TOPICAL REPORT
SLURRY REACTOR DESIGN STUDIES
DOE Project No. DE-AC22-89PC89867
REACTOR COST COMPARISONS

1.0 INTRODUCTION

The objective of these studies was to perform a realistic evaluation of the relative costs of tubular-fixed-bed and slurry reactors for methanol, mixed alcohols and Fischer-Tropsch syntheses under conditions where they would realistically be expected to operate. The slurry Fischer-Tropsch reactor was, therefore, operated at low H_2/CO ratio on gas directly from a Shell gasifier. The fixed-bed reactor was operated on 2.0 H_2/CO ratio gas after adjustment by shift and CO_2 removal. Every attempt was made to give each reactor the benefit of its optimum design condition and correlations were developed to extend the models beyond the range of the experimental pilot plant data.

For the methanol design, comparisons were made for a recycle plant with high methanol yield, this being the standard design condition. It is recognized that this is not necessarily the optimum application for the slurry reactor, which is being proposed for a once-through operation, coproducing methanol and power. Consideration is also given to the applicability of the slurry reactor to mixed alcohols, based on conditions provided by Lurgi for an Octamix™ plant using their standard tubular-fixed-bed reactor technology.

This report follows the same format as the Topical Report on "Reactor Selection Criteria", issued in April 1990, except for the addition of Section 6 "Capital and Operating Cost Comparisons", an Executive Summary and backup material on the Methanol designs in Appendix E and the Fischer-Tropsch designs in Appendix F. This backup material consists of the process flow diagrams and equipment lists used for the estimation of costs. Fischer-Tropsch material balances and utility balances are also included as well as Lurgi's process flow diagram for the Octamix™ mixed alcohols process.

Sections 2 through 5 and Appendices A through D are identical to the Topical Report except that Section 4, "Process and Reactor Design Bases," has been amended and expanded. Sections 2 and 3 contain a critical review of the literature on Fischer-Tropsch (F-T) and alcohol syntheses from the standpoint of reactor design. Bechtel was assisted in this work by two consultants who supplied design reviews:

Dr. Aydin Akgerman of Texas A&M University in Appendix A
Dr. Joe M. Smith of U. C. Davis in Appendix B

Section 5 covers areas for further development.

Appendix C consists of Bechtel's review of fixed-bed and slurry reactor kinetics and Appendix D is a reprint of the paper "Fischer-Tropsch Reactor Selection" presented at the Fischer-Tropsch Symposium at the AIChE Spring National meeting in Orlando, March, 1990.

2.0 SLURRY REACTOR DESIGN

2.1 Definition of the "Slurry Reactor"

For the purposes of this review, a slurry reactor is defined as a three phase bubble column reactor utilizing the catalyst as a fine solids suspension in a high molecular weight liquid. For methanol synthesis the liquid is Witco-70, a saturated mineral oil with molecular weight ~340; for Fischer-Tropsch synthesis it is the heavy portion of the product, molecular weight ~400. In the latter case product withdrawal includes a catalyst separation step (e.g. hydrocloning), returning the catalyst thus recovered to the reactor. Gas-liquid disengaging is provided by a settling zone at the top of the reactor and external cyclones.

The reacting feed gas (mixed with recycle) is introduced through spargers. It bubbles through the column, keeping the catalyst in suspension, aerating the liquid and supplying the agitation necessary for mass transfer as it reacts. Because the reactions in question are highly exothermic, cooling coils are provided in the reaction zone, contacting the liquid phase with cooling medium, normally in the form of steam generation.

Except for the presence of solids, this type of slurry reactor is identical to the bubble column reactor commonly used for gas-liquid contacting accompanied by chemical reaction. Where gas solubility is low (liquid phase mass transfer is important) and a large liquid holdup is required, this type of reactor is ideal. It has been selected for this study because:

1. It has been chosen by Air Products for the liquid phase methanol reactor after careful review and testing of other types of reactors including those with slurry circulation through an external exchanger, both ebullated-bed and entrained-bed versions.

2. It has long been considered for application to liquid phase Fischer-Tropsch synthesis since first being proposed by Kolbel and Ackermann in the 1930's.

3. It is amenable to modelling and scale-up, though more difficult to analyze than a fixed-bed reactor. The literature on this subject is extensive.

A sketch showing the slurry reactor proposed by Kolbel is presented as Figure 2.1.

2.2 Slurry Reactor Applications

Slurry reactors and bubble column reactors have a long history of commercial use in specific applications. Among these are:

- Stack gas scrubbing with lime or magnesia
- Fatty oil hydrogenation with catalyst suspensions
- Resid hydrocracking and hydrotreating in ebullated bed reactors
- Olefin polymerization using catalyst suspensions
- Waste water treatment
- Ethylene oxidation to acetaldehyde (Wacker process)
- Ethylene oxychlorination
- Oxidation of toluene to benzoic acid

For some of these applications special designs have been developed:

- o The ebullated-bed reactor is employed for resid hydrocracking and is proposed for coal liquefaction. In this design, larger catalyst particles are used and the liquid product overflows from the reactor free of the catalyst.
- o The pipeline loop reactor is used for polymerization of olefins to isotactic polymers (Figure 2.2). This design takes advantage of the improvement in product quality and conversion when plug flow characteristics apply. The product is removed as a solid which contains catalyst particles dispersed in it. External jackets cool the reactants.
- o Pipeline reactors are used in the homogeneous two-stage partial oxidation of ethylene to acetaldehyde The catalyst is circulated from the reactor to the oxidizer, where it is reoxidized with air. A bubble column is used for the single step process with in-situ oxygen addition. Heat removal is by water evaporation from the liquid phase.
- o Mechanically agitated reactors have been used for the olefin polymerization and oxychlorination processes, among others. Several such reactors can be placed in series if high conversions are required.
- o Some slurry reactors incorporate special internals such as porous plate distributors or internal draft tubes to promote circulation. The jet-bubbling reactor, used by Chiyoda/Bechtel for SO_2 scrubbing, employs a draft tube.
- o Several schemes are used for heat removal where the process is highly exothermic. Most reactors use internal coils or solvent evaporation but circulation through an external heat exchanger has sometimes been used where heat removal surface requirements are high compared to reactor volume. Air Products has looked at external circulation loops for their liquid phase methanol process, both with ebullated-bed and entrained-bed designs (Figure 2.3). These designs require a slurry pump and internal cooling coils are preferred as long as there is adequate space in the reactor..
- o A circulating design without a slurry pump has been used for xylene oxidation (Figure 2.4). The design achieves rapid circulation by virtue of differences in density between the contactor and the heat exchanger. It has not yet been applied to slurry systems but might be worthy of consideration in future development work.

The rapid internal circulation of the liquid phase in large scale slurry bubble columns has both advantages and disadvantages. From a reaction standpoint, it limits the conversion which can be achieved in a given size reactor. From a heat removal standpoint, however, it has the advantage that temperatures within the vessel are quite uniform and heat transfer coefficients are good. It is possible to use a reactor-to-coolant temperature difference of 50 °F with an overall heat flux of 6000 Btu/(hr·ft^2·°F) or more. Air Products has stated that the volume occupied by the heat exchanger in the La Porte slurry methanol reactor is only 3.5% of the total reactor volume. It would appear both feasible and prudent, however, to design with at least double this heat exchange volume.The heat release per unit of synthesis gas reacted for Fischer-Tropsch is roughly 1.6 times that for methanol synthesis but space time yields (STY) are lower, making the use of internal coils still feasible.

