

# **NOTICE**

**CERTAIN DATA  
CONTAINED IN THIS  
DOCUMENT MAY BE  
DIFFICULT TO READ  
IN MICROFICHE  
PRODUCTS.**

**TISSOT**

DOE/PC/89867-T2  
(DE91005752)

**SLURRY REACTOR DESIGN STUDIES: SLURRY VS. FIXED-BED REACTORS  
FOR FISCHER-TROPSCH AND METHANOL**

**Final Report**

**June 1990**

**Work Performed Under Contract No. AC22-89PC89867**

**For  
U.S. Department of Energy  
Pittsburgh Energy Technology Center  
Pittsburgh, Pennsylvania**

**By  
Bechtel Group, Inc.  
San Francisco, California**

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

DOE/PC/89867--T2

DE91 005752

**FINAL REPORT**  
**SLURRY REACTOR DESIGN STUDIES**

DOE Project No. DE-AC22-89PC89867  
Bechtel Job No. 20586

**SLURRY VS. FIXED-BED REACTORS  
FOR FISCHER-TROPSCH AND METHANOL**

**J. M. FOX, STUDY MANAGER**  
**B. D. DEGEN, LEAD PROCESS ENGINEER**  
**GROVER CADY, MECHANICAL SPECIALIST**  
**F. D. DESLATE, COST ENGINEER**  
**R. L. SUMMERS, COST ENGINEER**

**CONSULTANTS**  
**PROF. AYDIN AKGERMAN, TEXAS A&M**  
**PROF. J. M. SMITH, U.C. DAVIS**

**BECHTEL GROUP, INC.**

**JUNE 1990**

## EXECUTIVE SUMMARY

### Background

The objective of this study was to set the groundwork for further development of indirect coal liquefaction technology via Fischer-Tropsch (F-T) or methanol synthesis. In particular, it was desired to know exactly how the slurry reactor concept could be used to best advantage. In the slurry reactor, developed in Germany in the 1950's, powdered catalyst is suspended in a heavy oil - the heavy end of Fischer-Tropsch product, for example - and the synthesis gas is bubbled through the mixture at reaction temperature and pressure. The reactants dissolve in the oil and react over the catalyst. Agitation from the gas flowing through the column - as in a bubble column reactor - provides for good mass transfer and heat transfer characteristics. The heat of reaction can be removed by cooling tubes inserted into the liquid.

The slurry reactor has been proposed for Fischer-Tropsch operations in the wax producing mode, which is preferred from a selectivity standpoint. Production of light ends is minimized and the heavy wax portion of the product can readily be upgraded to useful products. Fluidized-bed reactors cannot operate in this mode. Tubular-fixed-bed reactors have been in operation at Sasol for many years for wax production and will be used by Shell in their Middle Distillate Process being installed in Malaysia. A key question, therefore, is how does the slurry reactor stack up against the tubular-fixed-bed reactor?

This study indicates that a key advantage for the slurry F-T reactor is its ability to convert the low  $H_2/CO$  ratio synthesis gas (0.7 ratio or less) produced by coal gasifiers without ratio adjustment. An iron based Fischer-Tropsch catalyst can accept such a gas, converting it to liquid hydrocarbons with  $CO_2$  as the primary byproduct. The tubular-fixed-bed reactors cited above have been operated on 2.0  $H_2/CO$  ratio gas and produce water as the byproduct. They would not be expected to be able to use a low ratio gas because of carbon formation. The main product from this study, therefore, is a cost comparison of slurry F-T reactors operating on low ratio gas versus fixed-bed F-T reactors operating on high ratio gas after composition adjustment. Designs have been prepared for those sections of a coal-based Fischer-Tropsch plant affected by reactor selection, equipment sized and costed with particular attention to the reactors themselves, and operating costs examined.

The slurry reactor has also been proposed for the synthesis of methanol and mixed alcohols. Chem Systems developed the original concept and Air Products has been piloting the so-called liquid phase methanol (LPMeOH<sup>TM</sup>) process at LaPorte, TX, and now is designing a demonstration unit for Great Plains as part of Clean Coal 3. A specific niche has been identified for the slurry reactor in the coproduction of methanol and electric power in a combined cycle operation. A low conversion, once-through operation is used with low ratio gas as produced in the gasifier. Unconverted gas is directed to gas turbines for power generation. Methanol can be stored and used for supplemental firing of the gas turbines or sold.

Since the coproduction type of operation has been well studied and since it was not certain how to design a tubular-fixed-bed reactor for such an operation, attention was directed to ascertaining how well the slurry reactor would compete costwise with the fixed-bed reactor in a conventional, high yield methanol plant design with recycle. It was recognized that this would probably not be the optimum application for a slurry reactor, with its superficial velocity limitation, but it was felt that something could be learned about its preferred range of applicability. A brief look was also taken at mixed alcohols operation, using Lurgi's Octamix<sup>TM</sup> process as a model.

## Reactor Design Criteria

Before attempting to perform an economic comparison, it was necessary to develop a rational basis for reactor comparison. Reaction kinetics, mass transfer, heat transfer and hydrodynamics were examined and effects of operating variables such as superficial velocity, slurry concentration, temperature and pressure were determined. It is necessary to allow for the effect of slurry concentration on mass transfer, for example, and this report provides a basis for doing so. A consistent process design basis was also developed based on the use of the Shell gasifier. This effort is the subject of Sections 2 through 5 of the report. This material should be of value to the DOE in setting the basis for the proposed baseline economic evaluation of advanced Fischer-Tropsch technology (RFP No. DE-RP22-90PC90027).

Scale-up of the slurry F-T reactor has been the subject of numerous technical articles. A high conversion per pass is preferred since recycle of unconverted syngas reduces the production from a slurry reactor, which has a superficial velocity limitation. Conversions of 90% or more have been demonstrated in high L/D pilot plant equipment but backmixing in a commercial reactor will limit the conversion which can be achieved. This study has taken a conservative approach by assuming that complete backmixing will occur and limits conversion per pass to 80%.

On the other hand, it has been assumed that superficial velocity and catalyst slurry concentration can be taken well beyond levels which have been demonstrated in F-T pilot plant operations to date. There is good reason for this since hydrodynamic studies sponsored by the DOE (e.g. Contract No. DE-AC22-86PC90012) have demonstrated reasonable gas holdup and gas dispersion under such conditions. Air Products' development work with the LPMeOH™ process in the LaPorte pilot plant is also considered very significant.

## Conclusions

The primary conclusion from this study is that the slurry reactor has both advantages and disadvantages and that proper applications must be sought. Coal-based Fischer-Tropsch, as described above, appears to be such an application. It was found that, in a project producing 20,000 BPSD of Fischer-Tropsch products from 7500 TPD of moisture free Illinois No. 5 coal, plant investment can be reduced by \$91 MM if the process scheme using slurry reactors is employed. This is a savings of about 8.5% on the total plant investment. The savings are roughly equally divided between the reactors themselves and the process simplifications resulting from the use of low H<sub>2</sub>/CO ratio gas.

The fact that the slurry reactor can be operated continuously at the end of run temperature required for the fixed-bed reactor proved a significant advantage and permitted operation at roughly the same space velocity despite the fact that conversion was much higher (80% per pass versus 37% per pass). This enabled the use of 6 slurry reactors for the same capacity as 8 fixed-bed reactors, despite an intrinsically lower catalyst loading.

In order to gain these reactor savings it is necessary to design to an inlet superficial velocity of 0.14 to 0.15 m/s (0.46 to 0.49 ft/s) and a slurry concentration of 35 wt%. Typical pilot plant operations have been at about half these values. If the more conservative approach of using demonstrated pilot plant conditions is taken, the number of reactors increases from 6 to 11 and the cost of the reactors approaches that of the fixed-bed system. The net savings in investment reduces to \$52 MM. There is thus a considerable incentive to demonstrate the higher levels of velocity and concentration.

There is even the possibility of going still further. It is understood that Air Products is designing the Great Plains demonstration unit for a superficial velocity of 0.24 m/s (0.8 ft/s). Slurry concentrations higher than 35 wt% are also possible. Again, the methanol system has been run up to 45 wt% slurry but under these conditions mass transfer resistance becomes a significant factor. This should not be true in the case of Fischer-Tropsch reactors which operate at only about one third the space velocity of a methanol reactor.

Operating cost was found not to vary greatly between the two reactors provided the slurry reactor catalyst is assumed to have an equivalent 60 day life (continuous replacement would be used) and the fixed-bed reactor catalyst, a life of one year. There is very little basis for either of these replacement rates and this is an item for further investigation. It was more difficult to balance energy requirements in the fixed-bed case leading to higher fuel gas requirement, but this is at least in part due to the use of the Shell gasifier. The Texaco or Dow type of gasifier would fit better into the fixed-bed processing scheme whereas the Shell gasifier appears a good choice for the slurry case..

For a conventional recycle methanol application the situation is reversed. The slurry methanol synthesis loop, at \$41 MM for 1640 TPD of production, is almost twice as expensive as a tubular-fixed-bed system. The reasons are apparent when the design conditions are examined:

- In order to achieve design production from the slurry reactor, pressure is raised to 100 atmospheres. This reduces recycle requirement to a minimum and permits higher mass flows at a given superficial velocity.
- Using a stoichiometric feed gas it is possible to run the fixed-bed reactor at 55 atmospheres. Pressure drop is a limitation, but Lurgi assures that the design capacity can be produced.
- Space velocity is roughly the same for both reactors per unit weight of catalyst present. Because of the lower catalyst loading per unit of reaction volume, the slurry reactor is over twice the height of the fixed-bed reactor.
- The entire shell of the slurry reactor must be designed for reaction pressure of 100 atmospheres. With the fixed-bed reactor only the heads and tube sheets need be designed for reaction pressure. Thus even if the fixed-bed operating pressure were 100 atmospheres, shell weight would be less.
- The combined effect of the above is to negate the lesser tube weight of the slurry reactor and produce a more massive and costly vessel.
- Finally, feed gas compression is required, whereas the fixed-bed reactor can operate at the pressure level available from a Texaco gasifier.

No conclusions can be drawn from this study concerning once-through methanol operations. Without recycle, pressure can be reduced in half, essentially cutting the weight of the slurry reactor in half. The comparison would then depend on what design conditions can be developed for the fixed-bed reactor operation.

It was not possible to design a slurry reactor mixed alcohol plant without a better feel for what limits conversion. Lurgi requires 100 atmospheres for the fixed-bed operation with quite a low space velocity. Production is 460 TPD from the same size reactor used for 1640 TPD of methanol production. The high pressure was stated to be essential. This being the

case, it does not appear that this is a good application for the slurry reactor in its present configuration

## RECOMMENDATIONS

Further development of the slurry reactor for the Fischer-Tropsch application can be recommended without qualification. It appears to have intrinsic cost advantages over the fixed-bed reactor for this application and is more amenable to further improvement. The reactor is not easy to scale-up, however, and further experimental pilot plant work is recommended to demonstrate operation at the design conditions used in this study in a reactor of sufficient size that axial dispersion effects can be determined. Conversion of the LaPorte reactor to Fischer-Tropsch synthesis should be possible and is recommended.

A number of design needs are listed in Section 5 of this report. Foremost among these are the demonstration of backmixing effects, the possibility of reducing backmixing by use of baffles, possible advantages of higher conversion levels than were used in this study and better experimental definition of the effects of pressure, superficial velocity and catalyst concentration.

Reactor modifications that will limit backmixing and give higher conversion may be worth pursuing. A better feel for the economics could be gained by an analysis of the two extreme models, plug flow and complete backmixing. This would define the incentive for further development efforts. It is also noted that, when operating conditions are chosen to maximize capacity or new more active catalysts are developed, the number of cooling tubes increases to the point where alternate reactor designs with external cooling may once again become worthy of consideration.

Finally, it is felt that this study represents a good first step towards DOE's proposed baseline study on indirect liquefaction. It is recommended that the design assumptions used here be carefully reviewed and used for the definition of design conditions for that study.



## Contents

		Page
Section	1.0 INTRODUCTION	1
Section	2.0 SLURRY REACTOR DESIGN	2
	2.1 Definition of the "Slurry Reactor"	2
	2.2 Slurry Reactor Applications	2
	2.3 Synopsis of Consultant's Review	8
	2.4 Results of Model Simulations	11
Section	3.0 FIXED-BED REACTOR DESIGN	20
	3.1 Types of Fixed-Bed Reactors	20
	3.2 Fixed-Bed Reactor Design Principles	20
	3.3 Comparison with the Slurry Reactor	22
Section	4.0 PROCESS AND REACTOR DESIGN BASES	24
	4.1 Methanol	24
	4.2 Mixed Alcohols	29
	4.3 Fischer-Tropsch	31
	4.4 Key Design Parameters	45
	4.5 Low Pressure Design	47
	4.6 Baffled Slurry Reactors	52
	4.7 Superficial Velocity and Catalyst Concentration	57
Section	5.0 AREAS NEEDING FURTHER DEVELOPMENT	60
Section	6.0 CAPITAL AND OPERATING COST COMPARISONS	62
	6.1 Fischer-Tropsch Comparison	62
	6.2 Methanol and Mixed Alcohols	71
	Table of Nomenclature	75

APPENDIX A AKGERMAN REPORTS

APPENDIX B SMITH REPORTS

APPENDIX C REVIEW OF FIXED-BED AND SLURRY REACTOR KINETICS

APPENDIX D FISCHER-TROPSCH REACTOR SELECTION (AIChE Paper)

APPENDIX E METHANOL AND MIXED ALCOHOLS DESIGN DATA SHEETS

APPENDIX F FISCHER-TROPSCH DESIGN DATA SHEETS

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

## 1.0 INTRODUCTION

The objective of these studies was to perform a realistic evaluation of the relative costs of tubular-fixed-bed and slurry reactors for methanol, mixed alcohols and Fischer-Tropsch syntheses under conditions where they would realistically be expected to operate. The slurry Fischer-Tropsch reactor was, therefore, operated at low H<sub>2</sub>/CO ratio on gas directly from a Shell gasifier. The fixed-bed reactor was operated on 2.0 H<sub>2</sub>/CO ratio gas after adjustment by shift and CO<sub>2</sub> removal. Every attempt was made to give each reactor the benefit of its optimum design condition and correlations were developed to extend the models beyond the range of the experimental pilot plant data.

