TOPICAL REPORT
SLURRY REACTOR DESIGN STUDIES
DOE Project No. DE-AC22-89PC89867
REACTOR SELECTION CRITERIA

1.0 INTRODUCTION

This Topical Report is a report on Task 2 of the Slurry Reactor Design Studies - "Survey Design and Scale-up Factors". In order to gain validity, Bechtel was assisted in this work by two consultants:

Dr. Aydin Akgerman of Texas A&M University, and
Dr. Joe M. Smith of the University of California - Davis

The work consisted of a critical review of the literature on Fischer-Tropsch (F-T) and alcohol syntheses from the standpoint of reactor design. No attempt was made to make this review exhaustive since several rather comprehensive reviews are available already. Rather, attention was placed on the availability of good models and good data for scale-up and reactor design purposes. At the same time a parallel effort was devoted to setting an appropriate process design basis for reactor comparison.

The reports of Drs. Akgerman and Smith are presented in Appendices A and B, respectively. Dr. Smith has provided two reviews of reactor modelling efforts, one for Fischer-Tropsch and one for methanol. His point of view is that of the theoretician and author of the book "Chemical Engineering Kinetics". Dr. Akgerman, who has performed diffusion studies on Fischer-Tropsch systems for the DOE and who has intimate knowledge of other Fischer-Tropsch work being carried out at Texas A&M University, supplied reports on the following specific issues:

1. Effect of H_2/CO ratio on carbon formation (via Boudouard reaction) in the Fischer-Tropsch synthesis reaction, showing the theoretical difference between slurry and fixed-bed reactors.
2. Design of slurry reactors:
   - 2A. Suspension of the solids
   - 2B Internal catalyst diffusion effect
   - 2C. Analysis of resistances
   - 2D. Effect of stoichiometry
   - 2E. Solids dispersion
   - 2F. Transport parameters.
3. Effect of solids on liquid phase mass transfer.
4. Model solutions for slurry reactors.
5. Diffusion effects in the fixed-bed gas phase Fischer-Tropsch reactor.

The remainder of this report follows the following format:

Section 2. - A discussion of slurry reactor design criteria.
Section 3. - A similar discussion of fixed-bed reactor design criteria.
Section 4. - Proposed process and reactor design bases.
Section 5. - Areas needing further development

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:

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

For some of these applications special designs have been developed:

- 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.
- 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.
- 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.
- 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.
- 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.
- 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..
- 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 $\mathrm{Btu/(hr \cdot ft^2 \cdot {}^\circ F)}$ 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)

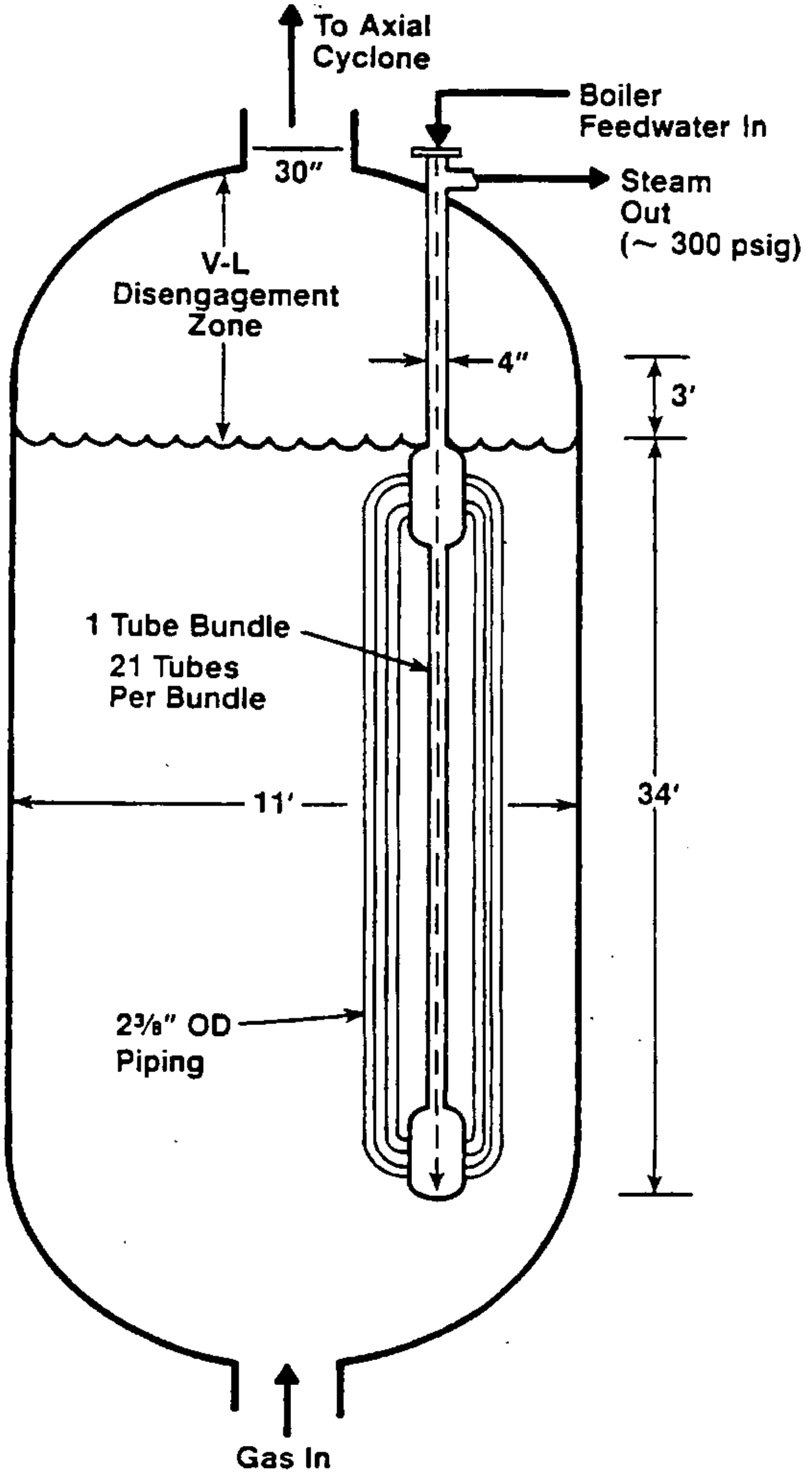


Figure 2.2

SLURRY REACTOR DESIGN
PIPELINE LOOP REACTOR
FOR POLYETHYLENE

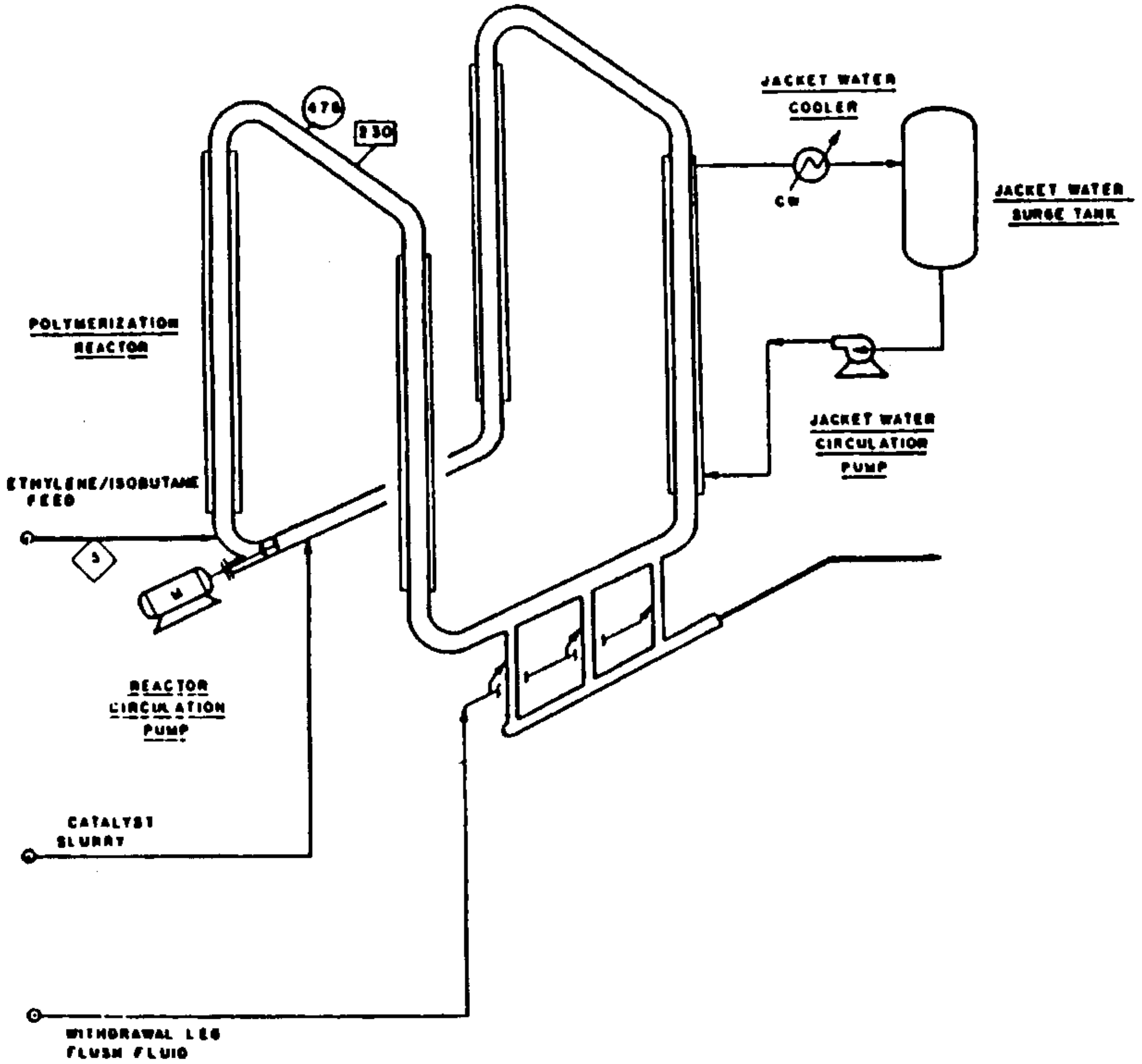


Figure 2.3

SLURRY REACTOR DESIGN
CIRCULATING LOOP LAYOUT
(CHEM SYSTEMS)