While the bubble column with internal heat exchange has been chosen for this study, the use of an external heat exchange loop may be worthy of further consideration as more active catalysts are developed and other design criteria are pushed to the limit.

Figure 2.1

SLURRY REACTOR DESIGN
BUBBLE COLUMN REACTOR
FOR METHANOL
(AIR PRODUCTS)

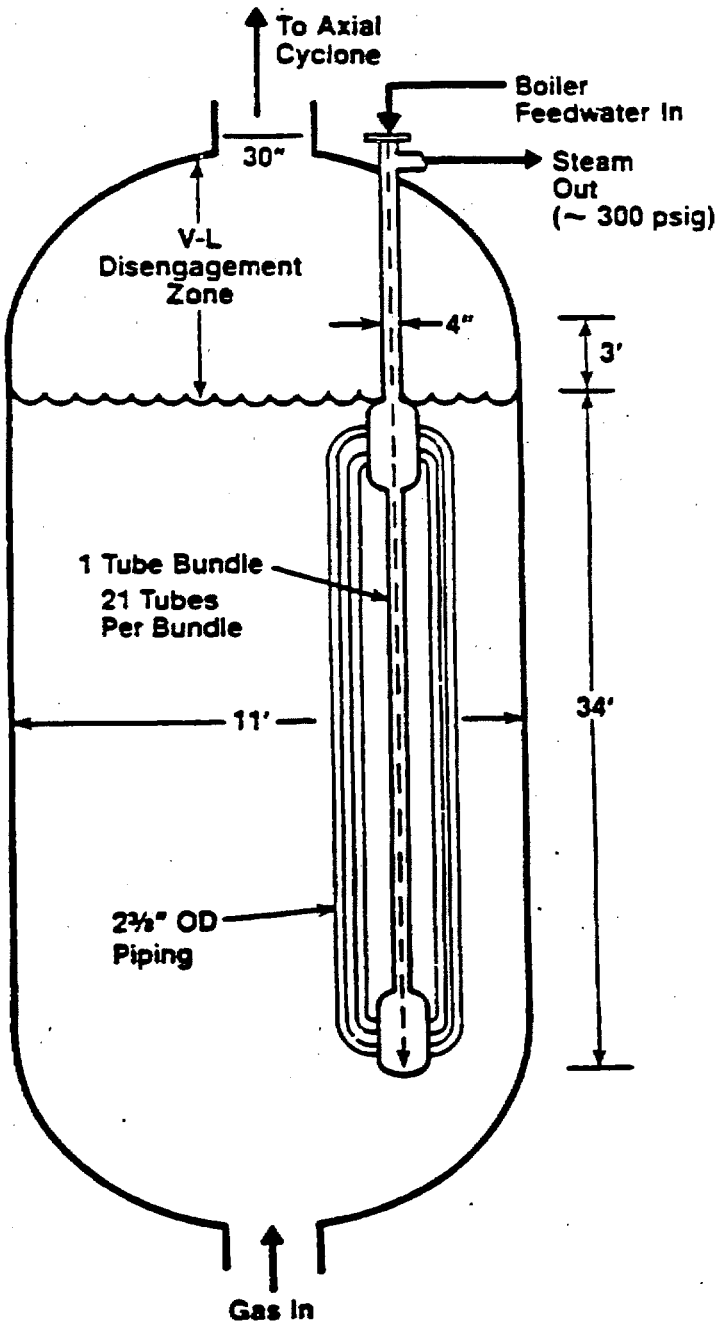


Figure 2.2

SLURRY REACTOR DESIGN
PIPELINE LOOP REACTOR
FOR POLYETHYLENE

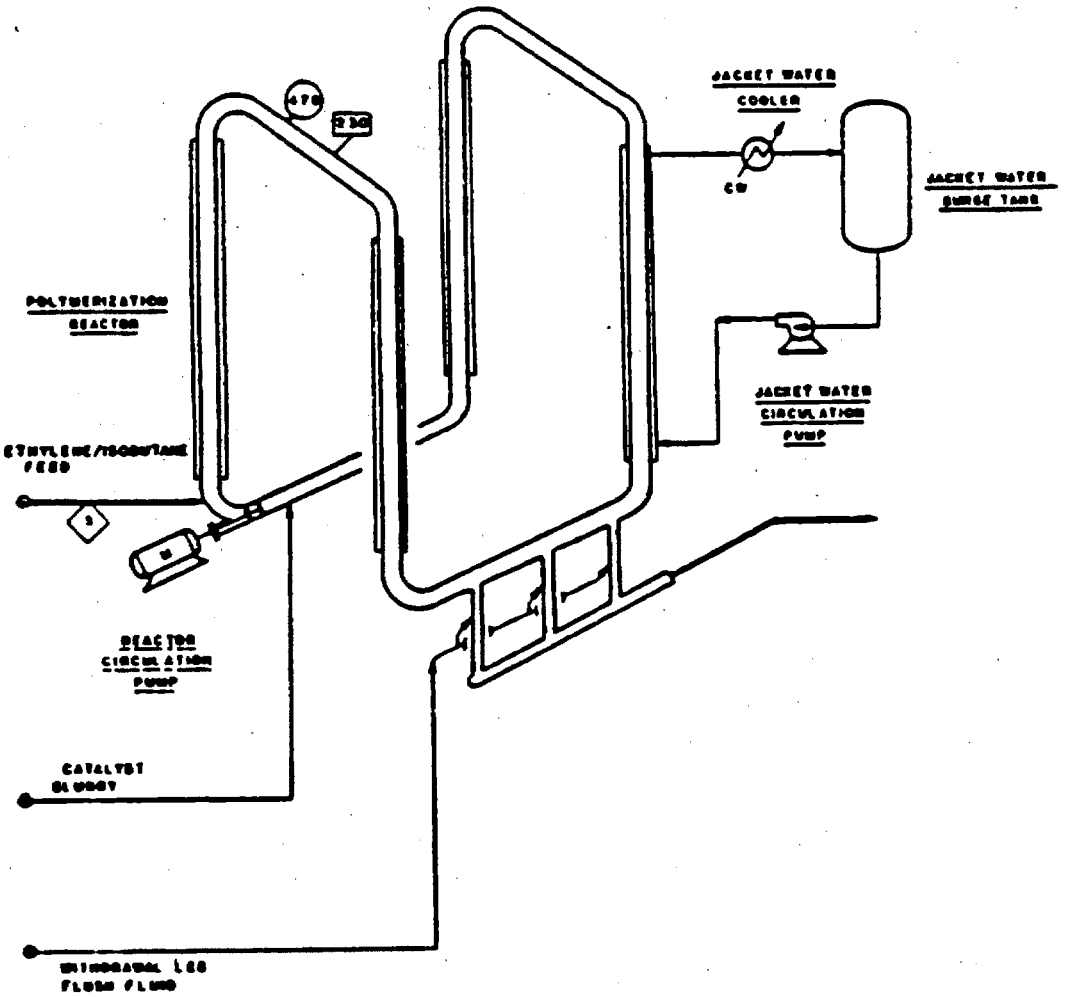


Figure 2.3

SLURRY REACTOR DESIGN
CIRCULATING LOOP LAYOUT
(CHEM SYSTEMS)