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

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

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

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

Section 5 covers areas for further development.

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

## 2.0 SLURRY REACTOR DESIGN

### 2.1 Definition of the "Slurry Reactor"

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

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

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

1. It has been chosen by Air Products for the liquid phase methanol reactor after careful review and testing of other types of reactors including those with slurry circulation through an external exchanger, both ebullated-bed and entrained-bed versions.
2. It has long been considered for application to liquid phase Fischer-Tropsch synthesis since first being proposed by Kolbel and Ackermann in the 1930's.
3. It is amenable to modelling and scale-up, though more difficult to analyze than a fixed-bed reactor. The literature on this subject is extensive.

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

### 2.2 Slurry Reactor Applications

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

- 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:

- o The ebullated-bed reactor is employed for resid hydrocracking and is proposed for coal liquefaction. In this design, larger catalyst particles are used and the liquid product overflows from the reactor free of the catalyst.
- o The pipeline loop reactor is used for polymerization of olefins to isotactic polymers (Figure 2.2). This design takes advantage of the improvement in product quality and conversion when plug flow characteristics apply. The product is removed as a solid which contains catalyst particles dispersed in it. External jackets cool the reactants.
- o Pipeline reactors are used in the homogeneous two-stage partial oxidation of ethylene to acetaldehyde. The catalyst is circulated from the reactor to the oxidizer, where it is reoxidized with air. A bubble column is used for the single step process with in-situ oxygen addition. Heat removal is by water evaporation from the liquid phase.
- o Mechanically agitated reactors have been used for the olefin polymerization and oxychlorination processes, among others. Several such reactors can be placed in series if high conversions are required.
- o Some slurry reactors incorporate special internals such as porous plate distributors or internal draft tubes to promote circulation. The jet-bubbling reactor, used by Chiyoda/Bechtel for SO<sub>2</sub> scrubbing, employs a draft tube.
- o Several schemes are used for heat removal where the process is highly exothermic. Most reactors use internal coils or solvent evaporation but circulation through an external heat exchanger has sometimes been used where heat removal surface requirements are high compared to reactor volume. Air Products has looked at external circulation loops for their liquid phase methanol process, both with ebullated-bed and entrained-bed designs (Figure 2.3). These designs require a slurry pump and internal cooling coils are preferred as long as there is adequate space in the reactor.
- o A circulating design without a slurry pump has been used for xylene oxidation (Figure 2.4). The design achieves rapid circulation by virtue of differences in density between the contactor and the heat exchanger. It has not yet been applied to slurry systems but might be worthy of consideration in future development work.

The rapid internal circulation of the liquid phase in large scale slurry bubble columns has both advantages and disadvantages. From a reaction standpoint, it limits the conversion which can be achieved in a given size reactor. From a heat removal standpoint, however, it has the advantage that temperatures within the vessel are quite uniform and heat transfer coefficients are good. It is possible to use a reactor-to-coolant temperature difference of 50 °F with an overall heat flux of 6000 Btu/(hr · ft<sup>2</sup> · °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)

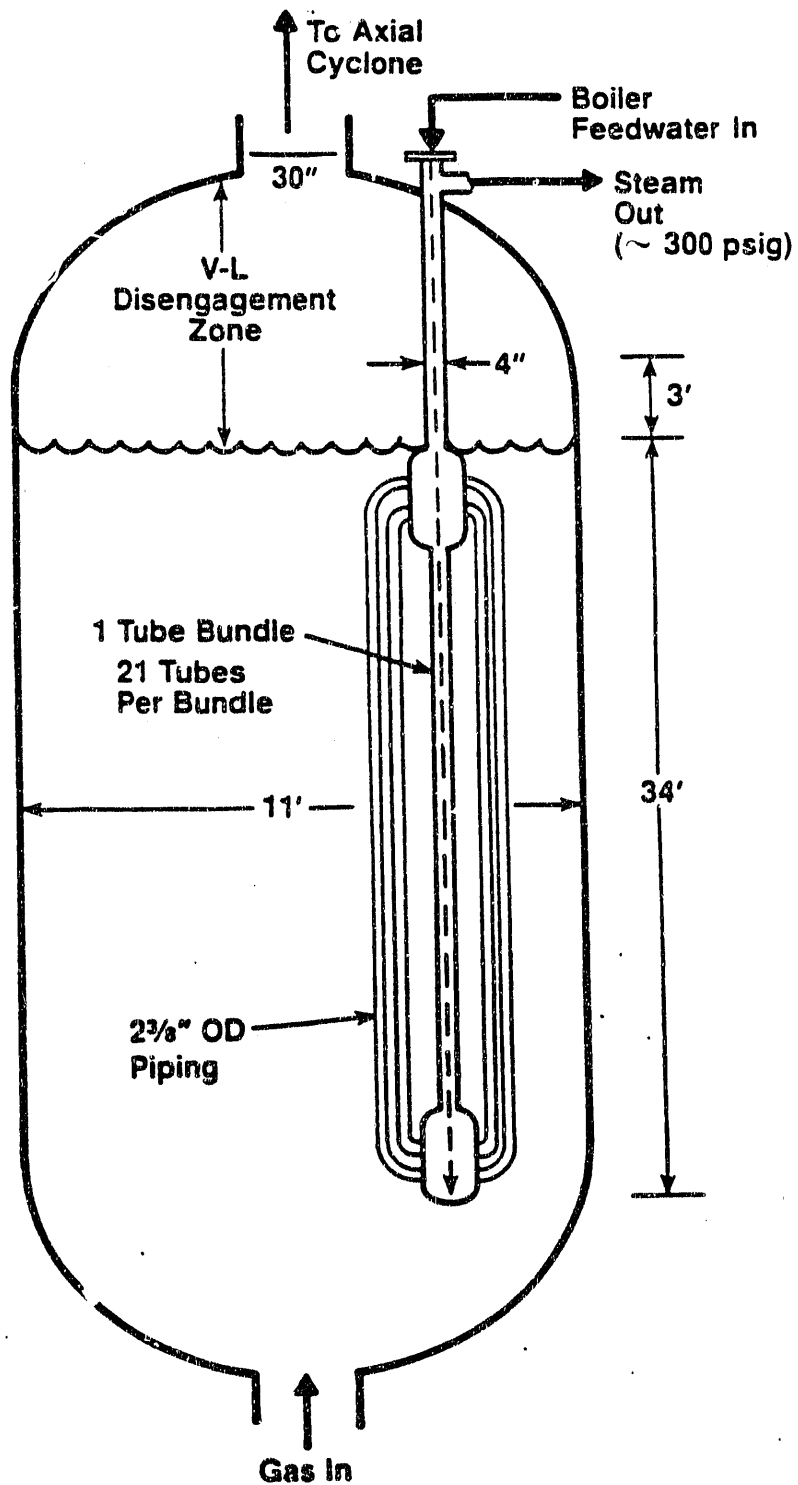


Figure 2.2

SLURRY REACTOR DESIGN  
PIPELINE LOOP REACTOR  
FOR POLYETHYLENE

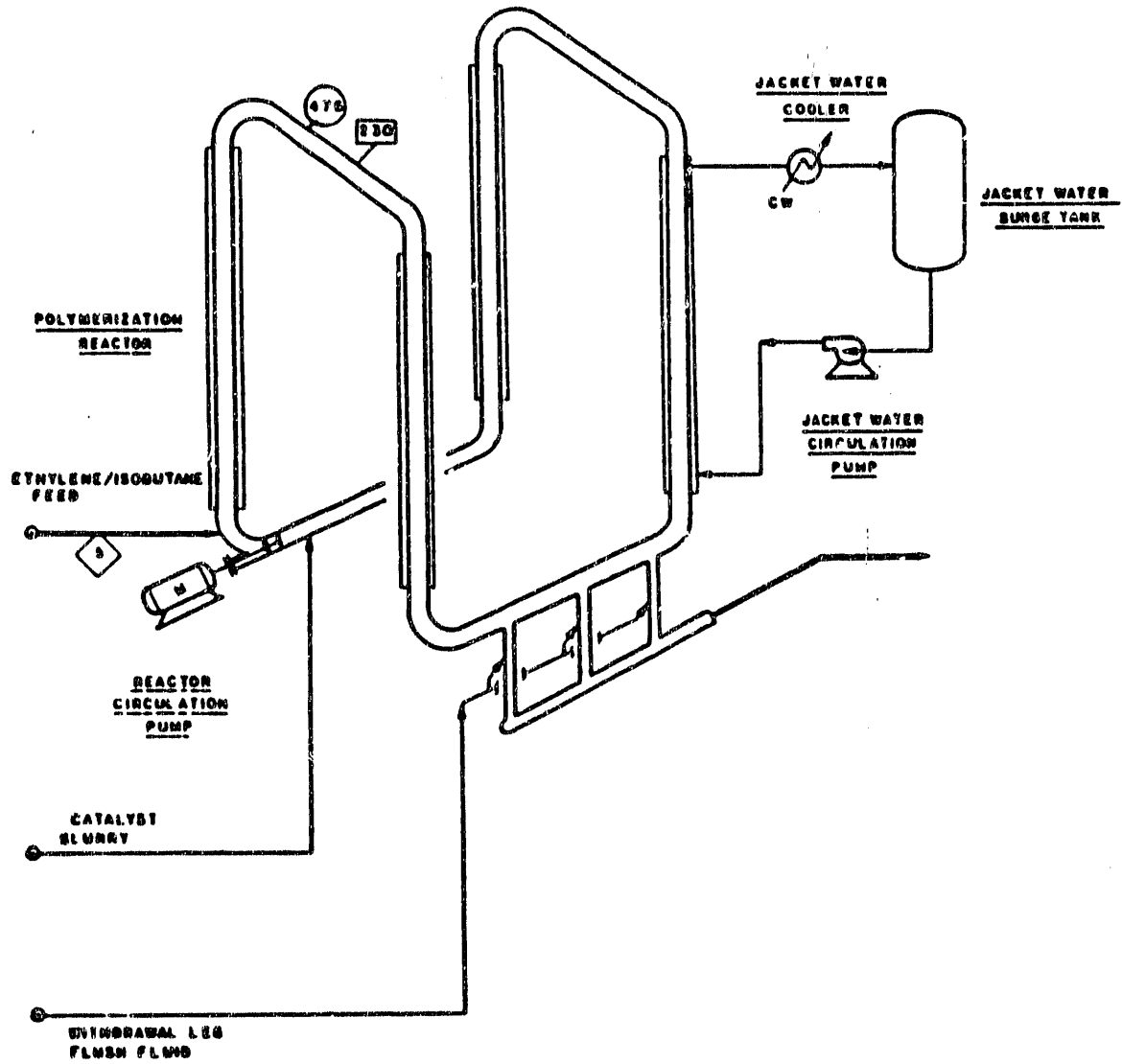


Figure 2.3

SLURRY REACTOR DESIGN  
CIRCULATING LOOP LAYOUT  
(CHEM SYSTEMS)