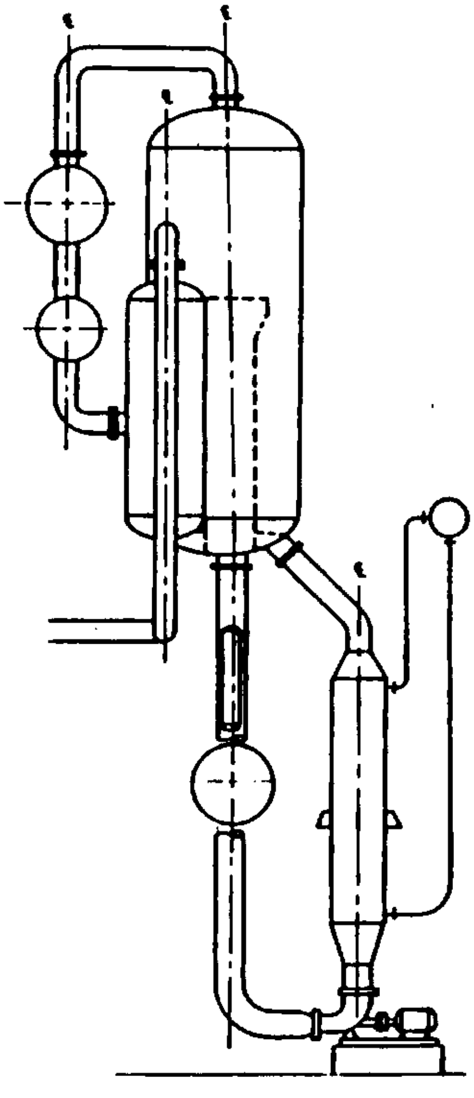
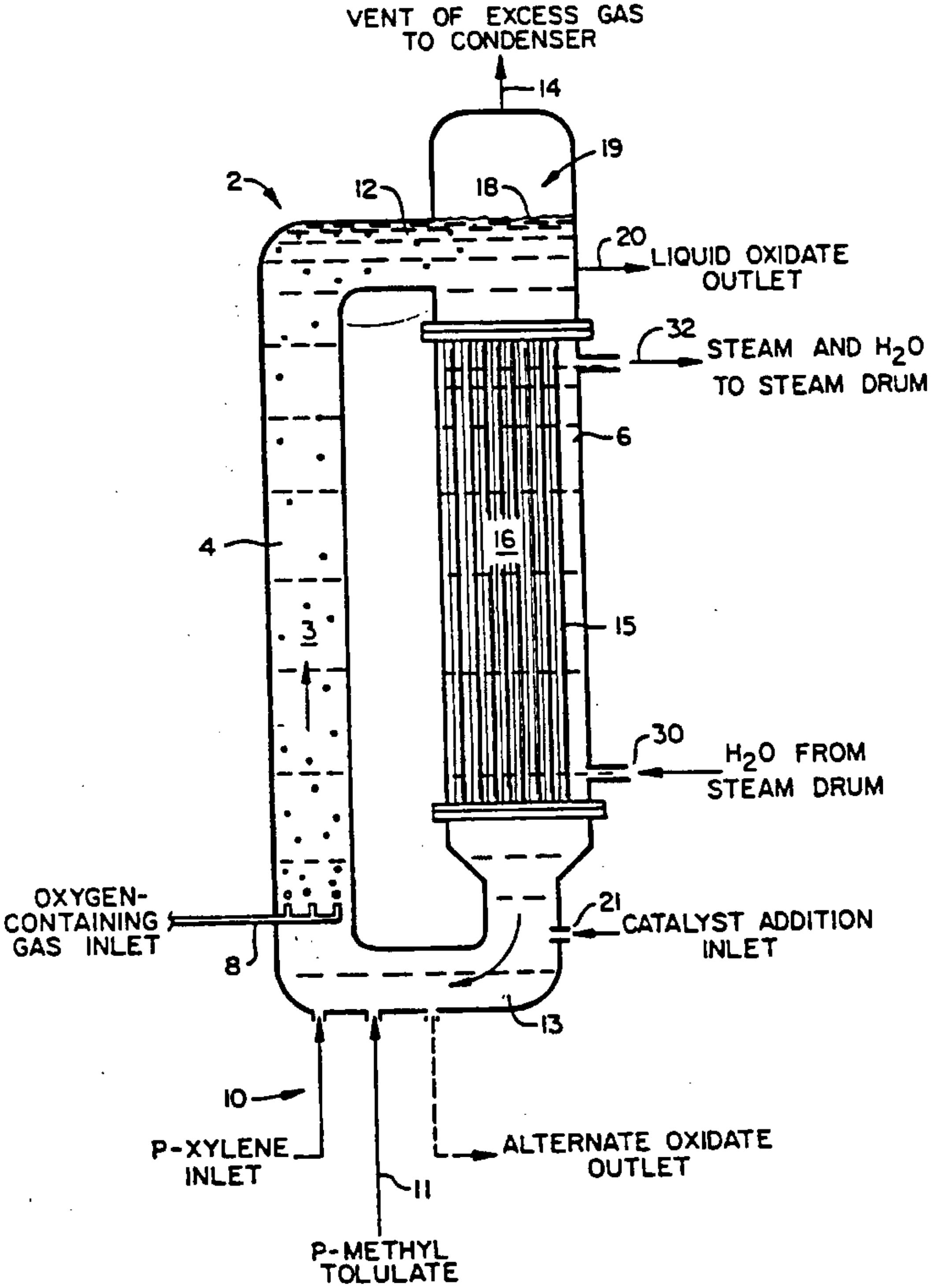


Figure 2.4

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_La.

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:

$$1/K_A = 1/k_La + 1/k_r\epsilon_L$$

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)[1] 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] 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[2] 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 supertficial velocity, d_R = column diameter, ρ_L = liquid density, σ_L = surface tension and g = gravitational acceleration in consistent units.

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

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

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 Ashita-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	l		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	<u>REACTOR MODEL</u>	<u>MODEL 1</u>	<u>MODEL 2</u>	<u>MODEL 3</u>	
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	0.078099982	
28	He - (kPa cm^3)/mol		19699754.02		
29	RTL/(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		2.886667106	
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		2.829329152		
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)		200.3034226		
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	141.1932862	123.0490317	112.5291474	
59	Heat Release - Btu/(h ft^3)	13651.48341	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	0.908448219		0.721400261	
33	Stanton No. - result	1.626820392		1.626622666	
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))	2.17763239	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-)	111.5766976	93.6694338	88.60324348	
57	Heat Release - kW	2001.355357	1680.152103	1589.27966	
58	Heat Release - kW/m^3	198.867668	166.9508263	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	0.40409665	
25	kH - (s*kgCat/m3)^-1		0.000507903	3.3e^9*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		12.57078878		
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))	1.604508665	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)	14868.17756	12384.53139	11875.29448	
60	Mass Transfer Resistance - %	13.93157752	12.81769975	12.60419168	
61	DL - cm2/s	50.16757931	51.16801093	51.36807309	

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		0.000585877		
18	muSlurry - poise		0.025154495		
19	rhoSlurry - g/cm^3		0.774238061		
20	kLa Correction Factor		0.812175666		
21	<u>REACTOR MODEL</u>	<u>MODEL 1</u>	<u>MODEL 2</u>	<u>MODEL 3</u>	
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		18.58019167		
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	1.568963898		1.568300863	
34	Average uG - cm/s	7.301608574		7.755649699	
35	Stanton No. - reaction		1.866437076		
36	StantonM - target		9.826638367		
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	0.734463285	
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	164.863771	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		1.40734217	
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-)	0.125746482	0.104332446	0.100079019	
57	Heat Release - kW	2.293708978	1.903101091	1.825515434	
58	Heat Release - kW/m^3	147.3510075	122.2578216	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	

3.0 FIXED-BED REACTOR DESIGN

3.1 Types of Fixed-Bed Reactors

A number of fixed-bed designs are in commercial use in methanol plants, but the two in most common use are the recycle-gas-quenched design of ICI and the tubular-fixed-bed reactor of Lurgi with steam generation. Topsoe, Mitsubishi and Kellogg have developed multi-bed designs with intercooling and Mitsubishi has also announced a fluidized-bed design. In each case, the objective is to remove heat efficiently and the tubular-fixed-bed and fluidized-bed designs do this most effectively at the expense of appreciably more expensive reactors. A sketch of the tubular fixed-bed ARGE reactors used at Sasol, South Africa, is shown in Figure 3.1[3].

The tubular-fixed-bed reactor has been chosen for comparison with the slurry reactor because it is the most comparable in terms of energy efficiency. In addition, this reactor is somewhat more flexible in terms of recycle to fresh feed ratio than other designs which remove the heat of reaction as sensible heat. The methanol reactor, being equilibrium limited, requires a recycle to fresh feed ratio in the range of 2 to 4. The Fischer-Tropsch reaction is not so limited and theoretically, at least, very high single pass conversions are feasible.

3.2 Fixed-Bed Reactor Design Principles

The design of a tubular-fixed-bed F-T reactor requires a careful balance between conversion, pressure drop and heat transfer. It is useful to review the design principles involved:

3.2.1 Heat Transfer

The heat transfer coefficient for an empty tube is obtained from the Nusselt type equation:

$$hD/k = 0.023\cdot(DG/\mu)^{0.8}\cdot(c\mu/k)^{1/3}$$

where h is the heat transfer coefficient, Btu/(h.ft$^{2}\cdot$°F), D is the tube internal diameter, ft, k is the thermal conductivity, Btu/(h·ft$^{2}\cdot$°F/ft), c is the heat capacity of the fluid, Btu/(lb·°F), m is the viscosity, lb/(h·ft) and G is the superficial mass velocity, lb/(h·ft^{2}).

For packed tubes Colburn [IEC 23, 910 (1931)] related the heat transfer coefficient to that of the empty tube times a factor which depends on the ratio of packing diameter to tube diameter, d/D:

d/D	0.05	0.10	0.20	0.30
h/h(empty)	5.5	7.0	7.5	6.6

The range of interest is 0.05 to 0.10 where the heat transfer coefficient is increasing.

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[3] From the Encyclopedia of Chemical Technology, 2nd Edition

3.2.2 Pressure Drop

The pressure drop in a packed-bed is given by the modified Ergun equation:

$$\Delta P/L = f \cdot C \cdot G^2/(\rho d)$$

where d is the effective particle diameter, ft, f is a friction factor dependent on the modified Reynolds Number, dG/μ, C is the pressure drop coefficient in $ft \cdot hr^2/in^2$, ρ is the fluid density, lb/ft^3 and $\Delta P/L$ is the pressure drop in psi/ft. Linde Bulletin F-2932 gives the value of C at a typical bed void fraction of 0.37 as $3.6 \cdot 10^{-10}$. At modified Reynold's Numbers above 500, which is typical, the friction factor, f, varies between 1.1 and 1.0.

3.2.3 Conversion

The conversion-space velocity relationship for a fixed-bed Fischer-Tropsch reactor is reviewed in Appendix C. Basically, the relationship is equivalent to that of a slurry reactor when space velocity is expressed per unit weight of catalyst, temperature is identical and mass transfer is not limiting the conversion.

3.2.4 Operating Variables

Operating variables at the disposal of the designer are tube diameter, particle diameter, pressure level, inerts level and conversion.These are, of course, interrelated. From a heat transfer standpoint, it is essential to maximize mass velocity within the limits imposed by pressure drop. Pressure drop can be minimized by increasing pressure level (increasing ρ) or by using larger diameter particles. Up to a limit, larger particles also improve heat transfer. There is a tradeoff on particle size, however, since intraparticle diffusion decreases the effectiveness of the catalyst.

Superficial velocity is a secondary variable in fixed-bed reactor design but is significant since pressure drop is proportional to mass velocity times superficial velocity. In general superficial velocities of 3 to 5 times those in a slurry reactor can be tolerated. This ratio increases as pressure is raised.

Tube diameter is important since smaller diameter tubes improve the ratio of heat transfer area to reaction volume without materially affecting the heat transfer coefficient unless the ratio of tube diameter to particle diameter gets too small. Also, for good gas distribution the ratio of tube diameter to particle diameter should be kept over 10. A typical choice might be 1/8" particles in a 1.25" tube.

The remaining variables are conversion per pass and the inerts level, which control the external recycle to fresh feed ratio and the ultimate conversion. Heat evolution in a given size reactor is proportional to the space time yield (STY) which is the product of volumetric space velocity and conversion. STY increases as conversion is lowered, but eventually lines out as recycle ratio becomes very large (see Appendix D). In low conversion per pass, high recycle ratio designs, high mass velocities are employed without a corresponding increase in heat evolution. The high mass velocity is conducive to improved heat transfer and if a temperature rise is allowed, sensible heat effects reduce the heat removal requirement. A low level of inerts is also very significant in this type of operation since it permits high ultimate conversion to be achieved without excessive buildup of inerts in the recycle gas.