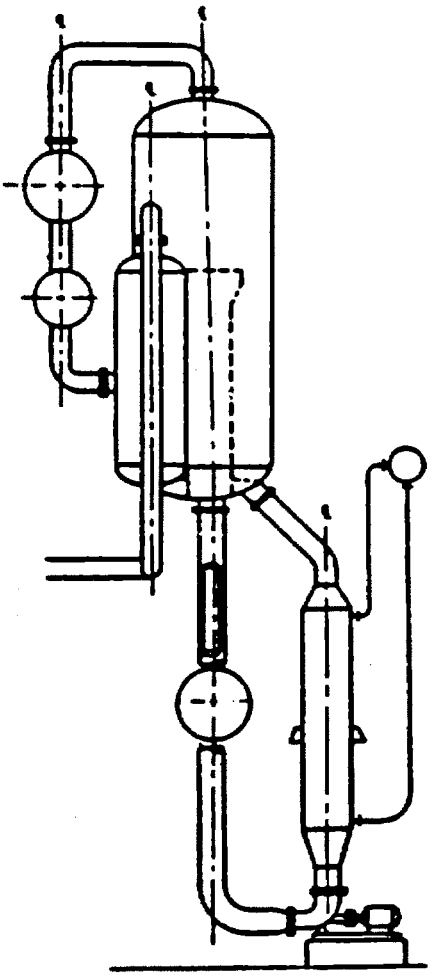
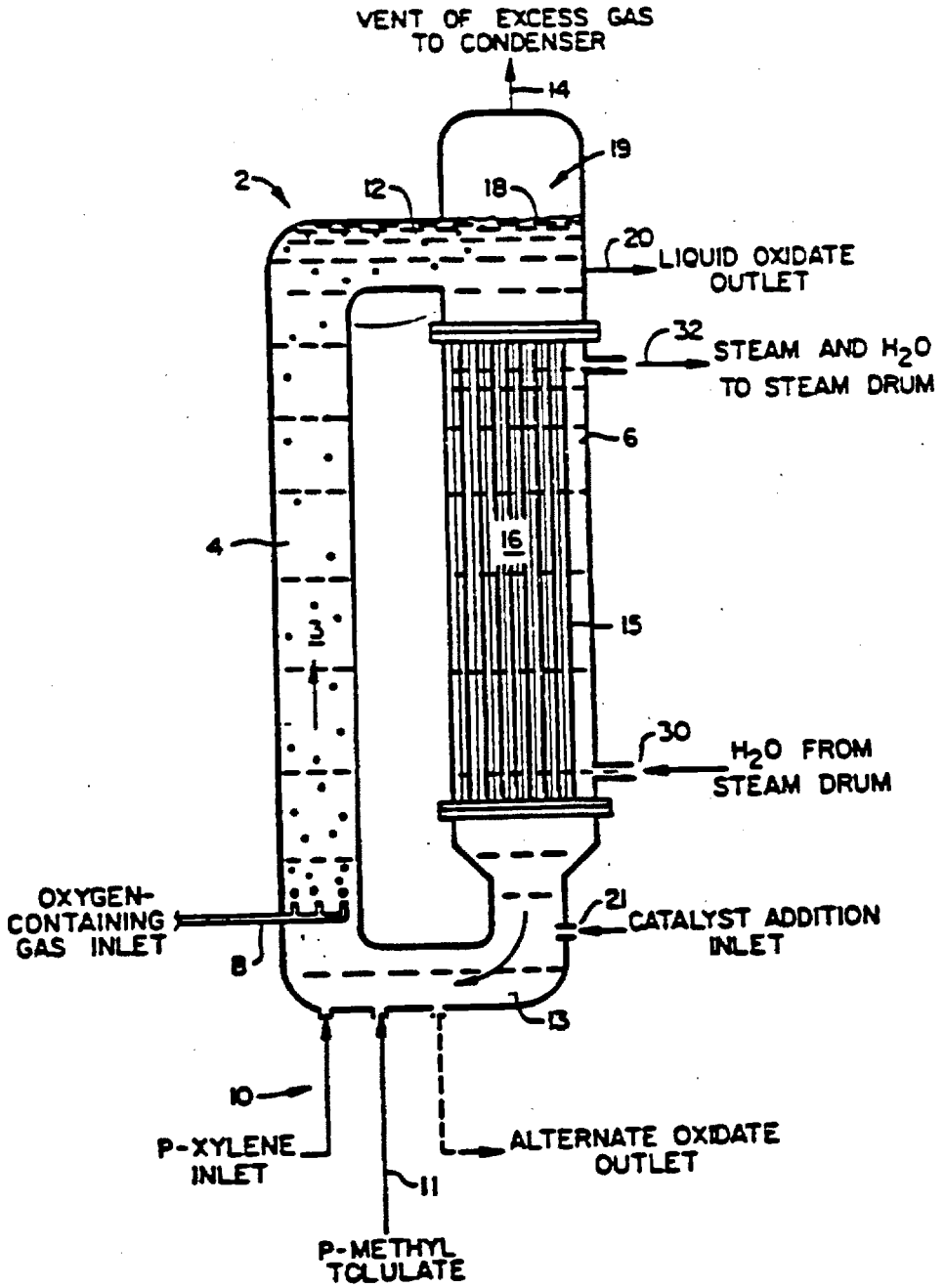


Figure 2.4

SLURRY REACTOR DESIGN
CIRCULATING LOOP REACTOR
WITHOUT PUMP
US PATENT 4,342,876



2.3 Synopsis of Consultants' Review

Both consultants devoted their primary effort to slurry reactor design principles. Attention was also directed at differences between the slurry reactor and the fixed-bed reactor. Dr. Akgerman's comments provide guidance on specific design aspects so they are covered first and in more detail. Dr. Smith's comments are in the nature of a review of the literature on reactor modelling for the two reactions of interest and are standalone documents.

2.3.1 Carbon Formation in Fischer-Tropsch Reactors

Dr. Akgerman has shown that the slurry reactor has a significant advantage over the fixed-bed reactor in terms of carbon forming tendency because the H_2/CO ratio the catalyst actually sees can be modified in the slurry reactor to higher H_2/CO ratio by a combination of gas solubility and diffusion rate differences. He shows that if reaction rate controls, the effective H_2/CO ratio the catalyst sees is controlled by solubility differences. The data are conflicting but the concensus shows basically no difference from the gas phase. If mass transfer controls, then differences in diffusion are important and here he concludes that the H_2/CO ratio the catalyst sees may be 2 to 3 times that in the gas phase. Dry (at SASOL) has found carbon formation to be related to $p_{CO}/p_{H_2}{}^2$, so that the actual effect on carbon formation is 4 to 9 times.