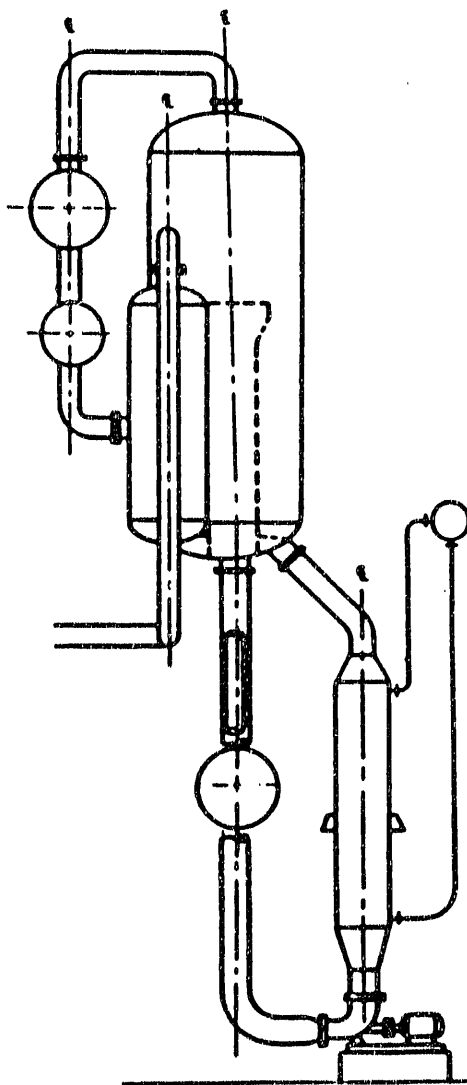
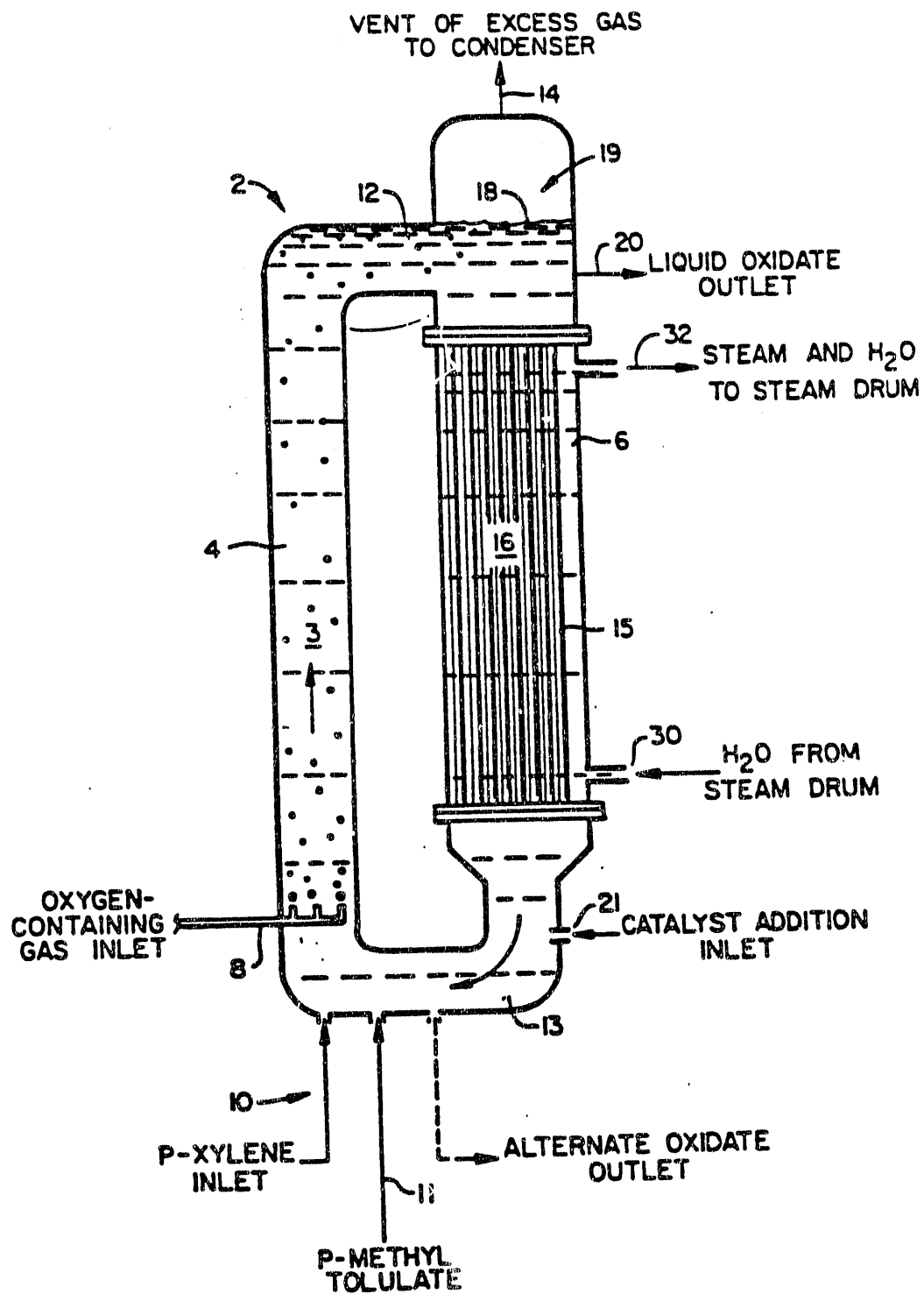


Figure 2.4

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 consensus 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:



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
- $k_L a$  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  $\mu\text{m}$  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  $k_L a$  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  $\text{H}_2/\text{CO}$  ratio and the  $\text{H}_2/\text{CO}$  usage ratio. (Most models use a mean gas velocity in the estimation of gas holdup and  $k_L a$ . 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  $k_L a$ . 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  $k_L a$  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<sub>2</sub>; may be different than the input ratio.
- Contraction factor is uniform with conversion
- Liquid phase batch (liquid flow is negligible compared to other effects)
- Catalyst is uniformly dispersed
- A mean gas velocity can be used to estimate gas holdup and  $k_L a$ .

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

### 2.3.6 Effectiveness Factors in Fixed-Bed Fischer-Tropsch

It is shown that for 1/16" to 1/8" diameter particles and first order rate constants typical of Fischer-Tropsch synthesis (0.01 to 0.4 sec<sup>-1</sup>), 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<sub>2</sub> ratio, I, the CO/H<sub>2</sub> consumption ratio, U, (assumed constant with conversion) and the contraction factor,  $\alpha$ . 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<sup>1</sup>:

$$1/K_A = 1/k_{L,a} + 1/k_r \epsilon_L$$

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

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

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

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

---

<sup>1</sup> A table of nomenclature follows Section 6.

<sup>2</sup> 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 ( $\text{Nm}^3$  syngas converted per hour per  $\text{m}^3$  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:

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

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<sup>3</sup> is as follows:

$$\epsilon_G = 0.24 \cdot (\text{Fr}_G)^{0.28} \cdot (\text{Bo})^{0.14}$$

where

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

with  $u_G$  = gas superficial velocity,  $d_R$  = column diameter,  $\rho_L$  = liquid density,  $\sigma_L$  = surface tension and  $g$  = gravitational acceleration in consistent units.

---

<sup>3</sup> Personal communication from A. Akgerman dated 1/29/90.

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

Akgerman has recommended (1) use of the Bukur expression for gas holdup, (2) the Akita-Yokida (1973) correlation for  $k_L a$  using liquid (not slurry) properties and (3) use of a correction to  $k_L a$  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:

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

where T is temperature in °K and  $\mu$  is liquid viscosity in poise. The diffusivity of CO in the same media is 1/3 that of hydrogen. In the Akita-Yoshida correlation,  $k_L a$  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:

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

where the units are  $(\text{s} \cdot \text{kgCat}/\text{m}^3)^{-1}$ . Division by the catalyst loading in kgCat/m<sup>3</sup> 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 <sub>2</sub> + CO Conversion		
	<u>Model 1</u>	<u>Model 2</u>	<u>Reported</u>
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.  $\text{Nm}^3/(\text{h}\cdot\text{kgCat})$ ), 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 <sub>2</sub> +CO Conversion		
	<u>Model 1</u>	<u>Model 2</u>	<u>Reported</u>
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<sub>2</sub> and its mass transfer coefficient is expected to be 0.5 to 0.7 times that of H<sub>2</sub>, its fractional mass transfer resistance can be as much as twice that of hydrogen. This is reflected in a lower H<sub>2</sub>/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 <sup>3</sup>		3.1		
14	muL - poise		0.022322897		
15	rhoL - g/cm <sup>3</sup>		0.66587		
16	sigmaL - dyne/cm		16.5		
17	DA - cm <sup>2</sup> /s		0.00057721		
18	muSlurry - poise		0.024537552		
19	rhoSlurry - g/cm <sup>3</sup>		0.754766799		
20	kLa Correction Factor		0.814139428		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Deckwer's Model	0.160004024	0.16639018	0.170103106	
23	kLa - s <sup>-1</sup> (uncorr) for H	0.315706921	0.324375011	0.332345955	
24	kLa - s <sup>-1</sup> (corr) for H	0.252958755	0.264086486	0.270575946	
25	kH - (s*kgCat/m <sup>3</sup> ) <sup>-1</sup>		0.000831233	3.3e <sup>9</sup> *exp(-130/RT)	
26	kH - s <sup>-1</sup>		0.094108054		
27	kH*epsilonL - s <sup>-1</sup>	0.079050386	0.078449398	0.078099982	
28	He - (kPa cm <sup>3</sup> )/mol		19699754.02		
29	RTL/(uGo*He) - s <sup>-1</sup>		22.47475295		
30	kA - s <sup>-1</sup>	0.060228725		0.060606353	
31	Stanton No. - target	1.353625718		1.362112813	
32	H2 Conversion	0.849596977		0.577117348	
33	Stanton No. - result	1.353627693		1.362117185	
34	Average uG - cm/s	2.730435058		2.986667106	
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 <sup>2</sup>		0.001734945		
44	Reactor Vol. - m <sup>3</sup>		0.005999438		
45	Feed Rate - m <sup>3</sup> /h		0.218603012		
46	Feed Rate - Nm <sup>3</sup> /h		1.201708011		
47	SV - Nm <sup>3</sup> /(m <sup>3</sup> 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 <sup>3</sup> /(h*m <sup>3</sup> )	176.1674192	153.5287614	140.4030603	
51	STY - Nm <sup>3</sup> /(kgCat h)	1.852440809	1.626757724	1.494336443	
52	GHSV - Nm <sup>3</sup> /(kgCat h)	2.106236419	2.122371969	2.131867378	
53	Catalyst - kg	0.570547542	0.566209895	0.563687978	
54	Catalyst Loading kg/m <sup>3</sup>	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 <sup>3</sup>	141.1832862	123.0490317	112.5291474	
59	Heat Release - Btu/(h ft <sup>3</sup> )	13651.48341	11897.17911	10880.0484	
60	Mass Transfer Resistance - %	23.8097018	22.90253414	22.39901737	
61	DL - cm <sup>2</sup> /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	l		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 <sup>3</sup>		3.1		
14	muL - poise		0.021828409		
15	rhoL - g/cm <sup>3</sup>		0.66476		
16	sigmaL - dyne/cm		16.5		
17	DA - cm <sup>2</sup> /s		0.000585877		
18	muSlurry - poise		0.025154495		
19	rhoSlurry - g/cm <sup>3</sup>		0.774238061		
20	kLa Correction Factor		0.812175666		
21	REFACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Bukur's Model	0.181155844	0.186080074	0.187454703	
23	kLa - s <sup>-1</sup> (uncorr) for H	0.631067377	0.649962057	0.655245612	
24	kLa - s <sup>-1</sup> (corr) for H	0.512537567	0.527883367	0.532174541	
25	kH - (s <sup>2</sup> kgCat/m <sup>3</sup> ) <sup>-1</sup>		0.000925334	3.3e <sup>9</sup> *exp(-130/RT)	
26	kH - s <sup>-1</sup>		0.128957233	No pressure correction	
27	kH*epsilonL - s <sup>-1</sup>	0.105595876	0.104960861	0.104783593	
28	He - (kPa cm <sup>3</sup> )/mol		19621139.04		
29	RTL/(uGo*He) - s <sup>-1</sup>		18.58019167		
30	kA - s <sup>-1</sup>	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 <sup>2</sup>		1.306981084		
44	Reactor Vol. - m <sup>3</sup>		10.06375434		
45	Feed Rate - m <sup>3</sup> /h		446.9875308		
46	Feed Rate - Nm <sup>3</sup> /h		2670.658039		
47	SV - Nm <sup>3</sup> /(m <sup>3</sup> h)		265.3739298		
48	H2+CO Conversion	0.936428424	0.788138344	0.743619389	
49	CO Conversion	0.955081895	0.801798065	0.758432141	
50	STY - Nm <sup>3</sup> /(h*m <sup>3</sup> )	248.503691	208.6206218	197.3371996	
51	STY - Nm <sup>3</sup> /(kgCat h)	2.17763239	1.839198198	1.742666801	
52	GHSV - Nm <sup>3</sup> /(kgCat h)	2.325465923	2.339535034	2.343492957	
53	Catalyst - kg	1148.439981	1141.533881	1139.605746	
54	Catalyst Loading kg/m <sup>3</sup>	114.1184561	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 - W	2001.355357	1680.152103	1589.27966	
58	Heat Release - kW/m <sup>3</sup>	198.867668	166.9508263	157.9211501	
59	Heat Release - Btu/(h ft <sup>3</sup> )	19227.817	16141.88958	15268.84187	
60	Mass Transfer Resistance - %	17.08302268	16.58557614	16.45062482	
61	DL - cm <sup>2</sup> /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	l		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		31.57333613		
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)		188.3424157		
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	
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)	14888.17756	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	l		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 <sup>3</sup>		3.1		
14	muL - poise		0.021828409		
15	rhoL - g/cm <sup>3</sup>		0.66476		
16	sigmaL - dyne/cm		16.5		
17	DA - cm <sup>2</sup> /s		0.000585877		
18	muSlurry - poise		0.025154495		
19	rhoSlurry - g/cm <sup>3</sup>		0.774238061		
20	kLa Correction Factor		0.812175666		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Bukur's Model	0.181512866	0.186398504	0.187749682	
23	kLa - s <sup>-1</sup> (uncorr) for H	0.63243559	0.651185634	0.656370908	
24	kLa - s <sup>-1</sup> (corr) for H	0.513648797	0.528877126	0.533095789	
25	kH - (s <sup>2</sup> kgCat/m <sup>3</sup> ) <sup>-1</sup>		0.000925334	3.3e <sup>9</sup> *exp(-130/RT)	
26	kH - s <sup>-1</sup>		0.12346715	With pressure correction	
27	kH*epsilonL - s <sup>-1</sup>	0.101056274	0.100453058	0.100286232	
28	He - (kPa cm <sup>3</sup> )/mol		19621139.04		
29	RTL/(uGo*He) - s <sup>-1</sup>		18.58019167		
30	kA - s <sup>-1</sup>	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 <sup>2</sup>		1.306981084		
44	Reactor Vol. - m <sup>3</sup>		10.06375434		
45	Feed Rate - m <sup>3</sup> /h		446.9875306		
46	Feed Rate - Nm <sup>3</sup> /h		2670.858039		
47	SV - Nm <sup>3</sup> /(m <sup>3</sup> 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 <sup>3</sup> /(h*m <sup>3</sup> )	245.6403251	206.0126517	194.9074082	
51	STY - Nm <sup>3</sup> /(kgCat h)	2.15347971	1.81691718	1.721834615	
52	GHSV - Nm <sup>3</sup> /(kgCat h)	2.326480285	2.310450687	2.344344027	
53	Catalyst - kg	1147.939253	1141.08708	1139.192034	
54	Catalyst Loading kg/m <sup>3</sup>	114.0667005	113.3858241	113.19752	
55	Reaction Enthalpy - kJ/gmol -CH2-		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 <sup>3</sup>	196.5762296	164.863771	155.9766642	
59	Heat Release - Btu/(h ft <sup>3</sup> )	19006.26587	15940.09953	15080.83828	
60	Mass Transfer Resistance - %	16.43979834	15.96190057	15.83345103	
61	DL - cm <sup>2</sup> /s	4675.840085	4747.348158	4766.982238	

