistance is sensitive to catalyst particle size. It is not clear what size is employed for the comparison, but calculations early in the paper are for 0.5 mm particles. For this size effectiveness factors ranged from 0.1 to 0.8. If larger particles (1/8"-1/16") are employed, effectiveness factors would be lower, shifting the comparison to favor the slurry reactor. On the other hand, for the same catalyst mass, reactor volumes for the slurry process would be larger than those for the fixed bed. This shifts the economics in the direction of the fixed bed. A normal solid fraction for a fixed-bed is 1-0.4 = 0.6, while a 30 wt. % slurry with a gas holdup of 0.3 suggests a very approximate solid fraction of 0.21. This indicates that the slurry reactor would require about three times the volume of the fixed-bed for the same amount of catalyst.

Also, the basis of equal intrinsic rates may not be appropriate for an overall comparison of the two reactors. For example, the kinetics may be more favorable for gas phase reactions because of higher adsorption rates. Since kinetics is an important factor in overall performance, this would favor the gas-phase fixed-bed process. In contrast, a higher catalyst loading than 30 wt. % might be employed without excessive settling and a significant increase

in mass transfer (gas-to-liquid) resistance. The Laporte experiments indicated that the upper limit could be higher than 30 wt. %.

As noted, the Graaf work (8) employed a multi-stage agitated slurry system instead of a single reactor. The comparison also presented an economic analysis of the two processes in which feed preparation and product separation costs were included. Methanol production rates for the same feed conditions were calculated when the slurry reactor was operated at a superficial gas velocity of 30 cm/s, 0.1 gas holdup, 25 wt. % catalyst loading, and isothermal conditions.*

I. Miscellaneous Comments

A. Catalyst Deactivation

For the fixed-bed process a catalyst life of 3-4 years seems to be possible. At constant temperature operation it is not known what residual activity exists after three years. As noted, in short (120 days) time tests, deactivation with the Laporte slurry reactor was less than 0.2% per day (17). If this rate of decrease is constant for three years the residual activity would be about 11%, assuming constant temperature. Normally the temperature would be raised to maintain catalyst activity. Also, the rate of activity decease could level off at long times (a common situation) leading to a higher residual activity.

B. Improved Catalysts

Adding alkali hydroxides can significantly improve the activity of Cu/ZnO catalysts for methanol production (5). The improvement in activity is greatest for cesium, and in decreasing order for Rb, K, Na and Li. There is an optimum amount of dopant. For example, for cesium at one set of

* Only Chap. 7 of reference (8) was available. The complete thesis (particularly Chap. 6) would give more detailed information. However, this may not be of interest since a mechanically agitated, multistage slurry system is employed for the calculations.

operating conditions, about 0.8 mole % Cs on a Cu/ZnO catalyst improved methanol productivity (STY) by more than 100% (22). The rate of the WGS reaction was also increased (23) by cesium.

C. Future Catalysis Research

Klier, et al (5) have listed several general and specific items regarding development and understanding of methanol catalysts. Items included are development of selective and stable homogeneous catalysts and understanding of the bi-functional nature of Cu/ZnO catalysts and their combination with alkali dopants.

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March 16, 1990

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Dear Joe:

This letter concerns the effect of pressure on F-T kinetics and conversion. While the literature indicates considerable uncertainty on the details of the mechanism for producing hydrocarbons, it seems clear that the first step is the adsorption of hydrogen on the metal (catalyst site) forming a metal (M) hydride:

$$(1) \qquad M + H_2 = 2MH$$

The paper by G. Henrici-Olive and S. Olive [Angeus Chemie International Ed. (1976)] seems to be a logical explanation of how hydrocarbons are produced from the metal hydride. The carbon atoms (from CO) are introduced into the chains attached to the catalyst (M). Then growth is determined by a "chain transfer" mechanism. That is a chain, $R\text{-}CH_2 - CH_2 - M$, leaves the catalyst and a new chain is started at the same site (MS according to the reaction:

$$(2) \qquad R - CH_2 - CH_2 - M \xrightarrow{\text{Olefin product}} R\text{-}CH = CH_2 + HM$$

Evidence for this process is that there are many more chains (hydrocarbon molecules) produced than there are metal hybride sites on the catalyst. The molecular weight distribution is determined by the frequency of chains leaving the site and the rate of inserting carbon atoms into the chain.

While these latter steps [after reaction (1)] may be affected by pressure, the effect of pressure on rate and conversion is primarily determined by reaction (1). This production of metal hybride is an activated adsorption process, and its rate increases with pressure (hydrogen pressure) on any one site. Also, as the pressure increases more of the sites in the catalyst are utilized for adsorption. The overall result is that the rate of reaction appears as a first-order process. This then means that as the pressure increases at low pressure, with a constant T and volumetric gas flow rate through the reactor, the conversion remains the same, but the spare-time-yield increases linearly with hydrogen pressure (see Deshuer paper, Fig. 4). This result has been verified up to 40-600 psia with experimental data [Industrial and Engineering Chemistry 46, 2278 (1954); 44, 391 (1952)].

The above results are based upon there always being available additional sites on the catalyst for formation of the metal hydride. However, such an activated adsorption process probably follows Langmuir concepts resulting in a flattening of the equilibrium adsorption isotherm as the pressure is increased to a high value. That is, a monolayer coverage of the catalyst surface is approached at high pressures. I believe this is the "saturation phenomenon" you mentioned during our telephone conversation.

Thus, at very high pressures (what the critical pressure is at which saturation access is unknown) the rate of reaction would no longer increase linearly with pressure, and so the conversion, at constant temperature and volumetric gas flow rate, would decrease with further pressure increase. I would expect the first-order form of the rate equation would be better represented by:

$$\text{rate} = \frac{k\, p_{H_2}}{1 + K p_{H_2}}$$ over a very wide pressure range.

Up to the critical or threshold pressure, $Kph_2 \ll 1$, but at at high pressures 1 and Kph_2 are about the same, and at very high pressures $Kph_2 \gg 1$ so that the rate = k/K and no longer increase with pressure.

Sincerely,

Joe Smith