Akgerman attributes carbon formation to the Boudouard reaction:

$$2CO \leftrightarrow CO_2 + C\downarrow$$

which is associated with catalyst particle swelling and eventually, in a fixed-bed reactor, leads to bed plugging and hot spots. While the methanol catalyst does not show this tendency, typical promoted iron catalysts used for fixed-bed Fischer-Tropsch synthesis must be run at low temperature and high H_2/CO ratio to minimize plugging problems while producing high yields of waxy distillate.

2.3.2 Design of Slurry Reactors

This section of Akgerman's review consists of a series of reports delineating what may be considered to be the more significant variables to be considered in slurry reactor modelling and what correlations are available for prediction. Assumptions are:

Plug flow in gas phase - assuming high gas velocities
Axial dispersion in the liquid phase (or fully mixed in large reactors)
Isothermal - due to high degree of liquid mixing
Non-uniform catalyst distribution - sedimentation model
Hydrostatic head effects (pressure drop) can be neglected
Stoichiometry can be modelled by a contraction factor
k_La and gas holdup are uniform over reactor length
Liquid flow can be neglected

2.3.2.1 *Suspension of the Solids*

It is shown that the critical solids loading (i.e. the maximum that can be held in complete suspension) is about 65% for methanol and Fischer-Tropsch syntheses. A concentration of 35 to 45%, as proposed by Air Products for slurry methanol, should be no problem.

2.3.2.2 *Internal Catalyst Diffusion Effect*

It is shown that internal diffusional resistance can be neglected for Fischer-Tropsch and methanol synthesis reactions in a slurry reactor where the particle diameter is 50 μm or less.

2.3.2.3 *Analysis of Resistances*

A simple model is developed for F-T and methanol synthesis which assumes plug flow in the gas phase and a perfectly mixed liquid phase. The effects of various parameters are then examined. It is shown that an overall rate constant for either reaction can be developed which can be analyzed as a series of resistances. Of these only k_La and the kinetic resistance are shown to be important and these are of comparable magnitude over the range of conditions normally used in the Fischer-Tropsch reaction (at low gas velocity or high temperature, mass transfer will become more predominant). Liquid-solid mass transfer and diffusion into the solid may be neglected.

2.3.2.4 *Effect of Stoichiometry*

The equations of Deckwer are given showing how stoichiometry can be handled in terms of an overall contraction factor, the inlet H_2/CO ratio and the H_2/CO usage ratio. (Most models use a mean gas velocity in the estimation of gas holdup and k_La. This can be calculated from the contraction factor and the estimated conversion and the calculation iterated until converged).

2.3.2.5 *Solids Dispersion*

It is shown that catalyst distribution over the reactor volume can be important and can be accounted for by adding a catalyst concentration term into the kinetic rate constant. Gas superficial velocity, reactor diameter and particle settling velocity are the key variables in the analysis, which uses a sedimentation model.

2.3.2.6 *Transport Parameters*

The Shah and Deckwer model is cited for the liquid axial dispersion coefficient. Numerous correlations are available for the liquid phase mass transfer coefficient but the Akita-Yoshida correlation is recommended as giving good results where the gas is distributed via single or multiple orifice spargers which is probably the most reasonable design for a large, high superficial velocity, commercial reactor.

2.3.4 Effect of Solids on Mass Transfer

Consideration needs to be given to the effect of solids on k_La. Starting with the Akita-Yoshida correlation, a correlation by Zheng on the effect of solids on gas holdup and the data of Joosten and of Sada on k_La and viscosity, a relationship is given showing the effect of volume fraction solids in lowering the mass transfer coefficient.

2.3.5 Model Solutions for Slurry Reactors

Model solutions are summarized for two slurry reactor models which incorporate simplifying assumptions. Model 1 is for non-backmixed gas and liquid phases (plug flow), a situation which may be approached in a high L/D laboratory reactor. Model 2 is for

liquid phase perfectly backmixed, gas phase plug flow. This should more closely represent a large diameter, commercial reactor. Other assumptions are:

Only gas/liquid mass transfer and the reaction resistance terms are important; liquid/solid mass transfer and intraparticle diffusion are negligible.
Reaction rate is first order in hydrogen concentration (known to be a good assumption up to 60% conversion and used in many models at higher conversions than this).
Constant usage ratio of CO and H_2; may be different than the input ratio.
Contraction factor is uniform with conversion
Liquid phase batch (liquid flow is negligible compared to other effects)
Catalyst is uniformly dispersed
A mean gas velocity can be used to estimate gas holdup and $k_L a$.

This analysis follows articles by Bukur and others. It has been used by Bechtel (Appendix D) to show graphically the effects of variables, leading to a better understanding of design conditions for a commercial Fischer-Tropsch slurry reactor. A third model, for a continuous stirred tank reactor (CSTR), has been added by Bechtel following the same assumptions. The development of this model is given in Appendix C.

2.3.6 Effectiveness Factors in Fixed-Bed Fischer-Tropsch

It is shown that for 1/16" to 1/8" diameter particles and first order rate constants typical of Fischer-Tropsch synthesis (0.01 to 0.4 sec^{-1}), catalyst effectiveness factors will vary from 1.0 to 0.62 for hydrogen diffusion, from 1.0 to 0.42 for CO diffusion. The intraparticle diffusion effect will not be large but should be taken into account. (An article by Post et.al., AIChEJ, 35, 1107 (1989) confirms this experimentally.)

2.3.7 Literature Summary for Design of F-T Bubble Column Reactors - J. M. Smith.

This summary concentrates on the models of Deckwer, Kuo and Stern, all of which include the axial mixing effect which is considered to be necessary for successful scale-up. All three models neglect or minimize solid/liquid mass transfer and intraparticle diffusion. Deckwer and Stern include heat transfer, but temperature variations shown are minor. Catalyst concentration changes with reactor length are included but for small particles are found to be negligible.The Stern model (and Kuo's multicomponent model) develop the reaction stoichiometry and consider the water gas shift reaction to have a finite rate.They can, therefore, be used to make predictions outside the range of applicability of Deckwer's assumptions mentioned in 2.3.2.4. The effects of these differences, of different methods for estimating gas holdup and kinetics and other limitations common to all the models are discussed.

2.3.8 Literature Summary on Methanol Production from Synthesis Gas

A brief review of methanol production, kinetic models and reactor design principles for both fixed-bed and slurry reactors is provided. Three comparisons of fixed-bed and slurry reactors for methanol synthesis are reviewed and the underlying principles are analyzed. In general, these comparisons are not indicating a great size and economic difference between reactor types for conventional methanol synthesis.