Table 2.5

	A	B	C	D	E
1	CASE	MOBIL PILOT PLANT - RUN CT256-11			4/18/80
2	uGo - cm/s		5.3		
3	alpha		-0.55		
4	l		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 <sup>3</sup>		3.1		
14	muL - poise		0.02474214		
15	rhoL - g/cm <sup>3</sup>		0.670865		
16	sigmaL - dyne/cm		16.5		
17	DA - cm <sup>2</sup> /s		0.00053911		
18	muSlurry - poise		0.029347783		
19	rhoSlurry - g/cm <sup>3</sup>		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 <sup>-1</sup> (uncorr) for H	0.465353124	0.500032005	0.506971136	
24	kLa - s <sup>-1</sup> (corr) for H	0.376662804	0.404732336	0.410348958	
25	kH - (s*kgCat/m <sup>3</sup> ) <sup>-1</sup>		0.000507903	3.3e <sup>9</sup> *exp(-130/RT)	
26	kH- s <sup>-1</sup>		0.067204155	With pressure correction	
27	kH*epsilonL - s <sup>-1</sup>	0.051293067	0.050218695	0.050004545	
28	He - (kPa cm <sup>3</sup> )/mol		20064929.63		
29	RTL/(uGo*He) - s <sup>-1</sup>		31.57383613		
30	kA - s <sup>-1</sup>	0.045145287		0.044572948	
31	Stanton No. - target	1.425409884		1.407338966	
32	H2 Conversion	0.89013958		0.708443642	
33	Stanton No. - result	1.425412028		1.407342177	
34	Average uG - cm/s	3.898831287		4.184838864	
35	Stanton No. - reaction		1.585596862		
36	StantonM - target		12.77895246		
37	H2 Conversion		0.738552982		
38	n		0.465788625		
39	Y		0.738553096		
40	StantonM - result		12.77769651		
41	Average uG - cm/s		4.137443751		
42	Pressure - kPa		1480		
43	Reactor Xsect - m <sup>2</sup>		0.002042821		
44	Reactor Vol. - m <sup>3</sup>		0.015566293		
45	Feed Rate - m <sup>3</sup> /h		0.389770175		
46	Feed Rate - Nm <sup>3</sup> /h		2.931793271		
47	SV - Nm <sup>3</sup> /(m <sup>3</sup> 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 <sup>3</sup> /(h*m <sup>3</sup> )	181.0631229	150.2289218	144.1043866	
51	STY - Nm <sup>3</sup> /(kgCat h))	1.545673745	1.309889364	1.261868835	
52	GHSV - Nm <sup>3</sup> /(kgCat h)	1.607814579	1.642211936	1.64924491	
53	Catalyst - kg	1.823464789	1.785270955	1.777657917	
54	Catalyst Loading kg/m <sup>3</sup>	117.1418765	114.6882522	114.1991803	
55	Reaction Enthalpy - kJ/gmol -CH2-		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 <sup>3</sup>	147.3510075	122.2578216	117.2736127	
59	Heat Release - Btu/(h ft <sup>3</sup> )	14246.85187	11820.67978	11338.77411	
60	Mass Transfer Resistance - %	11.98559725	11.0382639	10.86220579	
61	DL - cm <sup>2</sup> /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 3.14.

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

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
$h/h(\text{empty})$	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.

---

<sup>4</sup> 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,  $dG/\mu$ ,  $C$  is the pressure drop coefficient in  $\text{ft} \cdot \text{hr}^2 / \text{in}^2$ ,  $\rho$  is the fluid density,  $\text{lb}/\text{ft}^3$  and  $\Delta P/L$  is the pressure drop in  $\text{psi}/\text{ft}$ . 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 Reynolds 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  $\rho$ ) 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  $\Delta T$  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.

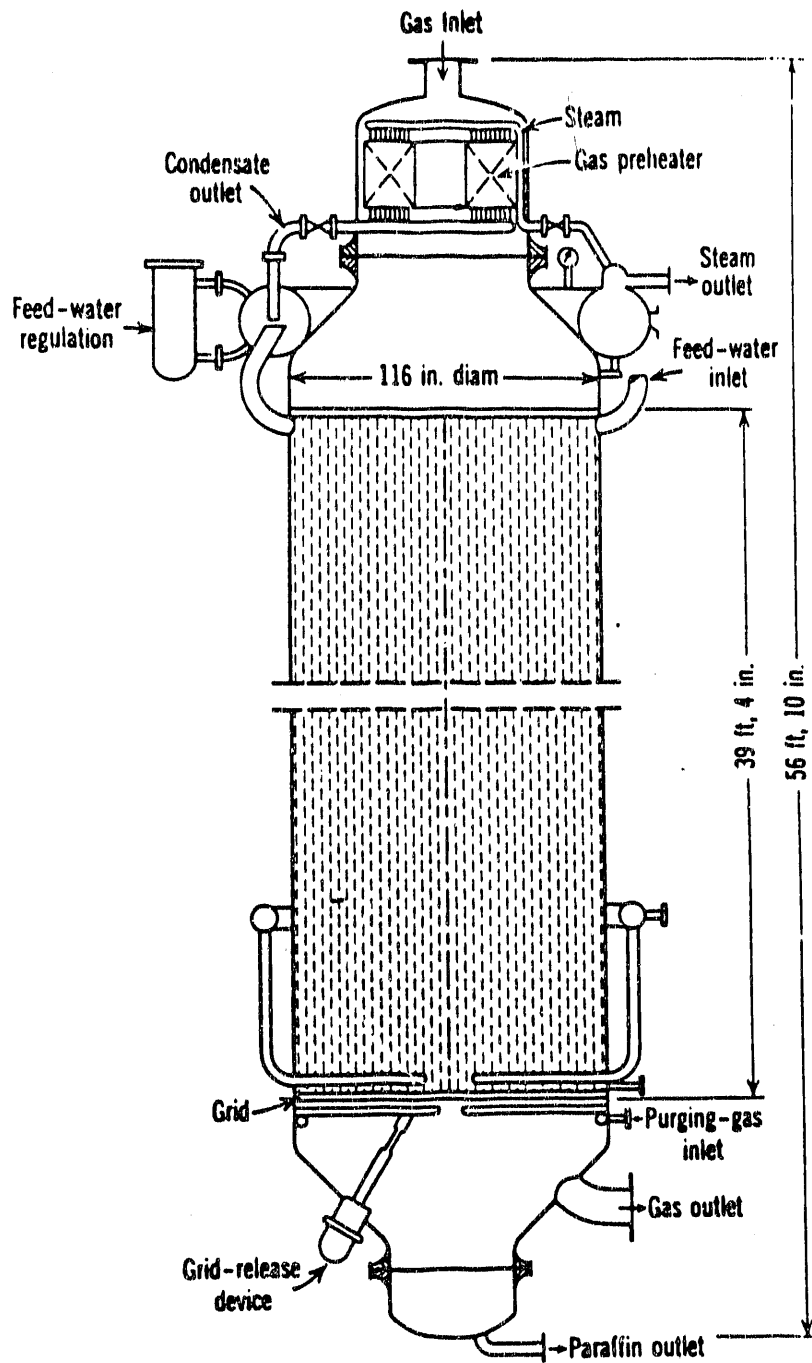
Increasing pressure level has significant advantages for either type of reactor, regardless of its effect on kinetics or equilibrium. At lower pressure, more slurry reactors are required because of the superficial velocity limitation. In the fixed-bed case, the limitation on superficial velocity is pressure 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<sup>5</sup>

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<sub>2</sub> 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

---

<sup>5</sup> Changes to Topical Report Sections 4 and 5 are shown in italics.

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<sub>2</sub> removal such that the ratio:

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

and the CO<sub>2</sub> 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<sub>2</sub>, H<sub>2</sub>S 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 4.0 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 (15.75 ft) and a tangent-to-tangent length of 7.77 meters (25.5 ft). Total weight of catalyst provided is 78200 kg and the GHSV is 9.07 Nm<sup>3</sup>/(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 25 psi (175 kPa) with a R/FF ratio of 4.0<sup>6</sup>. 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 1685 short tons per day (STPD) of methanol. At 0.146 m/s superficial velocity used for design, capacity is the same as a fixed-bed reactor of the same diameter which is 1640 STPD.

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 at the same space velocity (30 °F and 9.07 Nm<sup>3</sup>/(h·kgCat) in this study). Since the resulting CO conversion per pass is 88%, an allowance has been made for backmixing effects and the design approach is 45 °F giving a CO conversion of 83.6% at a GHSV of 8.7 Nm<sup>3</sup>/(h·kgCat). Ultimate conversion is now virtually identical to the fixed-bed case. The

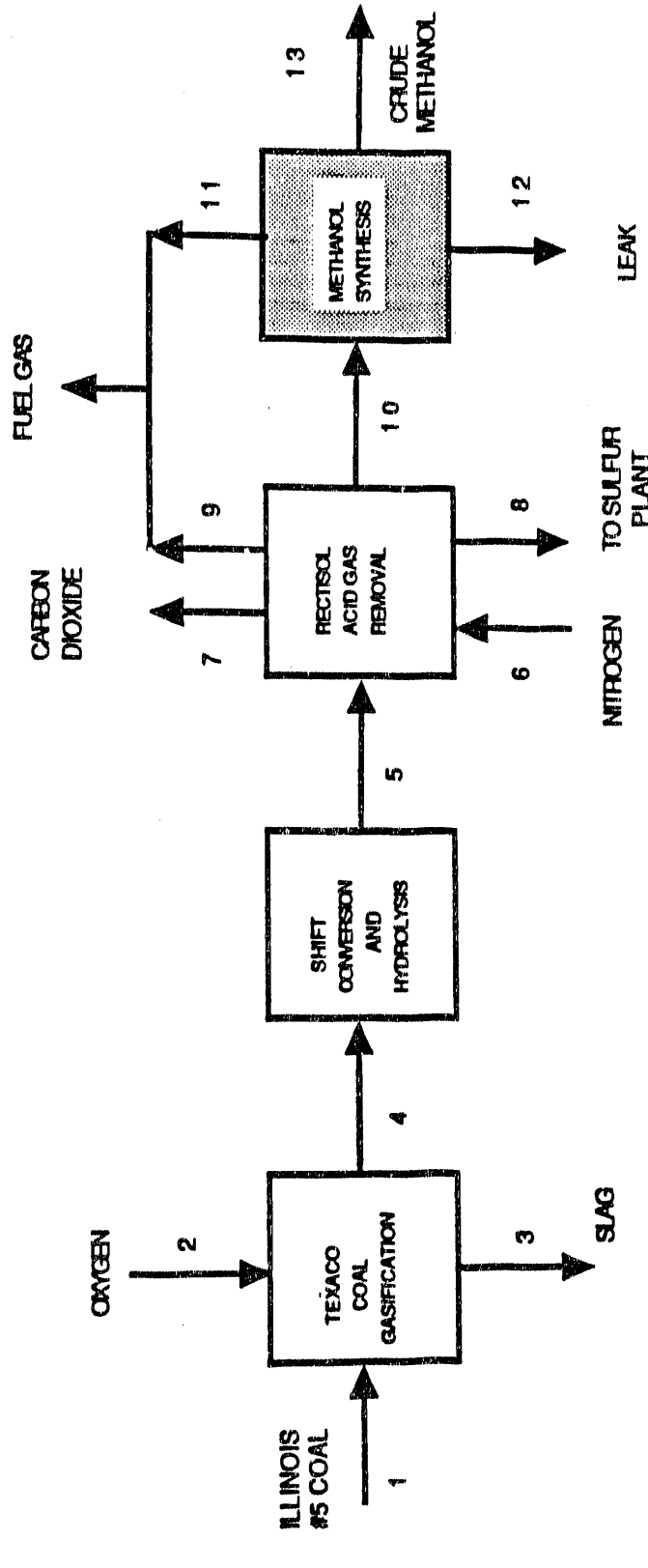
<sup>6</sup> Information from Lurgi; Bechtel had originally used R/FF = 3.0.