3.3 Comparison with the Slurry Reactor

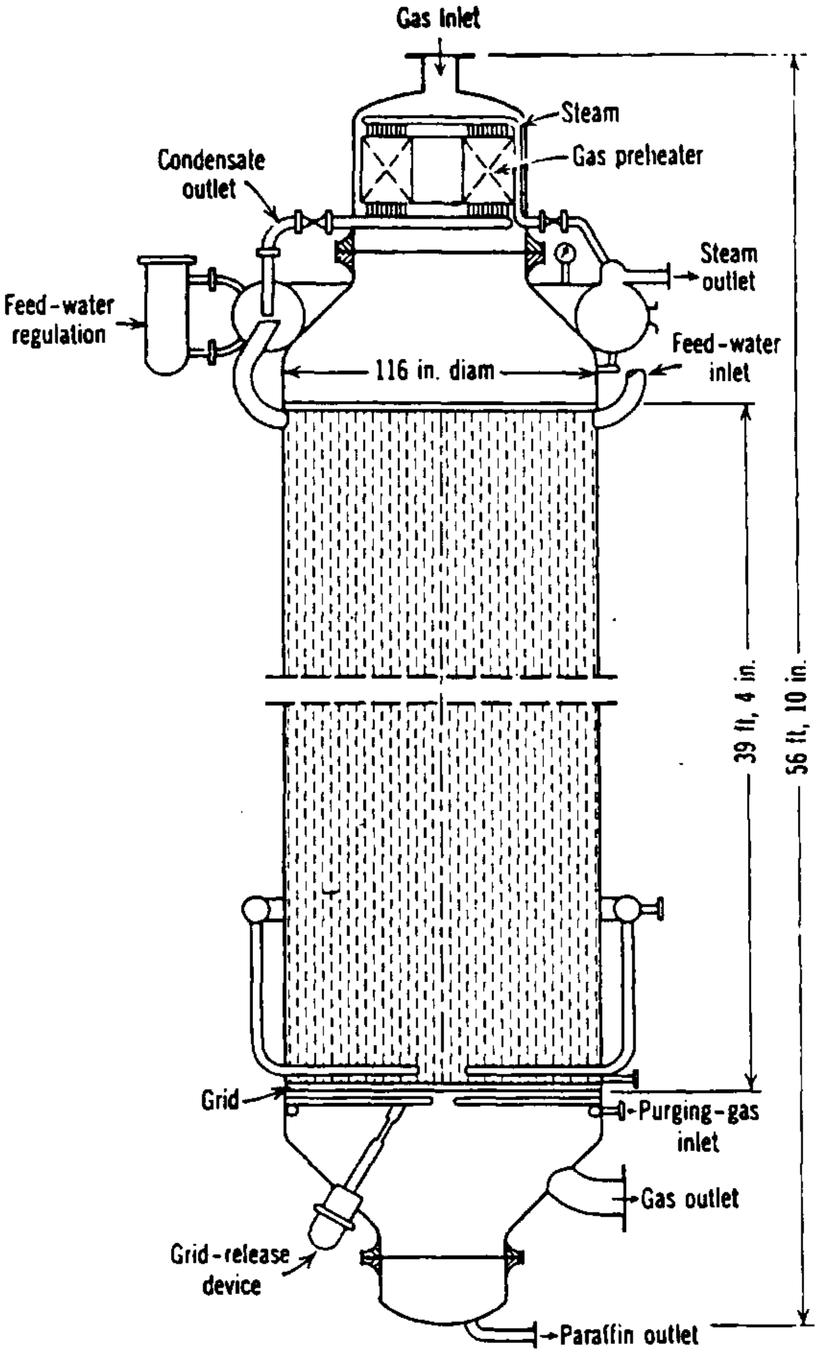
Some of the differences between a slurry reactor and a fixed-bed reactor have been pointed out elsewhere, but a review may be helpful at this point:

> A primary difference is the preferred conversion level. The slurry reactor, because of its superficial velocity limitation, fits best into the high conversion end of the scale where the recycle to fresh feed ratio is low, the only limitation being that due to backmixing. The fixed-bed reactor of the quenched or intercooled variety requires a high recycle ratio to limit the temperature rise, but even the externally cooled, tubular design requires a high mass velocity to achieve good heat transfer characteristics. A recycle to fresh feed ratio of at least 2 is preferred with pressure drop being the limiting factor.
>
> Cooling surface requirement in a slurry reactor is less than a quarter that in a tubular fixed-bed reactor. This is partially because the heat transfer film coefficient is improved but also because a higher ΔT is permissible between reactants and coolant. In the tubular fixed-bed reactor, hydrogen content of the gas improves the heat transfer coefficient significantly, another reason why that reactor may not be a good choice for very low H_2/CO ratio gases.
>
> Increasing pressure level has significant advantages for either type of reactor, regardless of its effect on kinetics or equilibrium. At lower pressure, more slurry reactors are required because of the superficial velocity limitation. In the fixed-bed case, the limitation on superficial velocity is pressure drop. The higher the pressure level, the higher the permissible superficial velocity, so there is a double advantage. A high mass velocity is required for good heat transfer and this can more readily be achieved at high pressure. Higher pressure will permit a higher recycle ratio to be used without causing an increase in compressor horsepower. In either case, the vessel must be designed for the higher pressure but in the fixed-bed case the shell thickness is set by steam pressure rather than reaction pressure so there is less of an effect on cost.
>
> Finally, in the fixed-bed reactor more catalyst can be loaded into a given volume. Since space velocity is normally expressed per unit weight of catalyst, this represents a significant potential advantage Since the fixed-bed reactor runs at lower conversion, space velocity would be expected to be higher as well. On the other hand, in F-T synthesis for distillate production, the slurry reactor is run at about 260 °C and, with catalyst addition, activity stays constant throughout the run. The fixed-bed reactor starts out at about 200 - 225 °C and temperature is gradually increased as activity declines. This temperature difference compensates for other effects and reaction volume requirements are actually somewhat less for the slurry reactor.

Some of these considerations are treated more fully in Appendix D.

Figure 3.1

FIXED-BED REACTOR DESIGN
ARGE REACTOR



4.0 PROCESS AND REACTOR DESIGN BASES

This section discusses some of the key process design issues and provides overall block flow diagrams for the F-T and methanol cases. Reactor design bases are then defined. The fairest comparison is obtained when the maximum size reactor is used in each case. A 4.8 meter shell diameter was fixed as the maximum practical dimension.

Since the study is aimed at defining differences between the slurry reactor and the fixed-bed reactor, only those sections of the overall facility which are materially affected by the choice of reactor are included in the evaluation.

4.1 Methanol

There is much activity at the present time in the development of new methanol plant concepts. Low temperature designs have been proposed using soluble catalyst in a bubble column. Designs have been developed which use adsorbents or solvents to remove the product from the gas phase and increase conversion. A recent paper (J. B. Hansen, Haldor Topsoe, AIChE Spring National Meeting, Orlando, March 20, 1990) describes a high conversion, once-through, tubular, fixed-bed design in which operating conditions are such that the product condenses in the reactor. There have also been advances in feed gas preparation for conventional methanol plants. Both Davy McKee and Lurgi have designs which produce a stoichiometric or close-to-stoichiometric synthesis gas from natural gas. ICI is also working on this. For coal-based plants, synthesis gas may be produced from new, high efficiency coal gasifiers, but extensive shifting and CO_2 removal are required to produce a stoichiometric gas.

More to the point, Chem Systems have developed a slurry reactor design in which the catalyst is held in suspension in a heavy hydrocarbon oil. This has been proposed primarily for low conversion operation on as-produced, coal-derived synthesis gas, producing as much methanol as possible once-through and coproducing power from the tail gas. Air Products has piloted this design in a 2' diameter reactor at La Porte, Texas. While a similar type of operation may be possible in a fixed-bed reactor, the slurry reactor should give superior heat transfer characteristics with either internal cooling coils or with an external loop cooler. The use of a fixed-bed reactor for this application would be developmental and the necessary data are lacking for design. The comparison of once-through methanol/power coproduction, in a slurry reactor, with conventional high yield methanol production, in a fixed-bed reactor, has been the subject of other studies and introduces complications which are not pertinent to a one-for-one comparison of reactor designs.

It is possible to design a slurry reactor for high conversions to methanol using a stoichiometric synthesis gas. This may not be the optimum application for the slurry methanol reactor but this case does provide a one-for-one comparison of the slurry reactor with the fixed-bed reactor under normal synthesis conditions. This is the case selected for study.

4.1.1 Process Design.

The block flow diagram and overall material balance for the coal based methanol plant is shown in Figure 4.1. The Texaco gasifier has been selected for the methanol application since it permits synthesis gas to be generated at 5,600 kPa (55 atmospheres), sufficient to supply the fixed-bed reactor without further gas compression. An oxygen concentration of 99.5% is used since it gives a synthesis gas with very low inerts. This is beneficial in a recycle methanol operation. The gas is adjusted in composition by shift and CO_2 removal such that the ratio:

$$\frac{H_2 - CO_2}{CO + CO_2} = 2.05$$

and the CO_2 content is 3%. The steam content of the gas from the Texaco gasifier, after quenching, can be used effectively in the water gas shift reactor. The Rectisol Process is used for removal of CO_2, H_2S and other impurities. Processing closely follows that used in EPRI Report AP-1962. It turns out that, with the selected 4.8 m shell diameter, capacities are virtually identical for a fixed-bed reactor operating at 5600 kPa and 3.0 recycle to fresh-feed (R/FF) ratio and a slurry reactor operating at 10,000 kPa with a R/FF ratio of 2.2.

Only the methanol synthesis loop changes between cases. In addition to the differences in pressure and recycle ratio, there are differences resulting from slurry oil volatilization and recovery and catalyst makeup provisions in the slurry reactor case. The assumption is made that reactor configuration does not affect product distribution, so downstream product recovery facilities (after depressuring) are unchanged.

4.1.2 Reactor Design.

Design of the fixed bed methanol reactor is confidential to Lurgi who have requested that only overall dimensions and capacity be released publicly. The reactor has a shell diameter (ID) of 4.8 meters and a tangent-to-tangent length of 7.5 meters. Total weight of catalyst provided is 82000 kg and the GHSV is 7.0 Nm^3 /(h ·kg Cat). Since a stoichiometric gas is used and the feed gas inerts are low, the reactor can be designed for a total pressure of 5600 kPa. Pressure drop is 200 kPa with a R/FF ratio of 3.0. Steam production is at 4100 kPa (40 atm).

The slurry reactor design is based on information developed by Air Products for the design of the internally-cooled La Porte pilot plant reactor (final report on DOE Contract DE-AC22-85PC80007), and on operating results from that reactor (Studer, et al, EPRI 14th Annual Conference on Fuel Science and Conversion, Palo Alto, May 18-19, 1989)). Cognizance has been taken of some stoichiometric-gas, high-conversion designs prepared by Chem Systems for an ongoing Bechtel study of IGCC power/methanol coproduction, but the design parameters have been independently established for this study, particularly the design heat flux. Reactor design variables are summarized in Table 4.1. Capacity at 0.15 m/s superficial velocity is 475 STPD of methanol. At 0.145 m/s superficial velocity used for design, capacity is the same as a fixed-bed reactor of the same diameter.

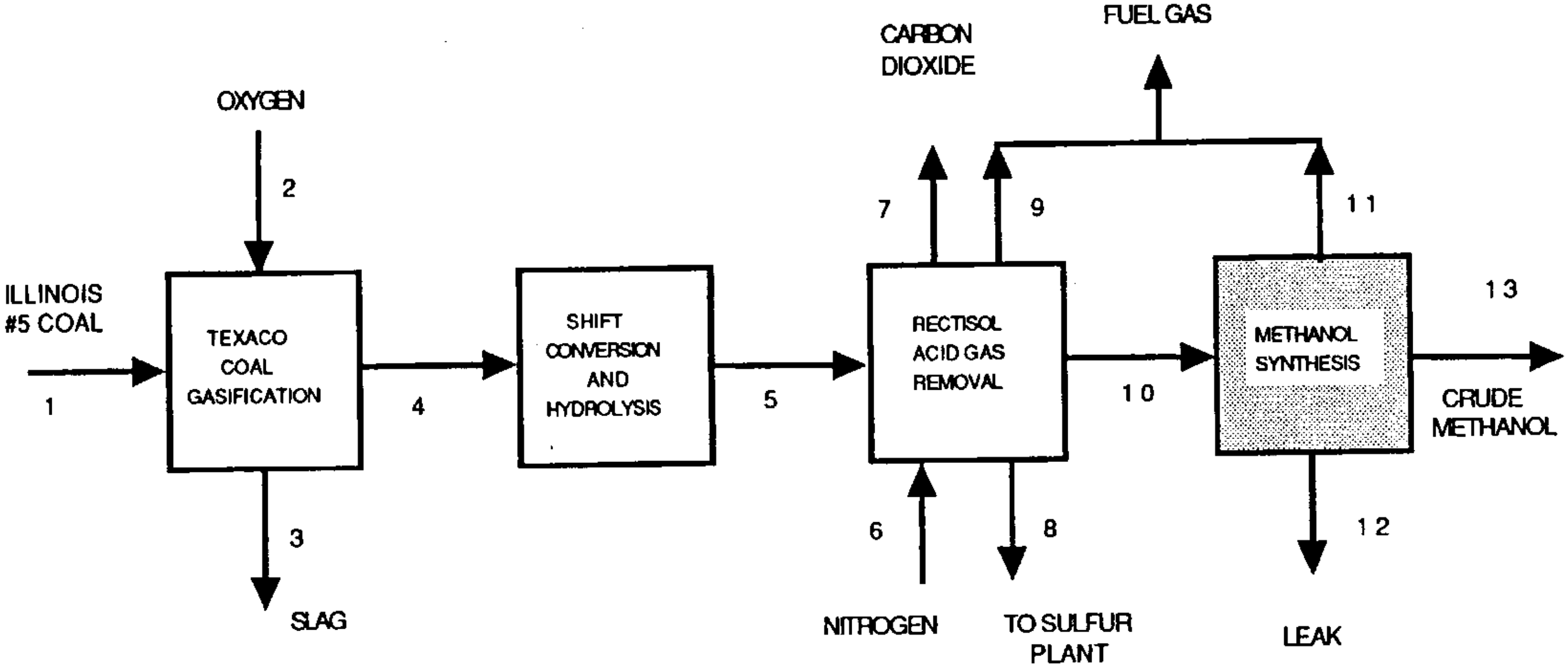
At the high design pressure (10,000 kPa), quite high conversions are theoretically possible and the R/FF ratio can be lowered, as indicated, to about 2.2. This combination of factors maximizes reactor throughput.