2.4 Results of Model Simulations

2.4.1 Axial Dispersion and Stoichiometry

Three simple Fischer-Tropsch models (Model 1 - plug flow of both gas and liquid, Model 2 - plug flow of gas, completely backmixed liquid and Model 3 - completely backmixed, both phases) have been used to generate values of conversion, space velocity (SV) and space time yield (STY) as determined by inlet gas superficial velocity, slurry concentration and reactor dimensions. Model 1 should approach the results from a high L/D pilot plant reactor, Model 2 should approach that of a large diameter, commercial reactor while Model 3 is representative of both lab scale and commercial mechanically-agitated reactors. The assumptions involved in the use of these models have been described in Section 2. Stoichiometry is handled by use of the inlet gas CO/H_2 ratio, I, the CO/H_2 consumption ratio, U, (assumed constant with conversion) and the contraction factor, α. The models are written in terms of hydrogen conversion but, with known values of U and I, the CO and synthesis gas conversions can readily be derived. Derivations of the three models are given in the Appendices.

The relationship between these models is developed in Appendix D, which reproduces a technical paper developed for the AIChE Fischer-Tropsch Symposium in Orlando (March, 1990). In Models 1 and 3, an overall rate constant is derived from the expression[1]:

$$1/K_A = 1/k_L a + 1/k_r \epsilon_L$$

This is the familiar summation of resistances. Other resistances, such as that at the liquid-solid interface could be added, but it is shown in Appendix A that these can be neglected with little loss in accuracy. Model 2 is somewhat more complicated but, as shown in Appendix D, reduces to either to Model 1 or Model 3 in the extreme as either surface reaction or mass transfer dominate. When $\alpha = 0$, Model 1 reduces to the familiar first order relationship that the log of one minus conversion is proportional to 1/SV.

From the difference between Models 1 and 2 at high conversion, it is apparent that the degree of internal mixing is an important variable. As described in Appendices A and B, mixing effects can be modelled by use of axial dispersion coefficients. This leads to boundary limit problems solvable by orthogonal collocation techniques. Models 1 and 2 are simpler to use and understand and lead to direct analytical solutions at the extreme conditions where D_L, the axial liquid dispersion coefficient, is zero and infinity, respectively.

The approach used in this study is to use the time available to develop best estimates of reaction kinetics, mass transfer and gas holdup and explore the effects of superficial velocity, slurry concentration and pressure on conversion and space time yield (STY).using the limiting models. For scaleup purposes several benchmarks are available in the form of reported pilot plant and demonstration unit results from Mobil, Rheinprussen and (for methanol) Air Products. Deckwer (1982)[2] gives the following expression for estimation of the axial dispersion coefficient for the liquid phase:

$$D_L = 3.676 \cdot u_G^{0.32} \cdot d_R^{1.34} \quad (cm^2/s)$$

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1 A table of nomenclature follows Section 6.

2 For reference citations see Appendices A and B.

where u_G is the superficial gas velocity, cm/s and d_R is the reactor diameter, cm

Pilot plant conditions result in values of D_L on the order of 40 to 50, the Rheinprussen demonstration reactor, on the order of 4700 and proposed commercial designs, on the order of 31000 cm/s. Clearly, if the conversions in these units fall in the proper range between Models 1 and 2, then the use of Model 2 should be reasonable for the commercial design.

In Appendix D, it is shown that Model 2 leads to a rapid fall-off in STY (Nm^3 syngas converted per hour per m^3 of reactor volume) at very high conversion levels, say above 90%. Some recycle of unconverted reactants will be required to maximize ultimate conversion and minimize unwanted byproduct gas production. Since external recycle gas requirements are only 12% higher at 80% than 90% conversion per pass, whereas STY is some 30% larger, 80% conversion per pass has been selected as the design level for this study.

2.4.2 Mass Transfer and Gas Holdup

Any slurry reactor model, no matter how complex, is no better than the methods used to predict gas holdup and mass transfer. Accurate prediction of gas holdup is very difficult but is essential since it (1) determines (along with slurry concentration) the amount of catalyst in a given reactor volume and (2) is required in most expressions for predicting the gas holdup. Most of the previous F-T reactor modelling efforts used a simple expression in terms of superficial gas velocity:

$$\varepsilon_G = 0.053 \cdot u_G^{1.1}$$

This expression was originally recommended by Deckwer and others for superficial velocities below 4 cm/s, at which velocity it gives a gas holdup of 0.24. At higher gas velocities than this it will predict too high and at 14.5 cm/s gives a gas holdup of 1.0. At this point the models indicate that the conversion drops to zero because the reactor contains no catalyst. This has led some writers to recommend a limit on superficial velocity at about 9 cm/s.

Fortunately, Bukur has recently been looking at the hydrodynamics of F-T slurry reactors for the DOE. His most recent expression for fractional gas holdup[3] is as follows:

$$\varepsilon_G = 0.24 \cdot (Fr_G)^{0.28} \cdot (Bo)^{0.14}$$

where

$$Fr_G = u_G^2/(g \cdot d_R) \quad \text{and} \quad Bo = d_R^2 \cdot \rho_L \cdot g/\sigma_L$$

with u_G = gas superficial velocity, d_R = column diameter, ρ_L = liquid density, σ_L = surface tension and g = gravitational acceleration in consistent units.

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[3] Personal communication from A. Akgerman dated 1/29/90.

The correlation is good for non-foaming wax, which is probably what will exist in a commercial scale reactor. Typically, density of the liquid wax is about 0.67 g/cm^3 and surface tension is about 0.014 to 0.017 N/m. At 15 cm/s superficial velocity the correlation predicts a gas holdup of 27% which is verified experimentally.

Akgerman has recommended (1) use of the Bukur expression for gas holdup, (2) the Akita-Yokida (1973) correlation for k_La using liquid (not slurry) properties and (3) use of a correction to k_La for slurry concentration which he has derived in Appendix A. He also recommends use of his own data for hydrogen diffusivity in F-T wax and n-octacosane obtained under DOE contract DE-AC22-84PC70032. Over the temperature range of interest for F-T synthesis, this has been fit to the equation:

$$D_H = 0.00000016 \cdot T/\mu^{0.5} \quad , m^2/s$$

where T is temperature in °K and μ is liquid viscosity in poise. The diffusivity of CO in the same media is 1/3 that of hydrogen. In the Akita-Yoshida correlation, k_La is directly proportional to diffusivity and is proportional to $e_G^{1.1}$.

2.4.3 Benchmark Simulations

As discussed in Section 2.4.1, the design approach employed in this study is to use the simplified models to check benchmark pilot plant and demonstration unit results looking for reported conversions to be bracketed between Models 1 and 2. Use of Model 2 for the commercial slurry reactor design should then provide a reasonable, possibly somewhat conservative, design basis. In following this approach, it was found that the kinetic expression used in Deckwer's reactor model had to be modified to fit the reported data. Since the literature indicates that an activation energy of 130,000 kJ/kgmole is typical of the reaction in the absence of mass transfer resistance, the following expression was developed:

$$k'_H = k_H / (kgCat/m^3) = 3.3 \cdot 10^9 \cdot e^{(-130000/RT)}$$

where the units are $(s \cdot kgCat/m^3)^{-1}$. Division by the catalyst loading in kgCat/m^3 of unexpanded slurry is in basic agreement with space velocity expressed per kg of catalyst, the most common way of reporting data. The preexponential term was chosen to check reported conversions for the Rheinprussen laboratory unit using Model 1.