*resulting slurry bed height requirement of 12.6 meters is based on the bottom head volume being 15% effective for mass transfer and reaction. A total of 1245 cooling tubes are required. Methanol productivity (or STY), at 1.19 kg/(h·kg), is somewhat higher than in the fixed-bed reactor, at 0.794 kg/(h·kg), due to differences in conversion level. A more detailed analysis of backmixing might lead to a lower design GHSV than this. If so, the slurry reactor would be somewhat taller, productivity would be lower and fewer cooling tubes would be required.*

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 9300 for the fixed-bed case and 13900 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 <sub>2</sub> Vent	Acid Gas	Fuel Gas	Methanol Syn Gas	Purge Gas	Leak Gas	Crude Methanol
Component - lb mph													
H <sub>2</sub>				5886.0	1192.6		0.7	0.3	17.1	8584.7	443.9	50.5	25.3
CO				7915.0	4028.4		5.8		52.3	3970.0	33.6	7.1	4.8
CO <sub>2</sub>				2103.2	5996.3		4727.3	320.8	488.1	452.1	21.9	2.5	28.0
H <sub>2</sub> O				2878.2	0.0		0.0	0.0	0.0	0.0	0.1	0.3	398.5
O <sub>2</sub>		4804.0		0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0
N <sub>2</sub> +Ar		38.0		118.6	118.6	550.6	542.7	8.2	2.4	113.0	91.0	8.8	10.3
CH <sub>4</sub>				31.5	31.5		0.8	0.0	2.4	28.3	21.1	2.0	5.2
H <sub>2</sub> S				148.8	158.3		0.0	158.2	0.0	0.0	0.0	0.0	0.0
CO <sub>2</sub>				9.9	1.4		0.0	1.4	0.0	0.0	0.0	0.0	0.0
CH <sub>3</sub> OH											3.7	0.3	4318.1
TOTAL - MPH	177846	4840.0	27211	18900.3	19917.2	550.6	5277.5	480.3	572.3	14128.0	815.3	71.4	4792.2
LBS/HR	154925	154925		387352	405820	238869	223441	19963	23541	154204	8025	715	147420
MMBtu	32.01			20.49	20.37	433.80	42.34	40.51	41.14	10.91	9.79	10.02	30.78

Table 4.1

## SLURRY METHANOL REACTOR

DIMENSIONS	Design Case
Diameter, m	4.8
Straight Length of Bed, m	12.60
Xsect, m <sup>2</sup>	18.10
Head Vol, m <sup>3</sup>	28.95
Head Volume Effectiveness - %	15.00
Tube OD, mm	38.1
Tube ID, mm	34
Tube Length, m	12.10
No. of tubes	1245
Tube Area (OD), m <sup>2</sup> /tube	1.448
Tube Xsect (OD), m <sup>2</sup> /tube	0.001140
Tube Area (ID), m <sup>2</sup> /tube	0.000908
Net Xsect of Reactor, m <sup>2</sup>	16.68
Total Tube Area - m <sup>2</sup> (OD)	1803.4
Reaction Volume, m <sup>3</sup>	214.44
CONDITIONS	
Feed Gas Temp., °C	150
Operating Temp, °C	250
Operating Pressure, atm	99
Slurry Concentration, wt%	35
Gas Holdup, %	25
Liquid Density, kg/m <sup>3</sup>	675
Particle Density, kg/m <sup>3</sup>	3000
Slurry Density, kg/m <sup>3</sup>	926.2
Catalyst Loading, kg/m <sup>3</sup>	243.1
Catalyst Weight, kg	52138.6
FF - kgmph	6324.3
TF - kgmph	20237.6
TF - m <sup>3</sup> /h	8777.7
TF - Nm <sup>3</sup> /h	453606
R/FF Ratio	2.20
MW of TF	9.72
MW of Effluent	11.99
CO <sub>2</sub> in TF	2.808
CO <sub>2</sub> Conversion per pass, %	30.02
CO in TF, %	10.434
CO Conversion per pass, %	83.64
Methanol Production, MTPD	1487.8
Heat Duty, MW	34.1
Inlet Superficial Velocity, m/s	0.146
GHSV, Nm <sup>3</sup> /h kgCat	8.70
Mass Velocity, kg/h m <sup>2</sup>	196649
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	2115
STY - kg Methanol/(h kgCat)	1.189
STY - kg Methanol/(h m <sup>3</sup> )	289
Heat Flux, kW/m <sup>2</sup>	18.912
Total Cooling Surface, m <sup>2</sup>	1803.4

## 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  $\text{Nm}^3/(\text{h}\cdot\text{kg Cat})$ ) 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  $\text{H}_2/\text{CO}$  ratio and a  $\text{CO}_2$  content of only 1.0%. Only a small amount of shifting is required and, while less  $\text{CO}_2$  must be scrubbed out, a higher level of removal is achieved. The Rectisol unit employed for this purpose is integrated with that required for  $\text{CO}_2$  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  $\text{Nm}^3/(\text{h}\cdot\text{kg Cat})$ , 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  $\text{Btu/h} \times \text{ft}^2 \times ^\circ\text{F}$  (15.76  $\text{kW/m}^2$ ) 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.

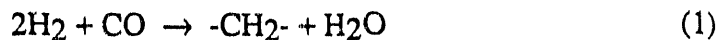
Table 4.2

## 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, m <sup>2</sup>	18.10	18.10
Head Vol, m <sup>3</sup>	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), m <sup>2</sup> /tube	2.067	5.048
Tube Xsect (OD), m <sup>2</sup> /tube	0.001140	0.001140
Tube Area (ID), m <sup>2</sup> /tube	0.000908	0.000908
Net Xsect of Reactor, m <sup>2</sup>	17.43	17.59
Total Tube Area - m <sup>2</sup> (OD)	1199.8	2252.7
Reaction Volume, m <sup>3</sup>	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/m <sup>3</sup>	675	675
Particle Density, kg/m <sup>3</sup>	3000	3000
Slurry Density, kg/m <sup>3</sup>	926.2	926.2
Catalyst Loading, kg/m <sup>3</sup>	259.3	243.1
Catalyst Weight, kg	81453.0	183520.3
FF - kgmph	2322.3	5232.4
TF - kgmph	9811.9	22106.9
TF - m <sup>3</sup> /h	4215.1	9496.9
TF - Nm <sup>3</sup> /h	219923	495505
R/FF Ratio	3.225	3.225
MW of TF	22.90	22.90
MW of Effluent	26.57	26.57
CO <sub>2</sub> 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, Nm <sup>3</sup> /h kgCat	2.7	2.7
Mass Velocity, kg/h m <sup>2</sup>	224706	506282
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	700	656
STY - kg Alcohols/(h kgCat)	.214	.214
STY - kg Alcohols/(h m <sup>3</sup> )	55	52
Heat Flux, kW/m <sup>2</sup>	15.76	18.912
Total Cooling Surface, m <sup>2</sup>	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<sub>2</sub>/CO ratio of about 0.75, the Shell gasifier produces something under 0.5 H<sub>2</sub>/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:



giving the overall reaction:



Because equilibrium in reaction 2 heavily favors CO<sub>2</sub> production at F-T conditions, reaction 3 predominates over reaction 1.

Since the fixed-bed reactor is not applicable to low H<sub>2</sub>/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<sub>2</sub>/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<sub>2</sub>/CO ratio but CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>/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<sub>2</sub> 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.

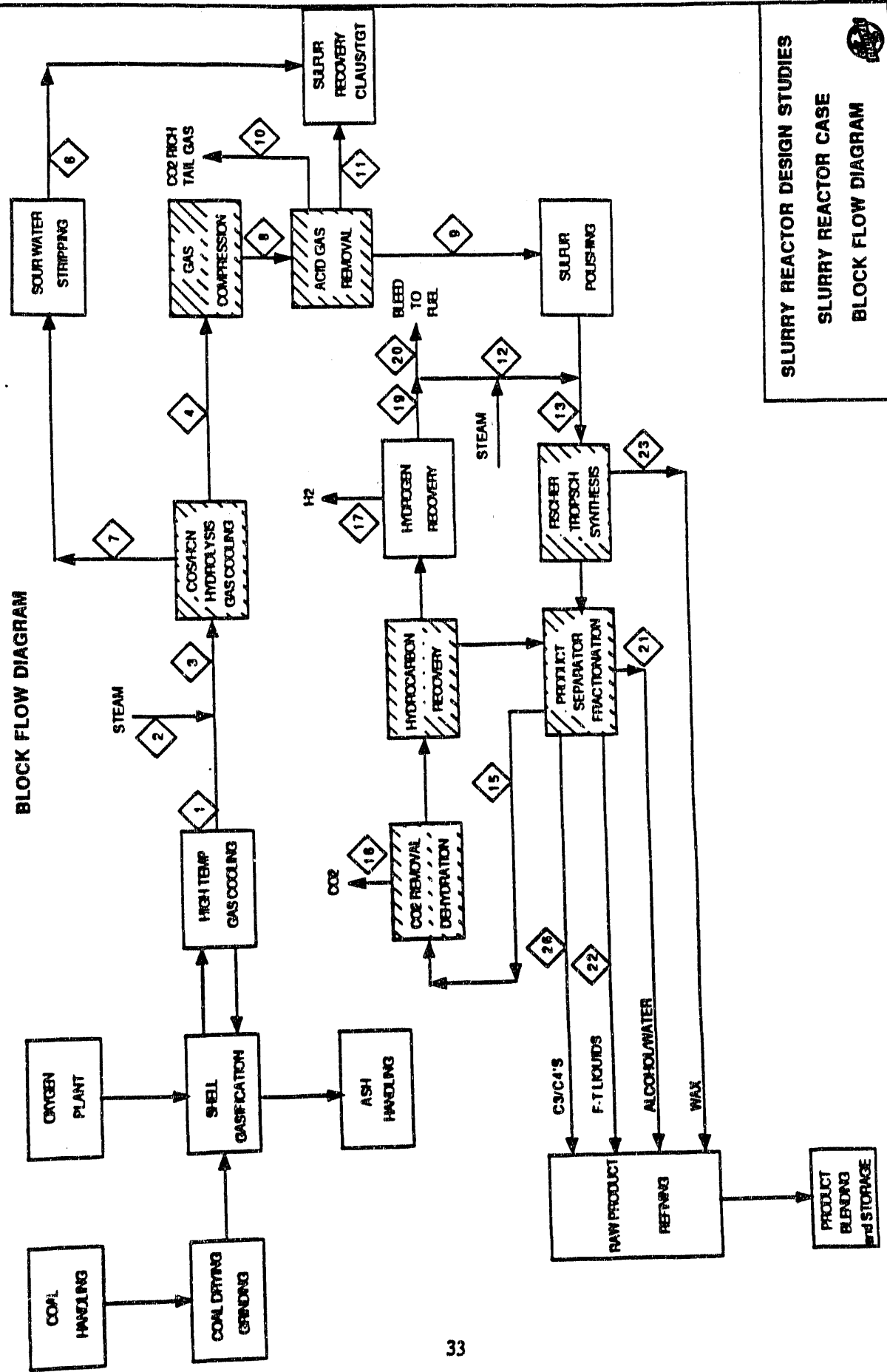
While the design follows that developed by MITRE ( Gray, et al, Sandia Report WP89W00144-1), there are some key differences. Both designs use Shell gasification of coal with CO<sub>2</sub> carrier gas to prepare synthesis gas. The Shell gasifier package includes a waste heat boiler and a scrubber for 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 H<sub>2</sub>S 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<sub>2</sub>/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<sub>2</sub> 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 C<sub>3</sub>/C<sub>4</sub>'s, heavy poly gasoline hydrotreating, isomerization of the C<sub>5</sub>/C<sub>6</sub>'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 COSHYDR	COSHYD INLET	COSHYD OUTLET	SOUR WATER	SELEXL OUTLET	SOUR GAS	RECYCLE GAS	REACTOR FEED	REACTOR PROD	OFF GAS	CO2 OFF GAS	H2 PROD
COMPONENT	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH	MPH
H2O	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
H2	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
CO2	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
N2	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
H2S	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
NH3	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
CO2S	46.3	0.0	46.3	0.5	0.0	0.4	0.1	0.0	0.0	1830.3	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	23.3	2052.2	0.0	0.0
C1	5.3	0.0	5.3	5.3	0.0	5.3	0.0	18.0	23.3	506.0	648.7	0.0	0.0
C2=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	506.0	506.0	162.9	208.9	0.0	0.0
C2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	162.9	162.9	301.0	454.4	0.0	0.0
C3=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	301.0	301.0	33.2	59.1	0.0	0.0
C3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	33.2	33.2	3.6	25.1	0.0	0.0
C4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.6	3.6	21.5	129.2	0.0	0.0
C4=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21.5	21.5	1.0	32.6	0.0	0.0
C5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	1.0	6.3	136.4	0.0	0.0
C5=	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.3	6.3	0.2	22.6	0.0	0.0
C6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.8	92.4	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	0.0	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	1096389	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

STREAMNO DESCRIPTION	18 H/C REC	19 AFTER H2 REC	20 BLEED	CHECK RECYCLE GAS	F-T STEAM ADDITION	21 ALCOHOLS	23 WAX TO HYDRO- CRACKER	26 CAT POLY FEED	30 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						
CO6	0.0	0.0	0.0	0.0						446.4
C8H17O.1	0.0	0.0	0.0	0.0						142.7
C1	0.0	2052.2	451.5	1600.7						45.9
C2=	0.0	648.7	142.7	506.0						153.4
C2	0.0	208.9	46.0	162.9						25.9
C3=	68.6	385.8	84.9	301.0				68.6		21.5
C3	16.5	42.5	9.4	33.2				16.5		107.8
C4	20.5	4.6	1.0	3.6				17.6		31.6
C4=	101.7	27.5	6.1	21.5				129.4		130.1
C5	31.3	1.3	0.3	1.0					31.3	22.4
C5=	128.3	8.1	1.8	6.3					128.3	91.7
C6	22.4	0.2	0.0	0.1					22.4	226.3
C6=	91.4	1.0	0.2	0.8					91.4	83.5
C7-C11										12.4
C12-C18										131.3
C19-C24										157.6
C25+						157.6				1830.4
ALCOHOLS						157.6				583.2
TOTAL	480.7	15156.4	3334.4	11822.0	3193.8	157.6	143.8	232.0	583.2	210696
LBHR	31389	307984	67756	240227	57539	10678	107474	10340	64938	

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<sub>2</sub> removal are required ahead of the F-T converters. A selective Rectisol unit is used for CO<sub>2</sub> and H<sub>2</sub>S removal in this case. This was chosen over Selexol since the latter would have required a double COS hydrolysis and CO<sub>2</sub> 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.