Air Products reports that the slurry methanol reactor can be designed to the same approach to equilibrium as a fixed-bed reactor (about 15 to 25 °C) at the same space velocity. Since the resulting CO conversion per pass is over 85%, an allowance has been made for backmixing effects and the design CO conversion is 70% at a GHSV of 7.0 Nm^3/(h·kgCat). Overall conversion is now virtually identical to the fixed-bed case. The resulting slurry bed height requirement of 15.62 meters is based on the bottom head volume being 15% effective for mass transfer and reaction. Methanol productivity (or STY), at 0.945 kg/(h·kg) is somewhat higher than in the fixed-bed reactor at 0.756 kg/(h·kg), due to differences in conversion level..

Based on Air Products' recommendation, catalyst makeup requirement for the slurry reactor has been set equal to that for a fixed-bed reactor. The resulting makeup rate of 0.2% per day is roughly equivalent to total replacement every 18 months, which typically is the guaranteed life of a fixed-bed catalyst (replacement every 3 years is, however, not uncommon). At this low makeup rate, catalyst carryover will probably account for most of the required withdrawal but a separate catalyst withdrawal system is provided to allow for dumping a load of catalyst and recovering the liquid for reuse. Conventional materials of construction are used in both reactors since carbonyl poisoning of the catalyst should not occur with a stoichiometric feed gas. Overall yield in kg of methanol per kg of catalyst consumed is 9000 for the fixed-bed case and 10000 for the slurry reactor case.

Figure 4.1

SLURRY REACTOR STUDIES
METHANOL BLOCK FLOW DIAGRAM



MATERIAL BALANCE

Stream Number	1	2	3	4	5	6	7	8	9	10	11	12	13
Description	Coal	Oxygen	Slag	Gasifier Outlet	Shifted Gas	Stripping Gas	CO_2 Vent	Acid Gas	Fuel Gas	Methanol Syn Gas	Purge Gas	Leak Gas	Crude Methanol
Component - lb mph													
H_2				5696.0	9582.6		0.7	0.3	17.1	9564.7	443.9	50.5	25.3
CO				7915.0	4028.4		5.8	0.4	52.3	3970.0	33.6	7.1	4.8
CO_2				2103.2	5998.3		4727.3	320.8	498.1	452.1	21.9	2.5	29.0
H_2O				2878.2	0.0		0.0	0.0	0.0	0.0	0.1	0.3	398.5
O_2		4804.0		0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0
N_2+Ar		36.0		116.6	116.6	550.6	542.7	9.2	2.4	113.0	91.0	8.8	10.3
CH_4				31.5	31.5		0.8	0.0	2.4	28.3	21.1	2.0	5.2
H_2S				149.9	158.3		0.0	158.2	0.0	0.0	0.0	0.0	0.0
COS				9.9	1.4		0.0	1.4	0.0	0.0	0.0	0.0	0.0
CH_3OH											3.7	0.3	4319.1
TOTAL - MPH		4840.0		18900.3	19917.2	550.6	5277.5	490.3	572.3	14128.0	615.3	71.4	4792.2
LBS/HR	177846	154925	27211	387352	405620	238869	223441	19863	23541	154204	6025	715	147420
Mol Wt		32.01		20.49	20.37	433.80	42.34	40.51	41.14	10.91	9.79	10.02	30.76

Table 4.1

SLURRY METHANOL REACTOR

DIMENSIONS	Design Case
Diameter, m	4.8
Straight Length of Bed, m	15.62
Xsect, m2	18.10
Head Vol, m3	28.95
Head Volume Effectiveness - %	15.00
Tube OD, mm	38.1
Tube ID, mm	34
Tube Length, m	15.12
No. of tubes	988
Tube Area (OD), m2/tube	1.810
Tube Xsect (OD), m2/tube	0.001140
Tube Area (ID), m2/tube	0.000908
Net Xsect of Reactor, m2	16.97
Total Tube Area - m2 (OD)	1788.1
Reaction Volume, m3	269.39
CONDITIONS	
Feed Gas Temp., oC	150
Operating Temp, oC	250
Operating Pressure, atm	99
Slurry Concentration, wt%	35
Gas Holdup, %	25
Liquid Density, kg/m3	675
Particle Density, kg/m3	3000
Slurry Density, kg/m3	926.2
Catalyst Loading, kg/m3	243.1
Catalyst Weight, kg	65499.3
FF - kgmph	6407.4
TF - kgmph	20455.8
TF - m3/h	8872.4
TF - Nm3/h	458495
R/FF Ratio	2.19
MW of TF	9.72
MW of Effluent	11.99
CO2 in TF	4.8
CO2 Conversion per pass, %	16.22
CO in TF, %	12.4
CO Conversion per pass, %	70.03
Methanol Production, MTPD	1486.2
Heat Duty, MW	33.8
Inlet Superficial Velocity, m/s	0.145
GHSV, Nm3/h kgCat	7.00
Mass Velocity, kg/h m2	198769
Space Velocity, Nm3/h m3	1702
STY - kg Methanol/(h kgCat)	.945
STY - kg Methanol/(h m3)	230
Heat Flux, kW/m2	18.912
Total Cooling Surface, m2	1788.1

4.2 Mixed Alcohols

The Lurgi Octamix process has been selected for the base case mixed alcohols process and Lurgi has provided the process design including a process flow diagram and equipment list. The data available to define the slurry reactor system for this application are very limited so only the reactors are sized. Relative costs may be compared by analogy with the methanol or Fischer-Tropsch systems. It is assumed that GHSV (in $Nm^3/(h\cdot kg\ Cat)$ and pressure level are identical regardless of which type of reactor is employed.

4.2.1 Process Design Basis

The overall block flow diagram is similar to that for methanol, the primary difference being that the synthesis gas has a 1.1 H_2/CO ratio and a CO_2 content of only 1.0%. Only a small amount of shifting is required and, while less CO_2 must be scrubbed out, a higher level of removal is achieved. The Rectisol unit employed for this purpose is integrated with that required for CO_2 removal from the gas recycled back to the synthesis reactor. Product recovery is somewhat more complicated than in a fuel grade methanol plant because of the higher alcohols in the product.

The synthesis loop is also more complicated since liquid methanol is recycled back to the reactor from the stabilizer reflux drum. Provisions may also be required for recovering heavier components of the product from the slurry oil. The assumption is made that syntheses gas preparation, the synthesis loop and product recovery are identical regardless of reactor selection.

4.2.2 Reactor Design.

Lurgi has given the capacity of the same tubular fixed-bed reactor used for 1640 STPD of methanol production as 460 STPD of mixed alcohols. The reactor is now designed for 10100 kPa rather than 5600 kPa operating pressure used for methanol. The primary effect is to increase the thickness of the heads and the tube sheets.

The slurry reactor design and sizing basis is summarized in Table 4.2. At the design GHSV of 2.7 $Nm^3/(h\cdot kg\ Cat)$, a slurry reactor designed for 0.15 m/s superficial velocity would have a slurry height of roughly 42.7 meters which is unrealistic. The superficial velocity is, therefore, reduced to 0.067 m/s, which should still be adequate to achieve the required agitation for heat and mass transfer. The slurry height is then reduced to 17.8 meters and the capacity is 460 STPD.

The heat release indicated by Lurgi in their fixed-bed design is about 50% higher per unit weight of product than in the methanol reactor. The same heat release has been used in the slurry reactor design. The design heat flux and gas holdup are reduced, at the lower superficial velocity, to 5,000 $Btu/h \times ft^2 \times {}^oF$ (15.76 kW/m^2) and 20%, respectively.

Since the reaction to mixed alcohols is controlled more by kinetics than equilibrium, the slurry reactor may benefit by a higher average temperature level, increasing the allowable space velocity. If the space velocity could be increased by 2.4 times, then it would be possible to double the capacity of the slurry reactor without increasing height, increasing the superficial velocity along with the space velocity. It is important, therefore, to obtain the kinetic data on which to base a valid design.

Table 4.2

SLURRY OCTAMIX REACTOR

DIMENSIONS	Design Case	Max. Sup. Vel.
Diameter, m	4.8	4.8
Straight Length of Bed, m	17.77	42.67
Xsect, m2	18.10	18.10
Head Vol, m3	28.95	28.95
Head Volume Effectiveness - %	15.00	15.00
Tube OD, mm	38.1	38.1
Tube ID, mm	34	34
Tube Length, m	17.27	42.17
No. of tubes	581	446
Tube Area (OD), m2/tube	2.067	5.048
Tube Xsect (OD), m2/tube	0.001140	0.001140
Tube Area (ID), m2/tube	0.000908	0.000908
Net Xsect of Reactor, m2	17.43	17.59
Total Tube Area - m2 (OD)	1199.8	2252.7
Reaction Volume, m3	314.07	754.80
CONDITIONS		
Feed Gas Temp., oC	200	200
Operating Temp, oC	245	245
Operating Pressure, atm	99	99
Slurry Concentration, wt%	35	35
Gas Holdup, %	20	25
Liquid Density, kg/m3	675	675
Particle Density, kg/m3	3000	3000
Slurry Density, kg/m3	926.2	926.2
Catalyst Loading, kg/m3	259.3	243.1
Catalyst Weight, kg	81453.0	183520.3
FF - kgmph	2322.3	5232.4
TF - kgmph	9811.9	22106.9
TF - m3/h	4215.1	9496.9
TF - Nm3/h	219923	495505
R/FF Ratio	3.225	3.225
MW of TF	22.90	22.90
MW of Effluent	26.57	26.57
CO2 in TF	0.96	0.96
CO in TF, %	62.49	62.49
CO Conversion per pass, %	16.2	16.2
Alcohols Production, MTPD	417.5	940.6
Heat Duty, MW	18.9	42.6
Inlet Superficial Velocity, m/s	0.0672	0.150
GHSV, Nm3/h kgCat	2.7	2.7
Mass Velocity, kg/h m2	224706	506282
Space Velocity, Nm3/h m3	700	656
STY - kg Alcohols/(h kgCat)	.214	.214
STY - kg Alcohols/(h m3)	55	52
Heat Flux, kW/m2	15.76	18.912
Total Cooling Surface, m2	1199.8	2252.7

4.3 Fischer-Tropsch

A modern coal gasifier of the Texaco or Dow design produces a synthesis gas with a H_2/CO ratio of about 0.75, the Shell gasifier produces something under 0.5 H_2/CO ratio. A 0.667 ratio is stoichiometric for the F-T reaction, without steam addition, where the catalyst has high water gas shift activity. Iron based catalysts have this activity. The reactions involved are:

$$2H_2 + CO \rightarrow -CH_2- + H_2O \qquad (1)$$

$$H_2O + CO \leftrightarrow H_2 + CO_2 \qquad (2)$$

giving the overall reaction:

$$H_2 + 2CO \rightarrow -CH_2- + CO_2 \qquad (3)$$

Because equilibrium in reaction 2 heavily favors CO_2 production at F-T conditions, reaction 3 predominates over reaction 1.

Since the fixed-bed reactor is not applicable to low H_2/CO ratio operation, this study evaluates fixed-bed operation at a 2 to 1 ratio versus slurry bubble column operation at the low ratio out of a Shell gasifier. Because of the hydrogen deficiency in the as-produced gas, steam is added to conform with stoichiometry. The two processing schemes are quite different between the gasifier and the downstream processing units.