The resulting simulations are shown in Tables 2.1, 2.2 and 2.3 showing results for the Rheinprussen demonstration unit, the Rheinprussen laboratory unit and the Mobil pilot plant, respectively. The results are summarized below:

	H_2 + CO Conversion		
	Model 1	Model 2	Reported
Rheinprussen Laboratory Unit	88.0	76.6	88
Rheinprussen Demonstration Unit	93.6	78.6	89
Mobil Pilot Plant	100	83.6	88

In each case the catalyst concentration was adjusted to match the reported holdup of catalyst (or Fe) in the reactor. For the Rheinprussen demonstration plant at 0.095 m/s superficial velocity, Bukur's prediction method was used for gas holdup since Deckwer's equation predicts a gas holdup of 50%, which is too high. For the other two cases, Deckwer's

equation was used since it seems to better fit reported gas holdup values for these small diameter reactors.

As expected, the Rheinprussen demonstration unit conversion falls between Models 1 and 2. The Mobil pilot plant predictions are too high indicating, perhaps, that the Mobil catalyst did not have quite the same level of activity.

2.4.4 Pressure Effect

The kinetic rate expression used in all these models is first order in hydrogen concentration, implying that if pressure is doubled the rate is doubled. In other words, if reaction rate controls and if GHSV is expressed in terms of flow at standard conditions (i.e. $Nm^3/(h \cdot kgCat)$, then it should be possible to double GHSV and obtain the same conversion level as pressure is doubled. No literature data were found to support this interpretation although in their slurry reactor modelling study, Deckwer, et al (1982) imply that it is correct.

Singleton and Regier have published data on Gulf-Badger fixed-bed F-T processing, using promoted cobalt catalyst,which indicate that the pressure effect is not linear but flattens out at pressure levels above 200 psia (Hydrocarbon Processing, p71, May 1983). This implies that the surface monolayer becomes filled at some pressure level and further increases have less impact on conversion. While this effect could be peculiar to the Gulf-Badger catalyst, it seems prudent to assume that a similar effect exists with precipitated iron catalyst and that the slurry reactor is no different in this respect than the fixed-bed reactor. For this reason it has been decided to make the arbitrary assumption that rate is not linear with pressure but decreases with pressure to the 0.5 power. The effect on the Models is shown in Tables 2.4 and 2.5 and is summarized as follows:

	H_2 +CO Conversion		
	Model 1	Model 2	Reported
Rheinprussen Demonstration Unit	92.6	77.6	89
Mobil Pilot Plant	96.1	79.8	88

The Rheinprussen laboratory unit is used as the base point, so it does not change. There is a significant improvement in the Mobil pilot plant prediction, since this was run at a higher pressure level.

2.4.5 Effect of Mass Transfer

In Tables 2.1 through 2.5, the fraction of the total resistance provided by mass transfer is shown on line 60. The variation is between 12 and 25%. Low superficial velocity and high temperature tend to increase the percentage. It should be remembered, however, that these percentages are based on hydrogen conversion rate. Since CO is consumed at 1.6 to 1.7 times the rate of H_2 and its mass transfer coefficient is expected to be 0.5 to 0.7 times that of H_2, its fractional mass transfer resistance can be as much as twice that of hydrogen. this is reflected in a lower H_2/CO ratio in the liquid phase as discussed in Appendix A.

Table 2.1

	A	B	C	D	E
1	CASE		RHEINPRUSSEN LABORATORY UNIT		4/17/90
2	uGo - cm/s		3.5		
3	alpha		-0.5		
4	I		1.5		
5	U		1.588		
6	alpha*		-0.5176		
7	T - oC		266		
8	Wt.% Slurry		15		
9	Vol.% Solids		3.652097413		
10	dR - cm		4.7		
11	L - cm		345.8		
12	dp - micron		26		
13	rhoS - g/cm^3		3.1		
14	muL - poise		0.022322897		
15	rhoL - g/cm3		0.66587		
16	sigmaL - dyne/cm		16.5		
17	DA - cm2/s		0.00057721		
18	muSlurry - poise		0.024537552		
19	rhoSlurry - g/cm^3		0.754766799		
20	kLa Correction Factor		0.814139428		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Deckwer's Model	0.160004024	0.16639018	0.170103106	
23	kLa - s^-1 (uncorr) for H	0.310706921	0.324375011	0.332345955	
24	kLa - s^-1 (corr) for H	0.252958755	0.264086486	0.270575946	
25	kH - (s*kgCat/m3)^-1		0.000831233	3.3e-9*exp(-130/RT)	
26	kH- s^-1		0.094108054		
27	kH*epsilonL - s^-1	0.079050386	0.078449398	0.078099882	
28	He - (kPa cm^3)/mol		19699754.02		
29	RTU/(uGo*He) - s^-1		22.47475295		
30	kA - s^-1	0.060228725		0.060606353	
31	Stanton No. - target	1.353625718		1.362112813	
32	H2 Conversion	0.849596977		0.677117348	
33	Stanton No - result	1.353627693		1.362117185	
34	Average uG - cm/s	2.730435058		2.686667106	
35	Stanton No. - reaction		1.763130833		
36	StantonM - target		5.935278532		
37	H2 Conversion		0.740418247		
38	n		0.419945153		
39	Y		0.741154967		
40	StantonM - result		5.934721427		
41	Average uG - cm/s		2.629329152		
42	Pressure - kPa		1100		
43	Reactor Xsect - m^2		0.001734945		
44	Reactor Vol. - m^3		0.005999438		
45	Feed Rate - m^3/h		0.218603012		
46	Feed Rate - Nm^3/h		1.201708011		
47	SV - Nm^3/(m^3 h)		200.3034228		
48	H2+CO Conversion	0.879502791	0.766480969	0.700951878	
49	CO Conversion	0.89944	0.783856117	0.716841565	
50	STY - Nm^3/(h*m^3)	176.1674192	153.5287614	140.4030603	
51	STY - Nm^3/(kgCat h))	1.852440809	1.626757724	1.494336443	
52	GHSV - Nm^3/(kgCat h)	2.106236419	2.122371969	2.131867378	
53	Catalyst - kg	0.570547542	0.566209895	0.563687978	
54	Catalyst Loading kg/m^3	95.10016102	94.3771523	93.95679331	
55	Reaction Enthalpy - kJ/gmol -CH2-	194.0133333	194.0133333	194.0133333	
56	kgmol/h of H2+CO Conv (=3* -CH2-)	0.047153812	0.041094241	0.037580953	
57	Heat Release - kW	0.847080399	0.738225065	0.675111669	
58	Heat Release - kW/m^3	141.1932882	123.0490317	112.5291474	
59	Heat Release - Btu/(h ft^3)	13851.48341	11897.17911	10880.0484	
60	Mass Transfer Resistance - %	23.8097018	22.90253414	22.39901737	
61	DL - cm2/s	40.32559878	40.78733634	41.05003932	