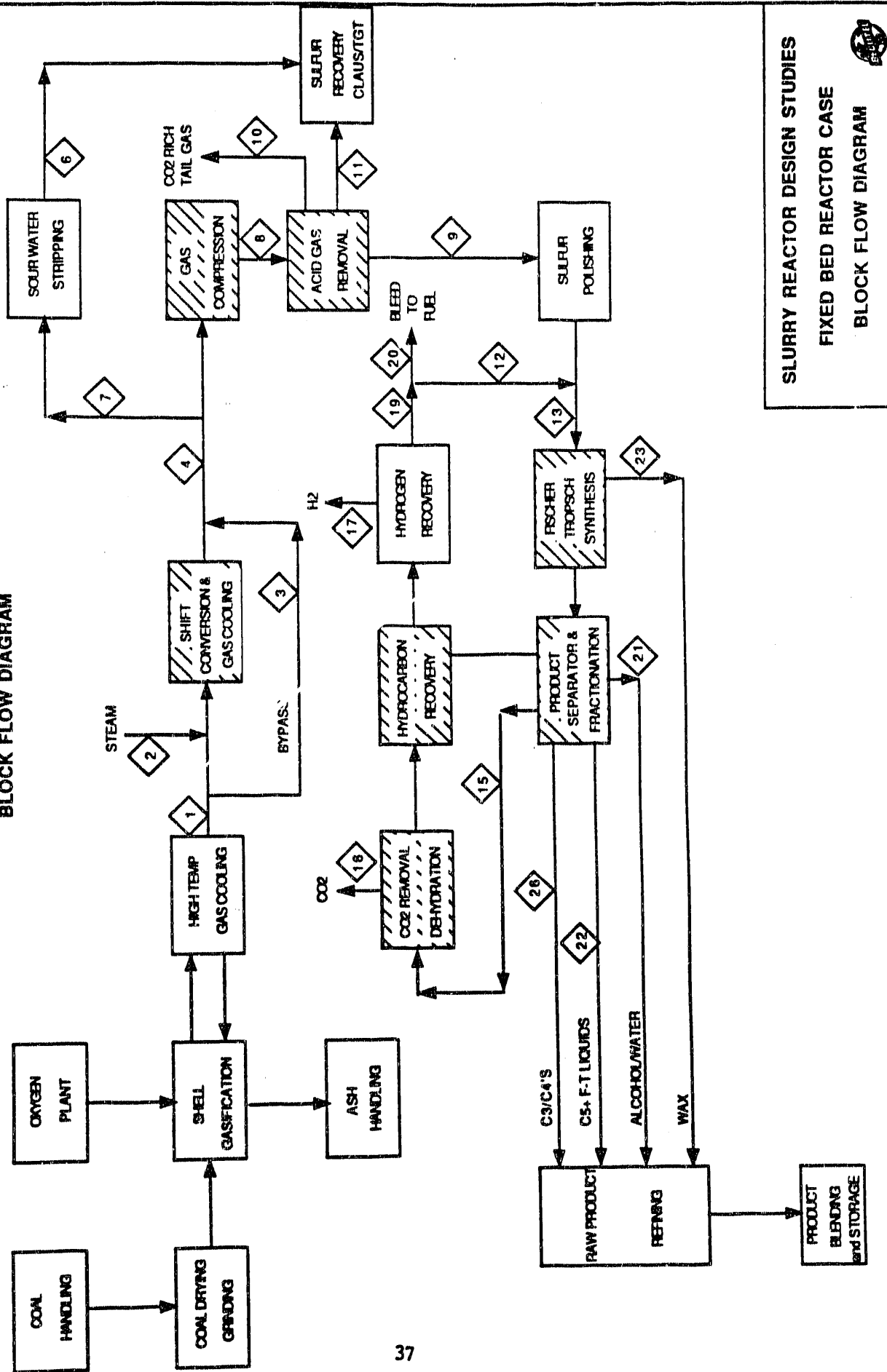
The recycle loop and product recovery are similar to that provided for the slurry reactor case except that:

- Much less CO<sub>2</sub> 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. DESCRIPTION	1 GASIFIER OUTLET MPH	2 STEAM TO SHIFT MPH	3 SHIFT BYPASS MPH	4 SHIFT OUTLET MPH	7 SOUR WATER MPH	9 RECTROL OUTLET MPH	10 CO2 OFF GAS MPH	11 SOUR GAS MPH	12 RECYCLE GAS MPH	13 REACTOR FEED MPH	14 REACTOR PROD MPH	15 OFF GAS MPH	16 CO2 OFF GAS MPH	17 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	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
CO2	46.3		18.6	46.3	0.0	0.0	0.0	46.3	0.0	0.0	0.0	0.0		0.0
C9H17O.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	9.0	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	21	23	26	30	30	30	30	NET F-T
DESCRIPTION	H/C REC MPH	AFTER H2 RECOV MPH	PURGE GAS MPH	CHECK RECYCLE GAS MPH	ALCOHOLS MPH	WAX TO HYD CRACK POLY FEED MPH	CAT MPH	FT PROD HTU FEED MPH	FT PROD HTU 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							
CO2	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							74.6
C3	87.8	649.1	14.7	634.5							102.4
C4	61.5	75.7	1.7	74.0							63.2
C4=	63.4	93.2	2.1	91.1							65.5
C5	76.1	17.6	0.4	17.2							76.4
C5=	84.5	30.0	0.7	29.3							85.2
C6	53.0	2.5	0.1	2.4							53.0
C6=	61.1	3.8	0.1	3.7							61.2
C7-C11											226.7
C12-C18											83.5
C19-C24											12.5
C25+											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		1880.2
LB/HR	34592	1784722	40335	1744388	10762	107458	13469	65518	212336		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 12.22 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, *uses the design GHSV from Table 4.5 but assumes the bottom head volume is 15% effective and allows for the reactor volume occupied by the cooling tubes. The straight length of bed in Table 4.6 is the height of the slurry-gas interface above the bottom tangent line of the reactor. The tube length is that active for heat transfer and is equal to the bed length.* Design heat flux is  $18.9 \text{ kW/m}^2$  [ $6,000 \text{ Btu/(h}\cdot\text{ft}^2)$ ]. The right hand column shows the maximum capacity at  $0.15 \text{ m/s}$  superficial velocity and under these circumstances the required bed height is 13.16 meters. The middle column is at 1/6th the flow given in Table 4.3 for the design material balance. Superficial velocity is  $0.136 \text{ m/s}$  and the required bed height is 11.69 meters. It is noted that 2481 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.

*Because of the large number of cooling tubes required, an alternate design with an external pumparound cooling loop becomes worthy of consideration. The left hand column of Table 4.6 shows that in this case the number of reactors can be decreased to 5 and the required bed length is 11.91 meters.*

Table 4.7 presents an analysis of fixed-bed F-T reactor design. Table 4.8 repeats the same data in metric units for comparison with the slurry reactor. Pressure drop and average heat transfer characteristics are shown in Table 4.7 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  $1920 \text{ Nm}^3/(\text{h}\cdot\text{m}^3)$ , 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  $850 \text{ kg/m}^3$  ( $53.1 \text{ lb/ft}^3$ ) 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		6/12/90
2	uGo - cm/s		15		
3	alpha		-0.5858		
4	l		2.2317		
5	U		2.5604		
6	alpha*		-0.623348182		
7	T - oC		257		
8	Wt.% Slurry		35		
9	Vol.% Solids		10.43659272		
10	dR - cm		480		
11	L - cm		1222		
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	0.233068105	0.241202372	0.242630391	
23	kLa - s^-1 (uncorr) for H	0.990384219	1.028471622	1.035171484	
24	kLa - s^-1 (corr) for H	0.758689567	0.787866644	0.792999112	
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	0.081972448	0.081103028	0.080950396	
28	He - (kPa cm^3)/mol		20064929.63		
29	RTL/(uGo*He) - s^-1		17.89073553		
30	kA - s^-1	0.073979364		0.07345229	
31	Stanton No. - target	1.323545234		1.314115489	
32	H2 Conversion	0.873587608		0.699774742	
33	Stanton No. - result	1.323542709		1.314115554	
34	Average uG - cm/s	10.91588064		11.72847515	
35	Stanton No. - reaction		1.45099283		
36	StantonM - target		14.09551375		
37	H2 Conversion		0.72608013		
38	n		0.500402287		
39	Y		0.726080164		
40	StantonM - result		14.09415988		
41	Average uG - cm/s		11.60549453		
42	Pressure - kPa		2600		
43	Reactor Xsect - m^2		18.09557368		
44	Reactor Vol. - m^3		221.1279104		
45	Feed Rate - m^3/h		9771.60979		
46	Feed Rate - Nm^3/h		129122.6672		
47	SV - Nm^3/(m^3 h)		583.9274967		
48	H2+CO Conversion	0.962441229	0.799930592	0.770949652	
49	CO Conversion	1.002265551	0.833022165	0.80284234	
50	STY - Nm^3/(h*m^3)	561.9958977	467.1014682	450.1787006	
51	STY - Nm^3/(kgCat h)	2.264935904	1.902675991	1.837200858	
52	GHSV - Nm^3/(kgCat h)	2.353323855	2.378551351	2.383036106	
53	Catalyst - kg	54868.20988	54286.26426	54184.10021	
54	Catalyst Loading kg/m^3	248.1288308	245.4971159	245.0351026	
55	Reaction Enthalpy - kJ/gmol -CH2-	214.6	214.6	214.6	
56	kgmol/h of H2+CO Conv (=3* -CH2-)	5544.435555	4808.243581	4441.290059	
57	Heat Release - kW	110169.988	91567.50671	88250.0784	
58	Heat Release - kW/m^3	498.218374	414.0929408	399.0908359	
59	Heat Release - Btu/(h ft^3)	48170.98637	40037.19342	38586.67321	
60	Mass Transfer Resistance - %	9.750939922	9.333240378	9.262594199	
61	DL - cm2/s	30932.6815	31545.0434	31651.62833	

Table 4.6

DIMENSIONS	SLURRY FISCHER-TROPSCH BASE CASE DESIGN		
	5 Reactors	6 Reactors	Max Capacity
Cooling Tube Design	External	Internal	Internal
Diameter, m	4.8	4.8	4.8
Straight Length of Bed, m	11.91	11.69	13.16
Xsect, m <sup>2</sup>	18.10	18.10	18.10
Head Vol, m <sup>3</sup>	28.95	28.95	28.95
Head Volume Effectiveness - %	15.00	15.00	15.00
Tube OD, mm	NA	38.1	38.1
Tube ID, mm	NA	34	34
Tube Length, m	NA	11.69	13.16
No. of tubes	NA	2481	2440
Tube Area (OD), m <sup>2</sup> /tube	NA	1.399	1.576
Tube Xsect (OD), m <sup>2</sup> /tube	NA	0.001140	0.001140
Tube Area (ID), m <sup>2</sup> /tube	NA	0.000908	0.000908
Net Xsect of Reactor, m <sup>2</sup>	18.10	15.27	15.31
Total Cooling Surface, m <sup>2</sup> (OD)	NA	3471.3	3844.7
Reaction Volume, m <sup>3</sup> (Effective)	219.92	182.80	205.93
Reaction Volume, m <sup>3</sup> (Total)	244.53	207.41	230.54
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, %	23.0	22.8	24.1
Liquid Density, kg/m <sup>3</sup>	675	675	675
Particle Density, kg/m <sup>3</sup>	3000	3000	3000
Slurry Density, kg/m <sup>3</sup>	926.2	926.2	926.2
Catalyst Loading, kg/m <sup>3</sup>	249.6	250.3	246.1
Catalyst Weight, kg (Effective)	54898.1	45748.4	50670.0
Catalyst Weight, kg (Total)	61041.3	51907.5	56725.4
FF - kgm <sup>3</sup> h	4608.4	3840.3	4253.4
TF - kgm <sup>3</sup> h	5826.8	4855.7	5378.1
TF - m <sup>3</sup> /h	8959.4	7466.2	8269.4
TF - Nm <sup>3</sup> /h	130603	108835	120544
R/FF Ratio	0.2644	0.2644	0.2644
MW of TF	20.90	20.90	20.90
MW of Effluent	38.04	38.04	38.04
Syngas in TF - %	90.8	90.8	90.8
Syngas Conversion/Pass - %	80	80	80
-CH <sub>2</sub> -Production, MTPD	474.9	395.8	438.4
Heat Duty, MW	78.8	65.6	72.7
Inlet Superficial Velocity, m/s	0.138	0.136	0.150
GHSV, Nm <sup>3</sup> /h kgCat	2.379	2.379	2.379
Mass Velocity, kg/h m <sup>2</sup>	121781	101484	112401
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	594	595	585
STY - kg -CH <sub>2</sub> -/(h kgCat)	.360	.360	.360
STY - kg -CH <sub>2</sub> -/(h m <sup>3</sup> )	90	90	89
Heat Flux, kW/m <sup>2</sup>	NA	18.912	18.912

Table 4.7

## FISCHER TROPSCH TUBULAR REACTOR DESIGN

4/17/90

CASE	Prototype	Design	Design
	ARGE Design	8 Reactors	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 - Nm <sup>3</sup> /hxm <sup>3</sup>	582	574	574
SV - TF Basis - Nm <sup>3</sup> /hxm <sup>3</sup>	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/hrxtxF - 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 - kt	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 BASE CASE DESIGN**