The Shell gasifier is believed to be the optimum choice in the case of the slurry reactor, which is capable of handling a very low H_2/CO ratio gas. The low oxygen requirement is a very definite advantage for this gasifier. It was considered appropriate to use the same gasifier for the fixed-bed case, leaving it to other studies to examine the difference between gasifiers. The Shell gas requires more shifting to achieve a 2.0 H_2/CO ratio but CO_2 removal requirements are virtually identical when compared to other gasifiers. The low inerts content resulting from the use of 99.5% oxygen and the CO_2 carrier gas favors the fixed-bed reactor because of the higher recycle ratio used in that design.

After consultation with catalyst experts, it was decided to go "generic" in terms of catalyst requirements and product distribution. In actual practice, fused or precipitated iron catalysts seem most appropriate for the slurry reactor, where high WGS activity is required, and cobalt type catalysts for fixed-bed synthesis where low WGS activity is needed. Some differences in product distribution can be expected when iron vs cobalt catalysts are compared, but it was decided that to identify such differences would confound the main purpose of the study. An attempt was made to rationalize space velocity requirements so that reactor sizing is not dependent on the particular catalyst chosen.This is described elsewhere in this report.

Basis for design is a plant which uses the gas produced from 7500 T/D of coal in three Shell gasifiers at 2500 TPD each. In either case, the plant produces roughly 20,000 BPSD of liquid distillates under conditions where the Schultz-Flory chain-growth probability factor is about 0.9. The detailed product distribution is given in Mobil's final report under DOE Contract DE-AC22-83PC60019 (October 1985). The only difference identified between cases was a higher degree of olefinicity at the lower H_2/CO ratio. There should also be much lower oxygenates production if a cobalt catalyst is used, but this has not been factored into the design. For the slurry reactor case, steam was added to the feed gas to compensate for the deficiency in product water and a close approach to WGS equilibrium was assumed. For the fixed bed reactor, an 8% yield of CO_2 on CO converted was assumed - a compromise between cobalt and iron based catalysts.

A catalyst makeup rate of 1.67% per day was used for the slurry reactor case, this being the level used by MITRE based on their review of the available design information. This corresponds to a catalyst life of 60 days without replacement. Sixty days is not a reasonable catalyst life for a fixed-bed system and it is believed that Shell expects to get over a year life in their Malaysian unit using a cobalt based catalyst. Catalyst life in a fixed-bed system is amenable to study by varying the operating cost and does not materially impact capital cost.

4.3.1 Process Design Basis.

The overall Block Flow Diagram for the slurry reactor Fischer-Tropsch case is given in Figure 4.2. The material balance is given in Table 4.3 which is keyed into Figure 4.2 by means of stream numbers. Plants for which process flow diagrams and equipment lists will be provided are shaded in the diagram.

While the design follows that developed by MITRE (Gray, et al, Sandia Report WP89W00144-1), there are some key differences. Both designs use Shell gasification of coal with CO_2 carrier gas to prepare synthesis gas. The Shell gasifier package includes a waste heat boiler and a scrubber for carbon removal. The gasifier product gas is subjected to COS/HCN hydrolysis, cooling and condensation of sour water. Bechtel's design eliminates the water-gas-shift step entirely. The gas is compressed such that the F-T synthesis pressure is 3050 kPa (440 psia). The Selexol process is used for selective H2S removal and, finally, zinc oxide beds are used for sulfur polishing. The gas is then sent to the Fischer-Tropsch reactor after combining with a small amount of recycle gas. Since the gas is below stoichiometric H_2/CO ratio, steam is added to the recycle gas to supplement the water produced by reaction 1, shifting additional CO to produce the required amount of hydrogen.

As described elsewhere in this report, conversion per pass is 80% in the F-T reactor, rather than the 90% conversion used by MITRE. This permits significant reduction in the number of F-T reactors at the expense of doubling the small amount of recycle gas. It was not found effective to carry out a partial oxidation of the recycle gas to convert hydrocarbon byproducts to synthesis gas. The gas is recycled after product separation, CO_2 removal, cryogenic hydrocarbon recovery and recovery of enough hydrogen to treat the liquid product. A small purge is taken for inerts removal.

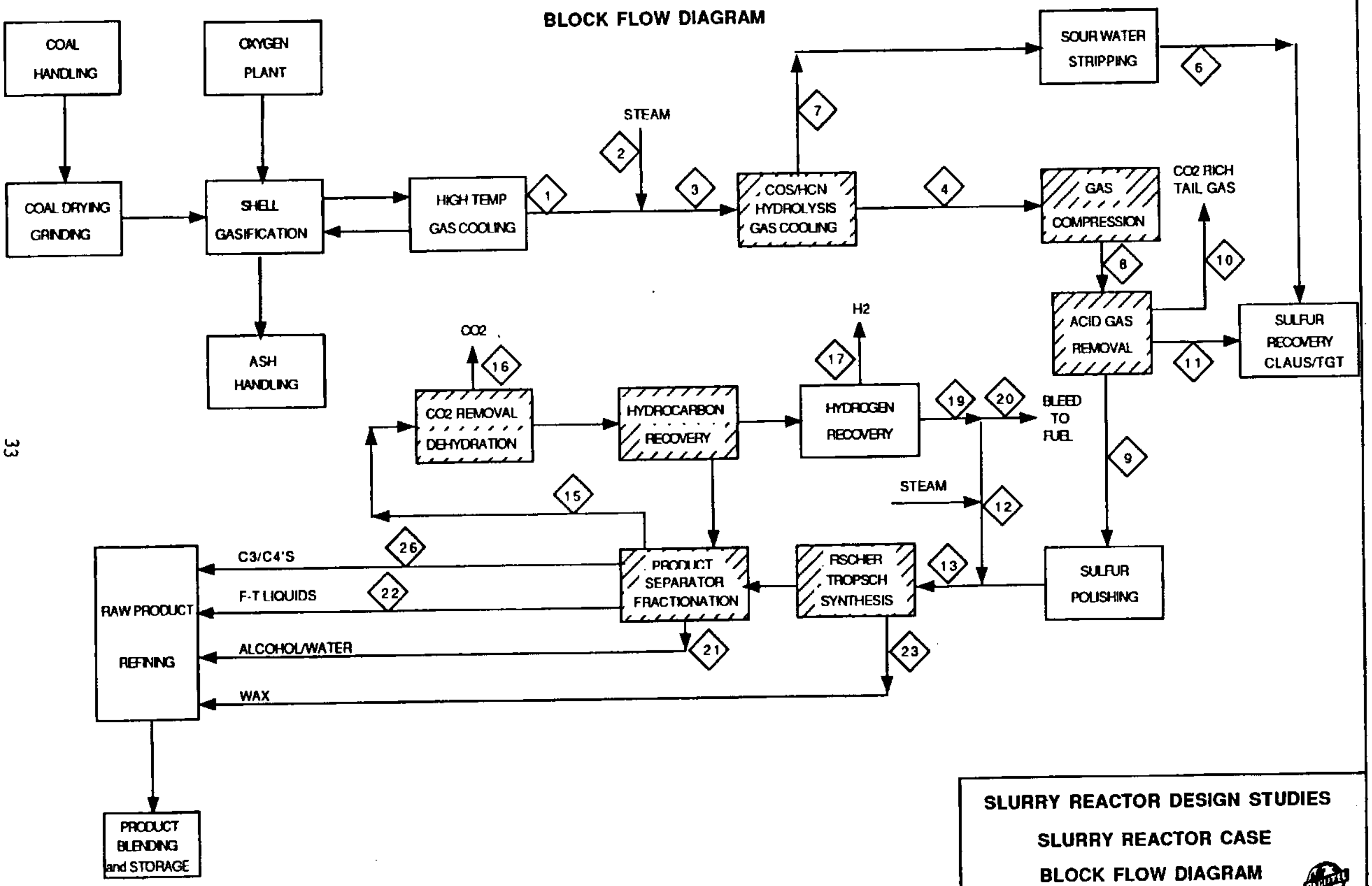
Product upgrading follows the sequence defined by MITRE and includes wax hydrocracking, distillate hydrotreating, catalytic polymerization of C3/C4's, heavy poly gasoline hydrotreating, isomerization of the C5/C6's and catalytic reforming of the naphtha from wax hydrocracking and middle distillate hydrotreating, and alkylation of cat poly olefins with isobutane from the cat reformer. MITRE shows "alcohols recovery" from the small amount of product water. Actually, there are other oxygenates present than just alcohols. This step has not been further defined but should be a minor part of the overall plant cost.

Figure 4.2

FISCHER TROPSCH SYNTHESIS

SLURRY REACTOR CASE

BLOCK FLOW DIAGRAM



SLURRY REACTOR DESIGN STUDIES

SLURRY REACTOR CASE

BLOCK FLOW DIAGRAM

Table 4.3

MATERIAL BALANCE -BASIS 3 SHELL GASIFIERS 2500 T/D M/F COAL EACH - SLURRY REACTOR CASE

STREAM NO	1	2	3	4	7	9	11	12	13	14	15	16	17
DESCRIPTION	GASIFIER OUTLET	STEAM TO COS HYDR	COS HYD INLET	COS HYD OUTLET	SOUR WATER	SELEXOL OUTLET	SOUR GAS	RECYCLE GAS	REACTOR FEED	REACTOR PROD	OFF GAS	CO2 OFFGAS	H2 PROD
COMPONENT	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH
H_2O	47.6	12879.0	12926.6	12880.9	12729.7	0.0	0.0	3193.8	3193.8	204.2	0.0	0.0	0.0
H_2	14621.3	0.0	14621.3	14621.3	0.0	14620.2	1.1	3093.8	17714.0	4909.9	4909.9	0.0	943.6
CO	34280.4	0.0	34280.4	34280.4	0.0	34268.4	12.0	5264.6	39533.1	6749.7	6749.7	0.0	0.0
CO_2	1920.9	0.0	1920.9	1966.7	15.5	1712.4	238.8	153.1	1865.6	19671.2	19671.2	19474.5	0.0
N_2	190.5	0.0	190.5	190.5	0.0	190.0	0.5	672.9	862.9	862.9	862.9	0.0	0.0
H_2S	433.9	0.0	433.9	479.7	1.7	0.4	477.5	0.0	0.0	0.0	0.0	0.0	0.0
NH_3	17.2	0.0	17.2	17.2	17.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
COS	46.3	0.0	46.3	0.5	0.0	0.4	0.1					0.0	
C8H170.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1830.3	0.0	0.0	0.0
C1	5.3	0.0	5.3	5.3	0.0	5.3	0.0	18.0	23.3	23.3	2052.2	0.0	0.0
C2=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	506.0	506.0	506.0	648.7	0.0	0.0
C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	162.9	162.9	162.9	208.9	0.0	0.0
C3=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	301.0	301.0	301.0	454.4	0.0	0.0
C3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	33.2	33.2	33.2	59.1	0.0	0.0
C4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.6	3.6	3.6	25.1	0.0	0.0
C4=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21.5	21.5	21.5	129.2	0.0	0.0
C5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	1.0	1.0	32.6	0.0	0.0
C5=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.3	6.3	6.3	136.4	0.0	0.0
C6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.2	22.6	0.0	0.0
C6=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.8	0.8	92.4	0.0	0.0
TOTAL	51563.5	12879.0	64442.4	64442.4	12764.1	50797.2	730.0	13432.8	64229.2	35287.9	36055.2	19474.5	943.6
LB/HR	1098389	232027	1330416	1330416	230372	1070180	27141.6	272358	1342499	1342498	1198365	857090	1902.3

Table 4.3 Cont.