Table 2.2

	A	B	C	D	E
1	CASE		RHEINPRUSSEN DEMONSTRATION UNIT		4/17/90
2	uGo - cm/s		9.5		
3	alpha		-0.5		
4	I		1.5		
5	U		1.577		
6	alpha'		-0.5154		
7	T - oC		268		
8	Wt.% Slurry		18		
9	Vol.% Solids		4.495575838		
10	dR - cm		129		
11	L - cm		770		
12	dp - micron		26		
13	rhoS - g/cm^3		3.1		
14	muL - poise		0.021828409		
15	rhoL - g/cm3		0.66476		
16	sigmaL - dyne/cm		16.5		
17	DA - cm2/s		0.000585877		
18	muSlurry - poise		0.025154495		
19	rhoSlurry - g/cm^3		0.774238061		
20	kLa Correction Factor		0.812175666		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Bukur's Model	0.181155844	0.186080074	0.187454703	
23	kLa - s^-1 (uncorr) for H	0.631067377	0.649962057	0.655245612	
24	kLa - s^-1 (corr) for H	0.512537567	0.527883367	0.532174541	
25	kH - (s*kgCat/m3)^-1		0.000925334	3.3e^9*exp(-130/RT)	
26	kH - s^-1		0.128957233	No pressure correction	
27	kH*epsilonL - s^-1	0.105595876	0.104960861	0.104783593	
28	He - (kPa cm^3)/mol		19621139.04		
29	RTL/(uGo*He) - s^-1		18.58019167		
30	kA - s^-1	0.087556909		0.087546037	
31	Stanton No. - target	1.626824149		1.626622151	
32	H2 Conversion	0.908446219		0.721400261	
33	Stanton No. - result	1.626820392		1.626622866	
34	Average uG - cm/s	7.275982492		7.733903951	
35	Stanton No. - reaction		1.95019292		
36	StantonM - target		9.80817413		
37	H2 Conversion		0.762648762		
38	n		0.39106324		
39	Y		0.762652396		
40	StantonM - result		9.807199463		
41	Average uG - cm/s		7.632921432		
42	Pressure - kPa		1200		
43	Reactor Xsect - m^2		1.306981084		
44	Reactor Vol. - m^3		10.06375434		
45	Feed Rate - m^3/h		446.9875306		
46	Feed Rate - Nm^3/h		2670.658039		
47	SV - Nm^3/(m^3 h)		265.3739298		
48	H2+CO Conversion	0.936428424	0.786138344	0.743619389	
49	CO Conversion	0.955081895	0.801798065	0.758432141	
50	STY - Nm^3/(h*m^3)	248.503691	208.6206218	197.3371996	
51	STY - Nm^3/(kgCat h))	2.17783239	1.839198198	1.742666801	
52	GHSV - Nm^3/(kgCat h)	2.325465923	2.339535034	2.343492957	
53	Catalyst - kg	1148.439981	1141.533681	1139.605746	
54	Catalyst Loading kg/m^3	114.1164561	113.4302013	113.2386291	
55	Reaction Enthalpy - kJ/gmol -CH2-	193.72	193.72	193.72	
56	kgmol/h of H2+CO Conv (=3* -CH2-)	111.5766978	93.8694338	88.60324348	
57	Heat Release - kW	2001.355357	1680.152103	1589.27966	
58	Heat Release - kW/m^3	198.867668	166.9506263	157.9211501	
59	Heat Release - Btu/(h ft^3)	19227.817	16141.88958	15268.84187	
60	Mass Transfer Resistance - %	17.08302268	16.58557614	16.45062482	
61	DL - cm2/s	4670.582428	4742.712163	4762.701051	

Table 2.3

	A	B	C	D	E
1	CASE	MOBIL PILOT PLANT - RUN CT256-11			4/17/90
2	uGo - cm/s		5.3		
3	alpha		-0.55		
4	I		1.5		
5	U		1.7		
6	alpha*		-0.594		
7	T - oC		257		
8	Wt % Slurry		19.4		
9	Vol % Solids		4.950943164		
10	dR - cm		5.1		
11	L - cm		762		
12	dp - micron		26		
13	rhoS - g/cm^3		3.1		
14	muL - poise		0.02474214		
15	rhoL - g/cm3		0.670865		
16	sigmaL - dyne/cm		16.5		
17	DA - cm2/s		0.00053911		
18	muSlurry - poise		0.029347783		
19	rhoSlurry - g/cm^3		0.791130093		
20	kLa Correction Factor		0.809412862		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Deckwer's Model	0.232678909	0.249020396	0.252383284	
23	kLa - s^-1 (uncorr) for H	0.456542511	0.491934082	0.499246637	
24	kLa - s^-1 (corr) for H	0.369531381	0.398177773	0.40409865	
25	kH - (s*kgCat/m3)^-1		0.000507903	3.3e*8*exp(-130/RT)	
26	kH- s^-1		0.077952607	No pressure correction	
27	kH*epsilonL - s^-1	0.059814679	0.058540818	0.058278672	
28	He - (kPa cm^3)/mol		20064929.63		
29	RTL/(uGo*He) - s^-1		31.57383613		
30	kA - s^-1	0.051481551		0.050933116	
31	Stanton No. - target	1.625470047		1.608153867	
32	H2 Conversion	0.928959846		0.741965294	
33	Stanton No. - result	1.625473217		1.608159138	
34	Average uG - cm/s	3.837724306		4.132072431	
35	Stanton No. - reaction		1.848358185		
36	StantonM - target		12.57199977		
37	H2 Conversion		0.773782283		
38	n		0.418632216		
39	Y		0.77378233		
40	StantonM - result		12.57078078		
41	Average uG - cm/s		4.081989308		
42	Pressure - kPa		1480		
43	Reactor Xsect - m^2		0.002042821		
44	Reactor Vol. - m^3		0.015566293		
45	Feed Rate - m^3/h		0.389770175		
46	Feed Rate - Nm^3/h		2.931793271		
47	SV - Nm^3/(m^3 h)		188.3424167		
48	H2+CO Conversion	1.003276634	0.835684866	0.801322517	
49	CO Conversion	1.052821159	0.876953254	0.840894	
50	STY - Nm^3/(h*m^3)	188.959546	157.3949072	150.9230195	
51	STY - Nm^3/(kgCat h))	1.604508685	1.365566642	1.315306142	
52	GHSV - Nm^3/(kgCat h)	1.599268447	1.634068891	1.64141917	
53	Catalyst - kg	1.833208975	1.794167485	1.786133198	
54	Catalyst Loading kg/m^3	117.7678564	115.2597775	114.7436439	
55	Reaction Enthalpy - kJ/gmol -CH2-	197	197	197	
56	kgmol/h of H2+CO Conv (=3* -CH2-)	0.131230467	0.109309149	0.104814489	
57	Heat Release - kW	2.393740924	1.993879848	1.911893926	
58	Heat Release - kW/m^3	153.7771968	128.0895733	122.8226854	
59	Heat Release - Btu/(h ft^3)	14866.17756	12384.53139	11875.29448	
60	Mass Transfer Resistance - %	13.93157752	12.81769975	12.60419168	
61	DL - cm2/s	50.16757931	51.16801093	51.36867309	