<b>DIMENSIONS</b>	<b>8 Reactors</b>
Diameter, m	4.8
Straight Length of Bed, m	12.65
Xsect, m <sup>2</sup>	18.10
Tube OD, mm	38.1
Tube ID, mm	34.04
Tube Length, m	13.56
No. of tubes	9602
Tube Area (OD), m <sup>2</sup> /tube	1.623
Tube Xsect (OD), m <sup>2</sup> /tube	0.001140
Tube Area (ID), m <sup>2</sup> /tube	1.450
Tube Xsect (ID), m <sup>2</sup> /tube	0.000910
Net Xsect of Reactor, m <sup>2</sup>	8.74
Total Tube Area - m <sup>2</sup> (ID)	13926
Total Tube Area - m <sup>2</sup> (OD)	15589
Reaction Volume, m <sup>3</sup>	110.29
<b>CONDITIONS - PER REACTOR</b>	
Feed Gas Temp., °C	200
Operating Temp, °C	225
Operating Pressure, atm	28.3
Catalyst Loading, kg/m <sup>3</sup>	850
Catalyst Weight, kg	93747.4
FF - kgmph	2825.9
TF - kgmph	9432.9
TF - m <sup>3</sup> /h	13628.3
TF - Nm <sup>3</sup> /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
-CH <sub>2</sub> -Production, MTPD	294.6
Heat Duty, MW	38.2
Inlet Superficial Velocity, m/s	0.433
GHSV, Nm <sup>3</sup> /h kgCat	2.26
Mass Velocity, kg/h m <sup>2</sup>	15127
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	1917
STY - kg -CH <sub>2</sub> -/(h kgCat)	.131
STY - kg -CH <sub>2</sub> -/(h m <sup>3</sup> )	111
Heat Flux, kW/m <sup>2</sup> (ID)	2.74

#### 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  $\text{Nm}^3/(\text{h}\cdot\text{kg Cat})$ ] 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	4.0
CO in Total Feed, %	10.4	10.0
CO Conversion, %	83.6	55.9
Superficial Velocity, m/s (based on empty shell)	0.135	0.317
GHSV, $\text{Nm}^3/(\text{h}\cdot\text{kgCat})$	8.7	9.1
SV, $\text{Nm}^3/(\text{h}\cdot\text{m}^3)$	2,115	11,333
STY, kg MeOH/(h·kgCat)	1,189	0.794
STY, kg MeOH/(h·m <sup>3</sup> ) (based on empty shell)	289 266	992 486
Effective X Sect Area, %	92	49
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 15.1 meters, the fixed-bed reactor, 7.77 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 0.135 and 0.317 m/s, respectively, a factor of 2.35 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·m<sup>3</sup>), 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  $\text{Nm}^3/(\text{h}\cdot\text{kgCat})$  to achieve the same approach to equilibrium. As discussed in Appendix D, the catalyst loading in kg/m<sup>3</sup> 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	11.69	12.65
Reaction Volume, m <sup>3</sup>	1097	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	0.136	0.433
(based on empty shell)	0.115	0.209
GHSV, Nm <sup>3</sup> /(h·kgCat)	2.38	2.26
SV, Nm <sup>3</sup> /(h·m <sup>3</sup> )	595	1917
STY, kg -CH <sub>2</sub> -(h·kgCat)	0.360	0.131
STY, kg -CH <sub>2</sub> -(h·m <sup>3</sup> )	90	111
(based on empty shell)	52.7	44.8
Effective Xsect Area, %	84	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 1.8 times that for the slurry reactor. *Actual fixed-bed superficial velocity is set by pressure drop considerations and will vary depending on mass and space velocity, molecular weight of the gas, pressure level, reactor length and other variables.* Owing to differences in conversion per pass and recycle ratio, the fixed-bed reactors must handle 2.4 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<sup>3</sup>/(h·kgCat), the SV, in Nm<sup>3</sup>/(h·m<sup>3</sup>) 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·m<sup>3</sup>) for the fixed-bed versus 90 for the slurry reactor. This ratio is only slightly less than the ratio in number of reactors and reaction bed heights are, therefore, roughly comparable.

#### 4.5 Low Pressure Design

*In order to ascertain the relative advantage for compressing the synthesis gas prior to acid gas removal and Fischer-Tropsch synthesis, designs have been prepared for both the slurry reactor and the fixed-bed reactor at half of the previous design pressure. The assumption is made that allowable GHSV increases as the square root of pressure in the fixed-bed case and that the reaction kinetic constant,  $k_H$ , decreases as the square root of pressure in the slurry reactor case. These are almost equivalent assumptions, since the GHSV in the slurry reactor also increases by  $P^{1/2}$  when mass transfer resistance is insignificant.*

##### 4.5.1 Slurry Reactor

*Keeping the superficial velocity constant, capacity must vary in direct proportion to pressure if the cross sectional area is constant. Actually, the area occupied by the cooling tubes increases as capacity increases so the exponent on pressure is slightly less than 1. Since GHSV varies as  $P^{1/2}$  and  $u$  is constant, reactor length must vary as  $P^{1/2}$ .*

*It turns out that if pressure is halved, the number of slurry reactors increases from 6 to 11. Table 4.9 shows that, as expected, the reactor length has been decreased from 12 meters to 8.5 meters and GHSV decreases from 2.42 to 1.71 to achieve 80% conversion per pass, Model 2. Table 4.10 shows how this fits into a slurry reactor design when the head volume and cooling tube volume corrections are made. Designs for 10, 11 and 12 reactors are shown. The 11 reactor design is under the limit of 0.15 m/s superficial velocity and results in a bed depth (to the tangent line) of 8.55 meters. In all cases the bottom head is assumed to be 15% effective.*

##### 4.5.2 Fixed-Bed Reactor

*The assumption that allowable GHSV increases as  $P^{1/2}$  turns out to be a good one from the standpoint of fixed-bed design since the reactor sizing does not change significantly but capacity increases in proportion to  $P^{1/2}$ . The reason is as follows:*

- *To keep  $\Delta P/L$  constant,  $uG$  is constant (superficial velocity times mass velocity).*
- *For the same reactor, capacity is proportional to GHSV.*
- *If reactor length is not varied,  $G$  varies as does GHSV (i.e. as  $P^{1/2}$ )*
- *Since gas density varies in direct proportion to  $P$ ,  $u$  varies as  $P^{1/2}/P = P^{-1/2}$ ,  $uG$  is constant,  $\Delta P$  is constant.*
- *Heat flux varies as  $P^{1/2}$ .*
- *The internal film coefficient varies as  $G^{0.8}$  or as  $P^{0.4}$ , film  $\Delta T$  varies as  $P^{0.1}$  but the effect on overall  $\Delta T$  is quite small.*

*The overall effect of halving the pressure is to increase the number of reactors from 8 to 11 ( $11/8 = 1.375$ ). The resulting reactor design is given in Tables 4.11 and 4.12. Overall reactor dimensions remain unchanged.*



Table 4.9

	A	B	C	D	E
1	CASE	COMMERCIAL DESIGN AT LOW PRESSURE			6/12/90
2	uGo - cm/s		15		
3	alpha		-0.5658		
4	l		2.2317		
5	U		2.5604		
6	alpha*		-0.623348182		
7	T - oC		257		
8	Wt.% Slurry		35		
9	Vol.% Solids		10.43659272		
10	dR - cm		480		
11	L - cm		864.5		
12	dp - micron		26		
13	rhoS - g/cm <sup>3</sup>		3.1		
14	muL - poise		0.02474214		
15	rhoL - g/cm <sup>3</sup>		0.670865		
16	sigmaL - dyne/cm		16.5		
17	DA - cm <sup>2</sup> /s		0.00053911		
18	muSlurry - poise		0.046982128		
19	rhoSlurry - g/cm <sup>3</sup>		0.924383927		
20	kLa Correction Factor		0.766055793		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Bukur's Model	0.233900696	0.241195733	0.243191644	
23	kLa - s <sup>-1</sup> (uncorr) for H	0.994276688	1.028440484	1.037805804	
24	kLa - s <sup>-1</sup> (corr) for H	0.761671401	0.78784278	0.795017148	
25	kH - (s*kgCat/m <sup>3</sup> ) <sup>-1</sup>		0.000507903	3.3e <sup>9</sup> *exp(-130/RT)	
26	kH - s <sup>-1</sup>		0.151156248	With pressure correction	
27	kH*epsilonL - s <sup>-1</sup>	0.115800696	0.114698006	0.114396312	
28	He - (kPa cm <sup>3</sup> /mol)		20064929.63		
29	RTL/(uGo*He) - s <sup>-1</sup>		12.65674375		
30	kA - s <sup>-1</sup>	0.100518386		0.10000625	
31	Stanton No. - target	1.272235449		1.265753475	
32	H2 Conversion	0.858672142		0.68940258	
33	Stanton No. - result	1.272236106		1.265754884	
34	Average uG - cm/s	10.98561211		11.77696616	
35	Stanton No. - reaction		1.451703272		
36	StantonM - target		9.97152431		
37	H2 Conversion		0.726202139		
38	n		0.500241442		
39	Y		0.726208105		
40	StantonM - result		9.970574259		
41	Average uG - cm/s		11.60492413		
42	Pressure - kPa		1300		
43	Reactor Xsect - m <sup>2</sup>		18.09557368		
44	Reactor Vol. - m <sup>3</sup>		156.4362345		
45	Feed Rate - m <sup>3</sup> /h		9771.60979		
46	Feed Rate - Nm <sup>3</sup> /h		64561.33359		
47	SV - Nm <sup>3</sup> /(m <sup>3</sup> h)		412.7006367		
48	H2+CO Conversion	0.946008693	0.80006501	0.759522526	
49	CO Conversion	0.985143233	0.833162144	0.790942495	
50	STY - Nm <sup>3</sup> /(h*m <sup>3</sup> )	390.4183801	330.1873393	313.45543	
51	STY - Nm <sup>3</sup> /(kgCat h)	1.575160343	1.344962645	1.280175317	
52	GHSV - Nm <sup>3</sup> /(kgCat h)	1.665059057	1.681066698	1.685500131	
53	Catalyst - kg	38774.20043	38404.98041	38303.96236	
54	Catalyst Loading kg/m <sup>3</sup>	247.8594589	245.4992838	244.853518	
55	Reaction Enthalpy - kJ/gmol -CH2-		214.6	214.6	214.6
56	kgmol/h of H2+CO Conv (=3* -CH2-)	2724.885466	2304.508969	2187.73031	
57	Heat Release - kW	54144.48342	45791.44674	43471.01152	
58	Heat Release - kW/m <sup>3</sup>	346.1121825	292.7163702	277.8832644	
59	Heat Release - Btu/(h ft <sup>3</sup> )	33484.37052	28301.71872	26867.55777	
60	Mass Transfer Resistance - %	13.1970802	12.70834588	12.57913114	
61	DL - cm <sup>2</sup> /s	30995.77875	31544.54725	31693.44566	

Table 4.10

## SLURRY FISCHER-TROPSCH - LOW PRESSURE DESIGN

DIMENSIONS	12 Reactors	11 Reactors	10 Reactors
Diameter, m	4.8	4.8	4.8
Straight Length of Bed, m	7.78	8.61	9.64
Xsect, m <sup>2</sup>	18.10	18.10	18.10
Head Vol, m <sup>3</sup>	28.95	28.95	28.95
Head Volume Effectiveness - %	15.00	15.00	15.00
Tube OD, mm	38.1	38.1	38.1
Tube ID, mm	34	34	34
Tube Length, m	7.78	8.61	9.64
No. of tubes	1865	1838	1805
Tube Area (OD), m <sup>2</sup> /tube	0.931	1.030	1.154
Tube Xsect (OD), m <sup>2</sup> /tube	0.001140	0.001140	0.001140
Tube Area (ID), m <sup>2</sup> /tube	0.000908	0.000908	0.000908
Net Xsect of Reactor, m <sup>2</sup>	15.97	16.00	16.04
Total Cooling Surface, m <sup>2</sup> (OD)	1735.6	1893.5	2082.7
Reaction Volume, m <sup>3</sup> (Effective)	128.51	142.03	158.92
Reaction Volume, m <sup>3</sup> (Total)	153.12	166.64	183.53
CONDITIONS - PER REACTOR			
Feed Gas Temp., °C	149	149	149
Operating Temp, °C	257	257	257
Operating Pressure, atm	14.15	14.15	14.15
Slurry Concentration, wt%	35	35	35
Gas Holdup, %	22.3	23.3	24.6
Liquid Density, kg/m <sup>3</sup>	675	675	675
Particle Density, kg/m <sup>3</sup>	3000	3000	3000
Slurry Density, kg/m <sup>3</sup>	926.2	926.2	926.2
Catalyst Loading, kg/m <sup>3</sup>	251.9	248.7	244.4
Catalyst Weight, kg (Effective)	32371.6	35316.1	38846.1
Catalyst Weight, kg (Total)	38570.6	41435.4	44861.7
FF - kgm <sup>3</sup> h	1920.1	2094.8	2304.2
TF - kgm <sup>3</sup> h	2427.8	2648.6	2913.4
TF - m <sup>3</sup> /h	7466.0	8145.1	8959.3
TF - Nm <sup>3</sup> /h	54417	59366	65300
R/FF Ratio	0.2644	0.2644	0.2644
MW of TF	20.90	20.90	20.90
MW of Effluent	38.04	38.04	38.04
Syngas in TF - %	90.8	90.8	90.8
Syngas Conversion/Pass - %	80	80	80
-CH <sub>2</sub> -Production, MTPD	197.9	215.9	237.5
Heat Duty, MW	32.8	35.8	39.4
Inlet Superficial Velocity, m/s	0.130	0.141	0.155
GHSV, Nm <sup>3</sup> /h kgCat	1.681	1.681	1.681
Mass Velocity, kg/h m <sup>2</sup>	50741	55356	60889
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	423	418	411
STY - kg -CH <sub>2</sub> -(/h kgCat)	.255	.255	.255
STY - kg -CH <sub>2</sub> -(/h m <sup>3</sup> )	64	63	62
Heat Flux, kW/m <sup>2</sup>	18.912	18.912	18.912