MATERIAL BALANCE -BASIS 3 SHELL GASIFIERS 2500 T/D M/F COAL EACH-SLURRY REACTOR CASE

STREAM NO	18	19	20	CHECK		21	23	26	30	
DESCRIPTION	H/C REC	AFTER H2 REC	BLEED	RECYCLE GAS	F-T STEAM ADDITION	ALCOHOLS	WAX TO HYDRO-CRACKER	CAT POLY FEED	FT PROD HTU FEED	NET F-T YIELD
COMPONENT	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH
H2O	0.0	0.0	0.0	0.0	3193.8					
H2	0.0	3966.3	872.6	3093.7						
CO	0.0	6749.7	1484.9	5264.7						
CO2	0.0	196.7	43.3	153.4						
N2	0.0	862.9	189.8	673.1						
H2S	0.0	0.0	0.0	0.0						
NH3	0.0	0.0	0.0	0.0						
COS										
C8H170.1	0.0	0.0	0.0	0.0						
C1	0.0	2052.2	451.5	1600.7						446.4
C2=	0.0	648.7	142.7	506.0						142.7
C2	0.0	208.9	46.0	162.9						45.9
C3=	68.6	385.8	84.9	301.0				68.6		153.4
C3	16.5	42.5	9.4	33.2				16.5		25.9
C4	20.5	4.6	1.0	3.6				17.6		21.5
C4=	101.7	27.5	6.1	21.5				129.4		107.8
C5	31.3	1.3	0.3	1.0					31.3	31.6
C5=	128.3	8.1	1.8	6.3					128.3	130.1
C6	22.4	0.2	0.0	0.1					22.4	22.4
C6=	91.4	1.0	0.2	0.8					91.4	91.7
C7-C11									226.3	226.3
C12-C18									83.5	83.5
C19-C24							12.4			12.4
C25+							131.3			131.3
ALCOHOLS						157.6				157.6
TOTAL	480.7	15156.4	3334.4	11822.0	3193.8	157.6	143.8	232.0	583.2	1830.4
LB/HR	31389	307984	67756	240227	57539	10678	107474	10340	64938	210696

The BFD for the fixed-bed case is given in Figure 4.3 which differs from Figure 4.2 only in the location of some steam additions and the addition of a water gas shift step. The material balance is given in Table 4.4. In this case, extensive shifting and CO_2 removal are required ahead of the F-T converters. A selective Rectisol unit is used for CO_2 and H_2S removal in this case. This was chosen over Selexol since the latter would have required a double COS hydrolysis and CO_2 removal sequence to achieve adequate COS removal. A zinc guard bed is again employed for polishing.

The fixed-bed converters operate at 37% CO conversion per pass and 97% ultimate conversion with a 2.3 recycle to fresh feed feed ratio. This high level of conversions is only possible because of the very low inerts level (0.4%) in the syntheses gas.

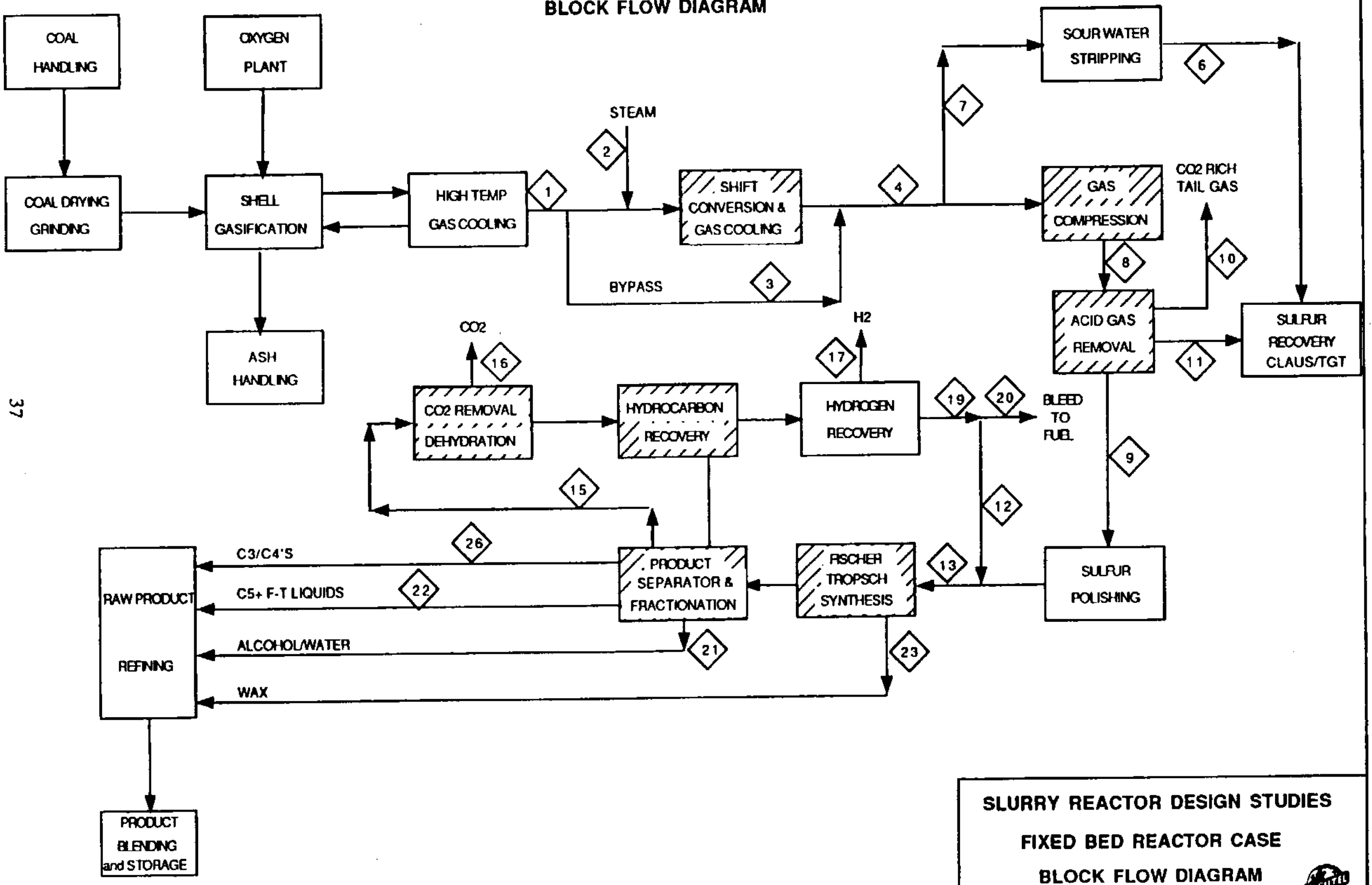
The recycle loop and product recovery are similar to that provided for the slurry reactor case except that:

- Much less CO_2 is removed from the recycle gas,
- Less hydrogen recovery is required to supply the treating units, and
- Considerably more water must be handled.

The question of oxygenates recovery from the product water is not addressed in this study. It could be more of a problem in the fixed-bed than in the slurry reactor case because of the larger quantity of water to be handled. On the other hand, if a cobalt based catalyst is used, oxygenates production could be so low that only a biotreatment step is required on the product water before its reuse as a utility.

Figure 4.3

FISCHER TROPSCH SYNTHESIS
FIXED BED REACTOR CASE
BLOCK FLOW DIAGRAM



SLURRY REACTOR DESIGN STUDIES
FIXED BED REACTOR CASE
BLOCK FLOW DIAGRAM

Table 4.4

MATERIAL BALANCE -BASIS 3 SHELL GASIFIERS 2500 T/D M/F COAL EACH - FIXED BED CASE

STREAM NO.	1	2	3	4	7	9	10	11	12	13	14	15	16	17
DESCRIPTION	GASIFIER OUTLET MPH	STEAM TO SHIFT MPH	SHIFT BYPASS MPH	SHIFT OUTLET MPH	SOUR WATER MPH	RECTISOL OUTLET MPH	CO2 OFF GAS MPH	SOUR GAS MPH	RECYCLE GAS MPH	REACTOR FEED MPH	REACTOR PROD MPH	OFF GAS MPH	CO2 OFFGAS MPH	H2 PROD MPH
H2O	47.6	46035.7	19.2	28904.7	28703.3	0.0	0.0	0.0	0.0	0.0	13535.6	0.0		0.0
H2	14621.3		5892.4	31799.9	0.0	31736.3	63.6	0.0	49908.3	81644.6	51645.9	51645.9		583.7
CO	34280.4		13815.0	17101.8	0.0	16930.8	171.0	0.0	26941.9	43872.7	27564.8	27564.8		0.0
CO2	1920.9		774.1	19099.5	15.3	977.1	17243.7	863.4	22.7	999.8	2304.5	2304.5	2281.4	0.0
N2	190.5		76.8	190.5	0.0	190.1	0.0	0.4	8224.4	8414.4	8414.4	8414.4		0.0
H2S	433.9		174.9	433.9	1.7	0.5	0.0	431.7	0.0	0.0	0.0	0.0		0.0
NH3	17.2		6.9	17.2	17.0	0.2	0.0	0.0	0.0	0.2	0.0	0.0		0.0
COS	46.3		18.6	46.3	0.0	0.0	0.0	46.3	0.0	0.0	0.0	0.0		0.0
C8H170.1	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1880.2	0.0		0.0
C1	5.3		2.1	5.3	0.0	5.2	0.1	0.0	21989.8	21994.9	21994.9	22498.5		0.0
C2=	0.0		0.0	0.0	0.0	0.0	0.0	0.0	1340.1	1340.1	1340.1	1371.1		0.0
C2	0.0		0.0	0.0	0.0	0.0	0.0	0.0	6557.3	6557.3	6557.3	6709.0		0.0
C3=	0.0		0.0	0.0	0.0	0.0	0.0	0.0	687.5	687.5	687.5	762.1		0.0
C3	0.0		0.0	0.0	0.0	0.0	0.0	0.0	634.5	634.5	634.5	736.9		0.0
C4	0.0		0.0	0.0	0.0	0.0	0.0	0.0	74.0	74.0	74.0	137.2		0.0
C4=	0.0		0.0	0.0	0.0	0.0	0.0	0.0	91.1	91.1	91.1	156.5		0.0
C5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	17.2	17.2	17.2	93.7	0.0	0.0
C5=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	29.3	29.3	29.3	114.6	0.0	0.0
C6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4	2.4	2.4	55.4	0.0	0.0
C6=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.7	3.7	3.7	64.9	0.0	0.0
TOTAL	51563.5	46035.7	20780.1	97599.1	28737.4	49840	17478.4	1341.8	116524	166364	136778	122629	2281.4	583.7
LB/HR	1098389	829379	442651	1927767	518141	586663	763831	55505	1744398	2331040	2331040	1920899	100408	1176.7

Table 4.4 Cont.

MATERIAL BALANCE -BASIS 3 SHELL GASIFIERS 2500 T/D M/F COAL EACH- FIXED BED CASE

STREAM NO.	18	19	20	CHECK	21	23	26	30	
DESCRIPTION	H/C REC MPH	AFTER H2 RECOV MPH	PURGE GAS MPH	RECYCLE GAS MPH	ALCOHOLS MPH	WAX TO HYDCRACK MPH	CAT POLY FEED MPH	FT PROD HTU FEED MPH	NET F-T YIELD MPH
H2O	0.0	0.0	0.0	0.0					
H2	0.0	51062.2	1154.0	49908.2					
CO	0.0	27564.8	623.0	26941.8					
CO2	0.0	23.0	0.5	22.5					
N2	0.0	8414.4	190.2	8224.3					
H2S	0.0	0.0	0.0	0.0					
NH3	0.0	0.0	0.0	0.0					
COS	0.0	0.0	0.0	0.0					
C8H170.1	0.0	0.0	0.0	0.0					
C1	0.0	22498.5	508.5	21990.0					503.6
C2=	0.0	1371.1	31.0	1340.1					31.0
C2	0.0	6709.0	151.6	6557.3					151.6
C3=	58.7	703.5	15.9	687.6			58.7		74.6
C3	87.8	649.1	14.7	634.5			87.7		102.4
C4	61.5	75.7	1.7	74.0			61.5		63.2
C4=	63.4	93.2	2.1	91.1			59.2		65.5
C5	76.1	17.6	0.4	17.2				76.0	76.4
C5=	84.5	30.0	0.7	29.3				84.5	85.2
C6	53.0	2.5	0.1	2.4				52.9	53.0
C6=	61.1	3.8	0.1	3.7				61.1	61.2
C7-C11								226.7	226.7
C12-C18								83.6	83.5
C19-C24						12.5			12.5
C25+						131.0			131.0
ALCOHOLS					158.8				158.8
TOTAL	271.3	119164.5	2693.1	116471.4	158.8	143.5	267.2	584.9	1880.2
LB/HR	34592	1784722	40335	1744388	10762	107458	13469	65518	212336

4.3.3 Reactor Design.

The design principles for both slurry and fixed-bed Fischer-Tropsch reactors are the subject of other sections of this report. In the following discussion, these principles (kinetics, heat, and mass transfer, hydraulics and batch-mixing effects) are translated into specific designs for the two F-T cases.