Table 2.4

	A	B	C	D	E
1	CASE		RHEINPRUSSEN DEMONSTRATION UNIT		4/17/90
2	uGo - cm/s		9.5		
3	alpha		-0.5		
4	I		1.5		
5	U		1.577		
6	alpha'		-0.5154		
7	T - oC		268		
8	Wt.% Slurry		18		
9	Vol % Solids		4.495575838		
10	dR - cm		129		
11	L - cm		770		
12	dp - micron		26		
13	rhoS - g/cm^3		3.1		
14	muL - poise		0.021828409		
15	rhoL - g/cm3		0.66476		
16	sigmaL - dyne/cm		16.5		
17	DA - cm2/s		0.000585377		
18	muSlurry - poise		0.025154495		
19	rhoSlurry - g/cm^3		0.774238061		
20	kLa Correction Factor		0.812175666		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Bukur's Model	0.181512866	0.186398504	0.187749682	
23	kLa - s^-1 (uncorr) for H	0.63243559	0.651185634	0.656379908	
24	kLa - s^-1 (corr) for H	0.513648797	0.528877126	0.533095789	
25	kH - (s*kgCat/m3)^-1		0.000925334	3.3e^9*exp(-130/RT)	
26	kH- s^-1		0.12346715	With pressure correction	
27	kH*epsilonL - s^-1	0.101056274	0.100453058	0.100286232	
28	He - (kPa cm^3)/mol		19621139.04		
29	RTL/(uGo*He) - s^-1		18.56019167		
30	kA - s^-1	0.084442826		0.084407461	
31	Stanton No - target	1.568963899		1.568306797	
32	H2 Conversion	0.89798069		0.712517738	
33	Stanton No - result	1.568953898		1.568300853	
34	Average uG - cm/s	7.301608574		7.755649699	
35	Stanton No - reaction		1.866437076		
36	StantonM - target		9.828638367		
37	H2 Conversion		0.753114877		
38	n		0.403504027		
39	Y		0.753119127		
40	StantonM - result		9.825671377		
41	Average uG - cm/s		7.656261815		
42	Pressure - kPa		1200		
43	Reactor Xsect - m^2		1.306981084		
44	Reactor Vol. - m^3		10.06375434		
45	Feed Rate - m^3/h		446.9875306		
46	Feed Rate - Nm^3/h		2670.658039		
47	SV - Nm^3/(m^3 h)		265.3739298		
48	H2+CO Conversion	0.925638495	0.776310815	0.734483285	
49	CO Conversion	0.944077032	0.791774774	0.749093649	
50	STY - Nm^3/(h*m^3)	245.6403251	206.0126517	194.9074082	
51	STY - Nm^3/(kgCat h))	2.15347971	1.81691718	1.721834615	
52	GHSV - Nm^3/(kgCat h)	2.326480285	2.340450687	2.344344027	
53	Catalyst - kg	1147.939253	1141.08708	1139.192034	
54	Catalyst Loading kg/m^3	114.0667005	113.3858241	113.19752	
55	Reaction Enthalpy - kJ/gmol -CH2-	193.72	193.72	193.72	
56	kgmol/h of H2+CO Conv (=3* -CH2-)	110.2910631	92.49847053	87.51228143	
57	Heat Release - kW	1978.294884	1659.148492	1569.711033	
58	Heat Release - kW/m^3	196.5762296	164.883771	155.9766842	
59	Heat Release - Btu/(h ft^3)	19006.26587	15940.09953	15080.83828	
60	Mass Transfer Resistance - %	16.43979834	15.96190057	15.83345103	
61	DL - cm2/s	4675.840085	4747.348158	4766.982238	

Table 2.5

	A	B	C	D	E
1	CASE	MOBIL PILOT PLANT - RUN CT256-11			4/18/90
2	uGo - cm/s		5.3		
3	alpha		-0.55		
4	I		1.5		
5	U		1.7		
6	alpha*		-0.594		
7	T - oC		257		
8	Wt % Slurry		19.4		
9	Vol.% Solids		4.950943164		
10	dR - cm		5.1		
11	L - cm		762		
12	dp - micron		26		
13	rhoS - g/cm^3		3.1		
14	muL - poise		0.02474214		
15	rhoL - g/cm3		0.670865		
16	sigmaL - dyne/cm		16.5		
17	DA - cm2/s		0.00053911		
18	muSlurry - poise		0.029347783		
19	rhoSlurry - g/cm^3		0.791130093		
20	kLa Correction Factor		0.809412862		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Deckwer's Model	0.236757506	0.252744191	0.255930759	
23	kLa - s^-1 (uncorr) for H	0.465353124	0.500032005	0.506971136	
24	kLa - s^-1 (corr) for H	0.376662804	0.404732336	0.410348958	
25	kH - (s*kgCat/m3)^-1		0.000507903	3.3e^9*exp(-130/RT)	
26	kH- s^-1		0.067204155	With pressure correction	
27	kH*epsilonL - s^-1	0.051293067	0.050218695	0.050004545	
28	He - (kPa cm^3)/mol		20064929.63		
29	RTL/(uGo*He) - s^-1		31.57383613		
30	kA - s^-1	0.045145287		0.044572948	
31	Stanton No. - target	1.425409884		1.407338966	
32	H2 Conversion	0.89013958		0.708443642	
33	Stanton No. - result	1.425412029		1.407342177	
34	Average uG - cm/s	3.898831287		4.184838864	
35	Stanton No. - reaction		1.585596862		
36	StantonM - target		12.77895246		
37	H2 Conversion		0.738552982		
38	n		0.465788625		
39	Y		0.738553096		
40	StantonM - result		12.77769651		
41	Average uG - cm/s		4.137443751		
42	Pressure - kPa		1480		
43	Reactor Xsect - m^2		0.002042821		
44	Reactor Vol. - m^3		0.015566293		
45	Feed Rate - m^3/h		0.389770175		
46	Feed Rate - Nm^3/h		2.931793271		
47	SV - Nm^3/(m^3 h)		188.3424167		
48	H2+CO Conversion	0.961350746	0.79763722	0.765119133	
49	CO Conversion	1.008824857	0.837026713	0.802902794	
50	STY - Nm^3/(h*m^3)	181.0631229	150.2289218	144.1043866	
51	STY - Nm^3/(kgCat h))	1.545673745	1.309889364	1.261868835	
52	GHSV - Nm^3/(kgCat h)	1.607814579	1.642211936	1.64924491	
53	Catalyst - kg	1.823464789	1.785270955	1.777657917	
54	Catalyst Loading kg/m^3	117.1418765	114.6882522	114.1991803	
55	Reaction Enthalpy - kJ/gmol -CH2-	197	197	197	
56	kgmol/h of H2+CO Conv (=3* -CH2-)	0.125745482	0.104332446	0.100079019	
57	Heat Release - kW	2.293708978	1.903101091	1.825515434	
58	Heat Release - kW/m^3	147.3510075	122.2578218	117.2736127	
59	Heat Release - Btu/(h ft^3)	14246.85187	11820.67978	11338.77411	
60	Mass Transfer Resistance - %	11.98559725	11.0382639	10.86220579	
61	DL - cm2/s	50.42182495	51.38943129	51.57707814	