Table 4.5, for the slurry reactor, follows the same format as Tables 2.1 through 2.5 but uses operating variables specific to the proposed process design to establish the slurry bed height requirement for the three simplified reaction models. A bed height of 12 meters is required to provide the design 80% CO conversion using Model 2, the model proposed for the commercial reactor. In this calculation, the reactor is treated as cylindrical, the head volume and the volume occupied by the cooling tubes being neglected. As long as the cooling tubes occupy the entire slurry bed height, and the bottom head is assumed ineffective for reaction, the bed height calculation in Table 4.5 is still valid. The cooling tubes simply reduce the effective diameter of the vessel. Capacity is reduced but the bed height / space velocity relationship is unchanged.

Table 4.6, following the format of Tables 4.1 and 4.2 for methanol and mixed alcohols, assumes the bottom head volume is effective to the extent indicated on line 5 and allows for the reactor volume occupied by the cooling tubes, which are designed to be 0.5 m shorter than the slurry bed height. The bed height is kept approximately constant at 12 m and the effective GHSV is back calculated. Design heat flux is 18.9 kW/m^2 [6,000 $Btu/(h{\cdot}ft^2)$]. The right hand column shows the maximum capacity at 0.15 m/s superficial velocity, assuming the bottom head is 100% effective. It is seen by comparison with Table 4.5, that the head volume slightly over-balances the cooling tube volume and the GHSV decreases from 2.42 to about 2.3 $Nm^3/(h{\cdot}kg\ Cat)$.

The left hand column in Table 4.6 reduces the capacity of the same reactor to 1/6 of the flow given in Table 4.3, the BFD material balance. Superficial velocity is reduced to 0.14 m/s and GHSV to 2.14. Again the bottom head is assumed 100% effective. The central column, which is the design case, assumes that the bottom head is 15% effective and the GHSV rises to 2.42, the same as in Table 4.5. It is noted that 2571 tubes are required in a 4.8 m diameter reactor. These are 38.1 mm in diameter (1.5 ") and reduce the effective cross sectional area of the reactor to 84% of that for the empty vessel.

Table 4.7 presents an analysis of fixed-bed F-T reactor design. Pressure drop and average heat transfer characteristics are shown for two design cases requiring 8 reactors and 7 reactors, respectively, to handle the flow shown in Table 4.4. These designs are compared with similar calculations for the ARGE reactors (based on information given in the Encyclopedia of Chemical Technology, 2nd Edition, Vol. 4). Design space velocity is roughly the same at 1920 $Nm^3/(h{\cdot}m^3)$, though the per pass conversion has been increased from 26% to 37%. This increased is justified by the analysis given in Appendix C. Part of the effect is due to the higher pressure level and part is an assumed higher catalyst activity. The same catalyst bulk density of 850 kg/m^3 (53.1 lb/ft^3) has been used, even though there are indications that a cobalt-based catalyst would have a lower value. Gas properties used in Table 4.7 are derived using API Technical Data Book methods for gas mixtures and are averaged between inlet and outlet conditions.

It will be noted that somewhat longer tubes of significantly smaller diameter are used in the present design than were used in the ARGE reactors. The smaller diameter is to accommodate the higher heat release per unit reactor volume and the longer length is to accommodate the space velocity at the design throughput. While either the 7 reactor or the 8 reactor design might be satisfactory, the 8 reactor design has the shorter tubes and the lower pressure drop and was chosen as the design case. The longer reactor in the 7 reactor case might give fabrication problems.

Table 4.5

	A	B	C	D	E
1	CASE		COMMERCIAL DESIGN		4/17/90
2	uGo - cm/s		15		
3	alpha		-0.5728		
4	l		2.2317		
5	U		2.5604		
6	alpha*		-0.63106016		
7	T - oC		257		
8	Wt.% Slurry		35		
9	Vol.% Solids		10.43659272		
10	dR - cm		480		
11	L - cm		1200		
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		0.046982128		
19	rhoSlurry - g/cm^3		0.924383927		
20	kLa Correction Factor		0.766055793		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Bukur's Model	0.232694165	0.240818841	0.242286696	
23	kLa - s^-1 (uncorr) for H	0.988636466	1.026672881	1.033558604	
24	kLa - s^-1 (corr) for H	0.757350692	0.786488708	0.791763556	
25	kH - (s*kgCat/m3)^-1		0.000507903	3.3e^9*exp(-130/RT)	
26	kH- s^-1		0.106883608	With pressure correction	
27	kH*epsilonL - s^-1	0.082012416	0.081144021	0.080987132	
28	He - (kPa cm^3)/mol		20064929.63		
29	RTL/(uGo*He) - s^-1		17.56864373		
30	kA - s^-1	0.073999154		0.073471909	
31	Stanton No. - target	1.300064776		1.2908018	
32	H2 Conversion	0.869515419		0.697487831	
33	Stanton No. - result	1.300062602		1.290803715	
34	Average uG - cm/s	10.88462595		11.69882413	
35	Stanton No. - reaction		1.425590403		
36	StantonM - target		13.8175399		
37	H2 Conversion		0.724165039		
38	n		0.507975529		
39	Y		0.724165091		
40	StantonM - result		13.81618348		
41	Average uG - cm/s		11.57256221		
42	Pressure - kPa		2600		
43	Reactor Xsect - m^2		18.09557368		
44	Reactor Vol. - m^3		217.1468842		
45	Feed Rate - m^3/h		9771.60979		
46	Feed Rate - Nm^3/h		129122.6672		
47	SV - Nm^3/(m^3 h)		594.6328341		
48	H2+CO Conversion	0.957954853	0.797820715	0.768430137	
49	CO Conversion	0.997583581	0.830825006	0.800218597	
50	STY - Nm^3/(h*m^3)	569.6314091	474.4103929	456.9337902	
51	STY - Nm^3/(kgCat h))	2.294589478	1.931471675	1.863922853	
52	GHSV - Nm^3/(kgCat h)	2.395300229	2.420934477	2.425624351	
53	Catalyst - kg	53906.67341	53335.87853	53232.75515	
54	Catalyst Loading kg/m^3	248.2498131	245.6212012	245.1462997	
55	Reaction Enthalpy - kJ/gmol -CH2-	214.6	214.6	214.6	
56	kgmol/h of H2+CO Conv (=3* -CH2-)	5518.590418	4596.088991	4426.775624	
57	Heat Release - kW	109656.4355	91325.99051	87961.67119	
58	Heat Release - kW/m^3	504.9873772	420.5724196	405.0791312	
59	Heat Release - Btu/(h ft^3)	48825.45754	40663.6715	39165.6798	
60	Mass Transfer Resistance - %	9.770791128	9.352346756	9.279526555	
61	DL - cm2/s	30904.31229	31516.37131	31626.00015	

Table 4.6

SLURRY FISCHER-TROPSCH

DIMENSIONS	6 Reactors	6 Reactors	Max Capacity
Diameter, m	4.8	4.8	4.8
Straight Length of Bed, m	12.00	12.00	12.00
Xsect, m2	18.10	18.10	18.10
Head Vol, m3	28.95	28.95	28.95
Head Volume Effectiveness - %	100.00	15.00	100.00
Tube OD, mm	38.1	38.1	38.1
Tube ID, mm	34	34	34
Tube Length, m	11.50	11.50	11.50
No. of tubes	2571	2571	2732
Tube Area (OD), m2/tube	1.376	1.376	1.377
Tube Xsect (OD), m2/tube	0.001140	0.001140	0.001140
Tube Area (ID), m2/tube	0.000908	0.000908	0.000908
Net Xsect of Reactor, m2	15.16	15.16	14.98
Total Tube Area - m2 (OD)	3538.2	3538.2	3761.3
Reaction Volume, m3	210.92	186.25	208.78
CONDITIONS - PER REACTOR			
Feed Gas Temp., oC	149	149	149
Operating Temp, oC	257	257	257
Operating Pressure, atm	28.3	28.3	28.3
Slurry Concentration, wt%	35	35	35
Gas Holdup, %	24.08	24.08	24.08
Liquid Density, kg/m3	675	675	675
Particle Density, kg/m3	3000	3000	3000
Slurry Density, kg/m3	926.2	926.2	926.2
Catalyst Loading, kg/m3	246.1	246.1	246.1
Catalyst Weight, kg	51911.5	45840.9	51384.2
FF - kgmph	3914.4	3914.4	4161.1
TF - kgmph	4949.4	4949.4	5261.3
TF - m3/h	7610.2	7610.2	8089.8
TF - Nm3/h	110935	110935	117927
R/FF Ratio	0.2644	0.2644	0.2644
MW of TF	20.47	20.47	20.47
MW of Effluent	37.64	37.64	37.64
Syngas in TF - %	90.8	90.8	90.8
Syngas Conversion/Pass - %	80	80	80
-CH2-Production, MTPD	403.4	403.4	428.8
Heat Duty, MW	66.9	66.9	71.1
Inlet Superficial Velocity, m/s	0.139	0.139	0.150
GHSV, Nm3/h kgCat	2.137	2.42	2.295
Mass Velocity, kg/h m2	101313	101313	107699
Space Velocity, Nm3/h m3	526	596	565
STY - kg -CH2-/(h kgCat)	.324	.367	.348
STY - kg -CH2-/(h m3)	80	90	86
Heat Flux, kW/m2	18.912	18.912	18.912
Total Cooling Surface, m2	3538.2	3538.2	3761.3

Table 4.7

FISCHER TROPSCH TUBULAR REACTOR DESIGN 4/17/90

CASE	Prototype ARGE Design	Design 8 Reactors	Design 7 Reactors
Pressure - psia	368	425	425
Temperature - F at Inlet	392	392	392
Temperature - F at Outlet	437	437	437
CO Conversion/Pass - %	26.0	37.2	37.2
CO Ultimate Conversion - %	63.0	96.3	96.3
C5+ Selectivity - %	78.00	87.24	87.24
Shell ID - inches	116.00	188.98	188.98
Shell T-T - feet	45	50	56
Tube ID - inches	1.80	1.34	1.34
Tube OD - inches	1.96	1.50	1.50
Tube Length - feet	39.5	44.5	50.5
No. of Tubes	2000	9602	9602
Tube xsection (ID) - sq ft	.0177	.0098	.0098
Tube Volume - cu ft	1396	4176	4739
Tube Area - sq ft	37228	149731	169920
Catalyst Bed Height - feet	36.5	41.5	47.5
Catalyst Volume - cu ft	1290	3894	4457
Catalyst Density - lb/cu ft	53.1	53.1	53.1
Catalyst Weight - pounds	68500	206776	236671
Catalyst Contact Area - sq ft	34400	156065	178629
Tube Xsect Area as % of Shell Area	57.099	60.176	60.176
Fresh Feed - lb mph per Reactor	2092.0	6230.0	7120.0
Total Feed - lb mph per Reactor	6903.6	20795.7	23766.6
Recycle/FF ratio	2.30	2.338	2.338
SV -FF Basis - Nm3/hxm3	582	574	574
SV -TF Basis - Nm3 /hxm3	1921	1917	1915
Prod - lb C5+/hrxlb cat	.062	.111	.111
C5+ HC - lb/hr	4281	22978	26260
Total HC - lb/hr	5544	26542	30334
MW of Inlet Gas	14.60	14.01	14.01
MW of Outlet Gas	16.38	17.04	17.04
Gas Viscosity - cp - Avg	0.0205	0.0201	0.0201
Gas Density - lb/cuft - Avg	.629	.705	.705
Gas Therm Cond - Btu/hrxftxF - Av	.060	.062	.062
Gas Sp. Ht. - Btu/lbxF - Avg	.556	.578	.578
Gas Prandtl No.	.458	.456	.456
Mass Velocity - lb/hrxsqft	2852	3105	3549
Reynold's Number - basis tube ID	8623	7958	9095
Catalyst Diam - feet	.0122	.0122	.0122
Reynold's Number - basis part diam	701	779	890
f	1.08	1.08	1.05
Press Drop - psi/ft	.41	.44	.55
Press. Drop - psi	15.0	18.1	26.3
Heat Release - MM Btu/hr	26.5	130.2	148.8
Heat Flux - Btu/hrxsqft	713	870	876
d/D	.081	.098	.098
Int Heat Trans Coef-Btu/hrxsqftxF	65	81	90
Film Temp Diff - F	11	11	10
Wall Resistance - k/t	938	953	953
Steam Side h - Btu/hrxsqftxF	250	250	250
Overall U	49.1	57.6	62.0
Overall Delta T - F	15	15	14
Gas Res. Time - sec	10.11	11.32	11.34
Tube area/tube volume	26.67	35.86	35.86
Heat Release/Unit Volume	19013	31188	31409

Table 4.8

FIXED-BED FISCHER TROPSCH

DIMENSIONS	8 Reactors
Diameter, m	4.8
Straight Length of Bed, m	12.65
Xsect, m2	18.10
Tube OD, mm	38.1
Tube ID, mm	34.04
Tube Length, m	13.56
No. of tubes	9602
Tube Area (OD), m2/tube	1.623
Tube Xsect (OD), m2/tube	0.001140
Tube Area (ID), m2/tube	1.450
Tube Xsect (ID), m2/tube	0.000910
Net Xsect of Reactor, m2	8.74
Total Tube Area - m2 (ID)	13926
Total Tube Area - m2 (OD)	15589
Reaction Volume, m3	110.29
CONDITIONS - PER REACTOR	
Feed Gas Temp., oC	200
Operating Temp, oC	225
Operating Pressure, atm	28.3
Catalyst Loading, kg/m3	850
Catalyst Weight, kg	93747.6
FF - kgmph	2825.9
TF - kgmph	9432.9
TF - m3/h	13628.4
TF - Nm3/h	211428
R/FF Ratio	2.338
MW of TF	14.01
MW of Effluent	17.04
Syngas in TF - %	75.45
Syngas Conversion/Pass - %	36.89
'-CH2-Production, MTPD	294.6
Heat Duty, MW	38.2
Inlet Superficial Velocity, m/s	0.530
GHSV, Nm3/h kgCat	2.26
Mass Velocity, kg/h m2	15127
Space Velocity, Nm3/h m3	1917
STY - kg -CH2-/(h kgCat)	.131
STY - kg -CH2-/(h m3)	111
Heat Flux, kW/m2 (ID)	2.74
Total Cooling Surface, m2	13916.7

4.4 Key Design Parameters

An AIChE paper, reproduced as Appendix D, gives some criteria for comparing the fixed-bed and the slurry reactor. In this paper it is pointed out that the same GHSV [in $Nm^3/(h.kg\ Cat)$] should be required regardless of reactor type, to achieve the same conversion per pass. Owing to the lower catalyst loading, the slurry reactor will require a greater reaction volume. It was also noted that the fixed-bed reactor will generally run at a lower conversion/pass. The following discussion briefly summarizes the key design parameters in the final reactor selections of Section 4 and rationalizes these against Appendix D.

4.4.1 Methanol Design Parameters

Key methanol reactor design variables are summarized below:

	Slurry	Fixed-Bed
Temperature, °C	250	255 (outlet at end of run)
Pressure, atm	99	54
R/FF Ratio	2.2	3.0
CO in Total Feed, %	12.4	12.6
CO Conversion, %	70.0	54.8
Superficial Velocity, m/s (based on empty shell)	0.136	0.388
GHSV, $Nm^3/(h \cdot kgCat)$	7.0	7.0
SV, $Nm^3/(h \cdot m^3)$	1702	8771
STY, kg MeOH/(h·kgCat)	0.945	0.756
STY, kg MeOH/$(h \cdot m^3)$	230	946
(based on empty shell)	216	457
Effective XSect Area, %	94	48
Methanol Production, MTD	1488	1488

Both reactors have the same shell diameter, 4.8 meters. The slurry reactor has a tangent to tangent height of 18 meters, the fixed-bed reactor, 7.5 meters. The slurry reactor pressure has been raised in order to increase capacity to that of the fixed-bed. End of run temperature is shown since this limits the equilibrium conversion and hence the design. Lower start of run temperatures improve conversion.

Once the shell diameter is set, the capacity of a given reactor depends on the allowable superficial velocity (corrected for the effective cross sectional area) and the total volume of gas to be handled. The allowable superficial velocities based on an empty reactor are 0.136 and 0.388 m/s, respectively, a factor of 2.85 in favor of the fixed-bed. This is balanced by the difference in total gas handled (owing to differences in recycle ratio, conversion per pass and pressure level) so that the capacities are equal in terms of methanol production.

The required height of the reactor can be calculated from the STY in kg MeOH/$(h \cdot m^3)$, the capacity in kg methanol per hour and the available cross sectional area. The STY can, in turn, be calculated from the space velocity, the conversion per pass and the concentration of reactants in the reactor feed. As best as can be determined, the slurry reactor and the fixed-bed reactor are designed to the same GHSV in $Nm^3/(h \cdot kgCat)$ to achieve the same approach to equilibrium. As discussed in Appendix D, the catalyst loading in kg/m^3 of reactor volume is highly significant and gives the fixed-bed reactor a significantly lower height requirement. When all factors are combined, the slurry reactor is about twice the height of the fixed-bed reactor.

4.4.2 Fischer-Tropsch Design Parameters

In similar fashion to methanol, F-T design parameters are summarized below:

	Slurry	Fixed-Bed
Number of Reactors	6	8
Height of Bed, m	12.0	12.65
Reaction Volume, m3	1118	887
Temperature, °C	257	225 (outlet at start of run)
Pressure, atm	28.3	28.3
R/FF Ratio	0.264	2.34
Syngas in Total Feed, %	90.8	75.5
Syngas Conversion, %	80.0	36.9
Superficial Velocity, m/s	0.139	0.53
(based on empty shell)	0.13	0.26
GHSV, $Nm^3/(h \cdot kgCat)$	2.42	2.26
SV, $Nm^3/(h \cdot m^3)$	596	1917
STY, kg $-CH_2-/(h \cdot kgCat)$	0.318	0.131
STY, kg $-CH_2-/(h \cdot m^3)$	78	111
(based on empty shell)	216	457
Effective XSect Area, %	94	48
Hydrocarbon Production, MTD	2294	2312

A key difference is the higher design temperature in the slurry reactor case as compared to the fixed-bed reactor. Equilibrium is no longer a consideration so the improved activity at the higher temperature is significant. The result is that 80% conversion per pass is achieved in the slurry reactor as compared to 37% in the fixed-bed reactor, at the same pressure level and at roughly the same GHSV in each case. Comparisons given in Appendix D assume temperature is the same and the allowable space velocity rises as conversion level drops.

The allowable superficial velocity for the fixed-bed reactor, based on the empty shell, is twice that for the slurry reactor. This velocity is set by pressure drop considerations. It is not as high as in the fixed-bed methanol reactor and the primary reason is the lower design pressure. Owing to differences in conversion per pass and recycle ratio, the fixed-bed reactors must handle 2.54 times the amount of gas as the slurry reactors for the same production. Consequently, six slurry reactors have roughly the same capacity as eight fixed-bed reactors.

At roughly the same value of GHSV in $Nm^3/(h \cdot kgCat)$, the SV, in $Nm^3/(h \cdot m^3)$ is about 3 times greater in the fixed-bed case due to the higher catalyst loading. At the lower gas concentration and conversion level in the fixed-bed, the difference in STY is not nearly as great; 111 $kg/(h \cdot m^3)$ for the fixed-bed versus 78 for the slurry reactor. This ratio is only slightly more than the ratio in number of reactors and reaction bed heights are, therefore, roughly comparable.

5.0 AREAS NEEDING FURTHER DEVELOPMENT

5.1 Backmixing Effects

One of the key issues left only partially defined in this study is the exact extent of backmixing effects on scale-up. The effect has been minimized by the choice of 80% rather than 90% as the design conversion per pass. There may be cases where higher conversions are desired and further study of backmixing effects is recommended.

Several more detailed slurry reactor models have been developed, and are discussed in Appendix A and B, which provide solutions to backmixing effects by incorporating axial dispersion coefficients. In order to use these models for scale-up, it is necessary to obtain axial dispersion data in a system which is physically and geometrically similar to the proposed design. This means that pilot plant data are required over a range of reactor diameters at superficial velocities and catalyst concentrations equal to those proposed for design. It is also important that cooling tubes be incorporated into the reactor design in the same fashion and with the same surface to volume ratio proposed for the commercial reactor.

It has not been possible to use published models directly for scale-up because of the way they handle gas holdup and other factors. All of the models proposed to date use an overly simplified expression in average gas velocity to estimate gas holdup. Most assume a constant contraction factor. All use a simplified expression for reaction rate which is first order in hydrogen concentration. These approaches may well be adequate for design purposes, but pilot plant confirmation is needed. In addition, none of the previous experimental work has been at the design superficial velocity and catalyst concentration proposed in this study.

The La Porte reactor offers the possibility of obtaining useful design information for model development if converted to Fischer-Tropsch operation. If backmixing effects are indeed significant, some consideration might be given to installing baffles or trays in the reactor to reduce backmixing. The presence of suspended catalyst is a potential problem, but if effective baffling can be provided in a fluidized-bed reactor (as in Mobil's MTG process) then its use in a slurry reactor may also be feasible.

5.2 Pressure Effect

As discussed in Section 2, Bechtel was unwilling to assume a linear pressure effect on the GHSV requirement for a given conversion level as predicted by the Fischer-Tropsch slurry reactor models. Gulf data on fixed-bed cobalt catalyst indicated that the "catalyst activity" is not linear with pressure but flattens off at pressures above 200 psia. For design purposes, a square root decrease in the rate constant with pressure level above 1100 kPa (160 psi) was assumed. Further data would be useful and some may be available in the literature (see Appendix B - part 3) but further measurements of the pressure effect at reactor design conditions are recommended.

It would be of interest in future studies to examine the effect of pressure on the reactor cost comparison. As described in Section 4, a compression step has been added to roughly double the pressure out of the Shell gasifier before F-T synthesis. It should be possible to gain a rough idea of the effect of pressure on cost by prorating from this study. The assumption of a square root effect of pressure on reactor size could then be compared with the linear assumption. This would set a reasonable goal for the proposed experimental studies.

5.3 Heat Removal

By increasing reactor pressure and catalyst concentration, heat removal requirements per unit reactor volume have been increased to the point where the reactor becomes quite packed with cooling tubes. A double tube sheet design with bayonet tubes has been adopted for this study, but at some point it may be worth again considering an external cooling loop. External cooling loops have been provided in bubble columns in which rapid circulation is provided by the difference in density between the aerated reactor and the exchanger. No pump is required. As far as is known, such a design has yet to be applied when a slurry is present, but the concept still seems applicable.

5.4 Improved Catalyst Activity

Allowable space velocity in a methanol reactor is roughly four times that in a F-T reactor, indicating that there may be room for improvement in F-T catalyst activity. If activity is improved, the mass transfer resistance will become more limiting. Some guidance could be provided by estimating the capacity of the reactor if the mass transfer resistance were completely controlling. Under these conditions, heat removal would become a problem and an external circulation loop might be a necessity.

5.5 Use of Steam at Low H2/CO Ratio

The slurry F-T reactor used in this study operates below 0.67 H_2/CO inlet ratio so that the inlet ratio is less than the expected consumption ratio. This has been compensated for by steam addition. This concept appears reasonable but it would be useful to have actual data under these conditions. If it is not feasible, the solution is an extra water gas shift reaction step, ahead of F-T synthesis, as provided by MITRE.

5.6 Catalyst Activity Maintenance

A primary consideration in choosing a slurry reactor is the expected life of the catalyst. If only a few months life is expected, there is considerable incentive to go to a system which can handle continuous catalyst replacement. This is primarily an operating problem and the relative economics can be defined by a sensitivity analysis.

5.7 Mixed Alcohols

Design data on the Octamix process in a slurry reactor are lacking. For one thing, the proper slurry liquid for mixed alcohol synthesis must be determined. Higher oxygenates will undoubtedly show some solubility in the hydrocarbon liquid used for the slurry methanol process. If the higher oxygenates form a stable liquid phase, then a portion of the product could be used for slurry liquid as in the Fischer-Tropsch design. Similar facilities would be required to recover product from catalyst .

The assumption that GHSV requirement is the same as the fixed-bed may be conservative. Since the equilibrium limitation is not as severe as when methanol alone is being produced, it may be possible to take advantage of a somewhat higher average temperature in the slurry reactor to reduce the GHSV requirement. In this case the height shown for the slurry reactor can be reduced. With the cooperation of Lurgi, test runs in the La Porte reactor are recommended.

5.8 Fixed-Bed Modelling

The gas phase fixed-bed reactor can be accurately modelled using stepwise integration procedures and providing an indication of temperature profiles. The difficult part will be to simulate accurately the two-phase behavior in the portion of the reactor where condensation is occurring. This is known to occur in F-T synthesis and, apparently, can also occur in high conversion methanol synthesis with a stoichiometric feed gas, enhancing the conversion. These phenomena may require experimental verification before an acceptable model can be developed.