Table 4.11

FISCHER-TROPSCH TUBULAR REACTOR DESIGN - LOW PRESSURE

6/12/90

CASE	Prototype	Design	Design
	ARGE Design	11 Reactors	10 Reactors
Pressure - psia	368	212	212
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	4530.9	4984.0
Total Feed - lb mph per Reactor	6903.6	15124.2	16636.6
Recycle/FF ratio	2.30	2.338	2.338
SV -FF Basis - Nm3/hxm3	582	418	401
SV -TF Basis - Nm3 /hxm3	1921	1394	1340
Prod - lb C5+/hrxlb cat	.062	.081	.078
C5+ HC - lb/hr	4281	16711	18382
Total HC - lb/hr	5544	19303	21234
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	.401	.401
Gas Therm Cond - Btu/hrxtxF - Av	.060	.062	.062
Gas Sp. Ht. - Btu/lbxF - Avg	.556	.578	.578
Gas Prandtl No.	.458	.456	.456
Mass Velocity - lb/hrxsqft	2852	2258	2484
Reynold's Number - basis tube ID	8623	5788	6367
Catalyst Diam - feet	.0122	.0122	.0122
Reynold's Number - basis part diam	701	566	623
f	1.08	1.11	1.10
Press Drop - psi/ft	.41	.42	.50
Press. Drop - psi	15.0	17.3	23.7
Heat Release - MM Btu/hr	26.5	94.7	104.2
Heat Flux - Btu/hrxsqft	713	633	613
d/D	.081	.098	.098
Int Heat Trans Coef-Btu/hrxsqftxF	65	63	68
Film Temp Diff - F	11	10	9
Wall Resistance - k/t	938	953	953
Steam Side h - Btu/hrxsqftxF	250	250	250
Overall U	49.1	47.7	50.6
Overall Delta T - F	15	13	12
Gas Res. Time - sec	10.11	8.85	9.21
Tube area/tube volume	26.67	35.86	35.86
Heat Release/Unit Volume	19013	22682	21986

Table 4.12

FIXED-BED FISCHER TROPSCH LOW PRESSURE DESIGN

DIMENSIONS	11 Reactors
Diameter, m	4.8
Straight Length of Bed, m	12.65
Xsect, m <sup>2</sup>	18.10
Tube OD, mm	38.1
Tube ID, mm	34.04
Tube Length, m	13.56
No. of tubes	9602
Tube Area (OD), m <sup>2</sup> /tube	1.623
Tube Xsect (OD), m <sup>2</sup> /tube	0.001140
Tube Area (ID), m <sup>2</sup> /tube	1.450
Tube Xsect (ID), m <sup>2</sup> /tube	0.000910
Net Xsect of Reactor, m <sup>2</sup>	8.74
Total Tube Area - m <sup>2</sup> (ID)	13926
Total Tube Area - m <sup>2</sup> (OD)	15589
Reaction Volume, m <sup>3</sup>	113.40
CONDITIONS - PER REACTOR	
Feed Gas Temp., °C	200
Operating Temp, °C	225
Operating Pressure, atm	14.15
Catalyst Loading, kg/m <sup>3</sup>	850
Catalyst Weight, kg	96387.5
FF - kgmph	2055.2
TF - kgmph	6860.3
TF - m <sup>3</sup> /h	19823.1
TF - Nm <sup>3</sup> /h	153766
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
-CH <sub>2</sub> -Production, MTPD	214.3
Heat Duty, MW	27.8
Inlet Superficial Velocity, m/s	0.630
GHSV, Nm <sup>3</sup> /h kgCat	1.60
Mass Velocity, kg/h m <sup>2</sup>	11001
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	1356
STY - kg -CH <sub>2</sub> -/(h kgCat)	.093
STY - kg -CH <sub>2</sub> -/(h m <sup>3</sup> )	79
Heat Flux, kW/m <sup>2</sup> (ID)	2.00

#### 4.6 Baffled Slurry Reactors

The backmixing effects in a slurry reactor cause a decrease in the conversion level achievable with a given GHSV. One way of cutting down on backmixing would be to install baffles or trays. This has been done in gas/solid fluidized beds such as the fluid-bed MTG reactor, piloted by Mobil and UDHE in 1986. Extensive cold-model tests were run to check out the principle (Krambeck, F. J., Avidan, A. A., Lee, C. K. and Lo, M. N., "Predicting Fluid-Bed Reactor Efficiency using Adsorbing Gas Tracers", *AICHE Journal*, 33, No.10, 1727-1734, 1987). Horizontal baffles were found to be particularly effective in improving fluid-bed reactor performance. The extension to slurry reactors would require piloting on a substantial scale plus similar cold-flow model testing. There are questions as to the extent of erosion of the baffles and whether salting out of the solids in inactive zones can be tolerated.

Preliminary reactor designs have been prepared to study the effect of backmixing using the simplified models described elsewhere in this report (Model 1 - plug flow vs Model 2, liquid phase fully backmixed, gas phase plug flow). These results give an indication of the maximum benefits to be achieved by baffling. These benefits should be balanced against the cost of reactor development and the cost of baffle installation and maintenance. It should also be understood that these are the maximum benefits to be expected and may be reduced somewhat when tested against more sophisticated reactor models.

Two cases are considered: (1) where conversion is kept constant and the size of the reactor is reduced and (2) where reactor size is kept roughly constant and conversion per pass is increased.

##### 4.6.1 80% Conversion per Pass

Table 4.13 shows that in a plug flow reactor, 80% conversion should be achievable with an 8.7 meter bed height and a GHSV of 3.34, (Model 1). This compares with 12 meters and a GHSV of 2.42 for a liquid backmixed reactor, Table 4.5 - Model 2. Table 4.14 shows how this translates into a slurry reactor design. Because of the shorter bed length, more tubes are required and these take up more of the volume and more of the cross sectional area. The right hand column shows the maximum capacity case. The middle column, the design case, shows a 6 reactor design at a superficial velocity of 0.146 m/s, meeting the design GHSV requirement with a bed length of 9.01 meters. The number of cooling tubes increases to 3407.

The left hand column of Table 4.14 shows an alternate design with an external cooling loop. In this case the number of reactors can be decreased to 5 and the required height decreases to 8.54 meters.

##### 4.6.2 95.5% Conversion Once-Through

Table 4.5 shows that the design slurry reactor should be capable of 95.5% conversion per pass if it were baffled to achieve 100% plug flow, (Model 1). The way to take advantage of higher conversion per pass is to relax on the inerts level in the synthesis gas. If 95% oxygen were used instead of 99.5% oxygen to the gasifier, the main effect would be a 10 fold increase in nitrogen content of the synthesis gas from 0.37% up to 3.7%. (Gasifier oxygen requirement would be increased, but negligibly). With once-through operation, total inerts in the F-T reactor feed gas are approximately the same and total feed gas is actually down from 64229 mph to 52510 mph.

*Table 4.15 shows that the bed height must be increased to 11.99 meters, but that a 5 reactor design is feasible. The number of cooling tubes increases to 2955 (versus 2481 in the base design). Superficial velocity in the 5 reactor design is 0.138 m/s. Again, an external circulation loop decreases the number of reactors, this time from 5 to 4. Superficial velocity is 0.141 m/s with 4 reactors and the required bed height is 12.26 meters.*

Table 4.13

	A	B	C	D	E
1	CASE	DEVELOPMENTAL DESIGN - BAFFLED REACTOR			6/12/90
2	uGo - cm/s		15		
3	alpha		-0.5658		
4	l		2.2317		
5	U		2.5604		
6	alpha'		-0.623348182		
7	T - oC		257		
8	Wt.% Slurry		35		
9	Vol.% Solids		10.43659272		
10	dR - cm		480		
11	L - cm		873.6		
12	dp - micron		26		
13	rhoS - g/cm <sup>3</sup>		3.1		
14	muL - poise		0.02474214		
15	rhoL - g/cm <sup>3</sup>		0.670865		
16	sigmaL - dyne/cm		16.5		
17	DA - cm <sup>2</sup> /s		0.00053911		
18	muSlurry - poise		0.046982128		
19	rhoSlurry - g/cm <sup>3</sup>		0.924383927		
20	kLa Correction Factor		0.766055793		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Bukur's Model	0.241197971	0.246449548	0.24805185	
23	kLa - s <sup>-1</sup> (uncorr) for H	1.028450982	1.053109211	1.060643168	
24	kLa - s <sup>-1</sup> (corr) for H	0.787850832	0.806740411	0.812511843	
25	kH - (s <sup>*</sup> kgCat/m <sup>3</sup> ) <sup>-1</sup>		0.000507903	3.3e <sup>-9</sup> *exp(-130/RT)	
26	kH - s <sup>-1</sup>		0.106883608	With pressure correction	
27	kH*epsilonL - s <sup>-1</sup>	0.081103499	0.080542191	0.080370931	
28	He - (kPa cm <sup>3</sup> )/mol		20064929.63		
29	RTL/(uGo*He) - s <sup>-1</sup>		12.78997263		
30	kA - s <sup>-1</sup>	0.073533737		0.073136514	
31	Stanton No. - target	0.940494479		0.935414013	
32	H2 Conversion	0.726161003		0.598797798	
33	Stanton No. - result	0.940496206		0.935415654	
34	Average uG - cm/s	11.80511644		12.20055361	
35	Stanton No. - reaction		1.03013242		
36	StantonM - target		10.31818778		
37	H2 Conversion		0.628823785		
38	n		0.61043005		
39	Y		0.628856383		
40	StantonM - result		10.31720848		
41	Average uG - cm/s		12.06017878		
42	Pressure - kPa		2800		
43	Reactor Xsect - m <sup>2</sup>		18.09557368		
44	Reactor Vol. - m <sup>3</sup>		158.0829317		
45	Feed Rate - m <sup>3</sup> /h		9771.60979		
46	Feed Rate - Nm <sup>3</sup> /h		129122.8672		
47	SV - Nm <sup>3</sup> /(m <sup>3</sup> h)		816.8033435		
48	H2+CO Conversion	0.800019691	0.69278219	0.659702225	
49	CO Conversion	0.833114949	0.721441242	0.686992823	
50	STY - Nm <sup>3</sup> /(h*m <sup>3</sup> )	653.4587585	565.8668093	538.8469831	
51	STY - Nm <sup>3</sup> /(kgCat h)	2.861762304	2.321033759	2.214915339	
52	GHSV - Nm <sup>3</sup> /(kgCat h)	3.327120987	3.350308065	3.357447125	
53	Catalyst - kg	38809.12888	38540.53558	38458.58546	
54	Catalyst Loading kg/m <sup>3</sup>	245.4985397	243.7994739	243.2810743	
55	Reaction Enthalpy - kJ/gmol -CH2-	214.6	214.6	214.6	
56	kgmol/h of H2+CO Conv (=3* -CH2-)	4608.756862	3990.982608	3800.415403	
57	Heat Release - kW	91577.70579	79302.30256	75515.66161	
58	Heat Release - kW/m <sup>3</sup>	579.3018665	501.6499991	477.69648	
59	Heat Release - Btu/(h ft <sup>3</sup> )	56010.64541	48502.77817	46186.79742	
60	Mass Transfer Resistance - %	9.33345928	9.077400021	9.001285911	
61	DL - cm <sup>2</sup> /s	31544.71453	31935.37053	32053.85093	

Table 4.14

SLURRY FISCHER-TROPSCH BAFFLED 80% CONVERSION			
DIMENSIONS	5 Reactors	6 Reactors	Max Capacity
	External	Internal	Internal
Cooling Tubes			
Diameter, m	4.8	4.8	4.8
Straight Length of Bed, m	8.50	9.03	9.30
Xsect, m <sup>2</sup>	18.10	18.10	18.10
Head Vol, m <sup>3</sup>	28.95	28.95	28.95
Head Volume Effectiveness - %	15.00	15.00	15.00
Tube OD, mm	NA	38.1	38.1
Tube ID, mm	NA	34	34
Tube Length, m	NA	8.53	8.80
No. of tubes	NA	3401	3391
Tube Area (OD), m <sup>2</sup> /tube	NA	1.021	1.054
Tube Xsect (OD), m <sup>2</sup> /tube	NA	0.001140	0.001140
Tube Area (ID), m <sup>2</sup> /tube	NA	0.000908	0.000908
Net Xsect of Reactor, m <sup>2</sup>	18.10	14.22	14.23
Total Cooling Surface, m <sup>2</sup> (OD)	NA	3471.3	3572.5
Reaction Volume, m <sup>3</sup> (Effective)	158.07	132.71	136.70
Reaction Volume, m <sup>3</sup> (Total)	182.68	157.32	161.31
CONDITIONS - PER REACTOR			
Feed Gas Temp., °C	149	149	149
Operating Temp, °C	257	257	257
Operating Pressure, atm	28.3	28.3	28.3
Slurry Concentration, wt%	35	35	35
Gas Holdup, %	23.0	23.8	24.1
Liquid Density, kg/m <sup>3</sup>	675	675	675
Particle Density, kg/m <sup>3</sup>	3000	3000	3000
Slurry Density, kg/m <sup>3</sup>	926.2	926.2	926.2
Catalyst Loading, kg/m <sup>3</sup>	249.6	247.0	246.1
Catalyst Weight, kg (Effective)	39457.0	32782.0	33636.6
Catalyst Weight, kg (Total)	45600.2	38861.4	39692.1
FF - kgmph	4608.4	3840.3	3952.3
TF - kgmph	5826.8	4855.7	4997.3
TF - m <sup>3</sup> /h	8959.4	7466.2	7683.9
TF - Nm <sup>3</sup> /h	130603	108836	112010
R/FF Ratio	0.2644	0.2644	0.2644
MW of TF	20.90	20.90	20.90
MW of Effluent	38.04	38.04	38.04
Syngas in TF - %	90.8	90.8	90.8
Syngas Conversion/Pass - %	80	80	80
-CH <sub>2</sub> -Production, MTPD	474.9	395.8	407.3
Heat Duty, MW	78.8	65.6	67.6
Inlet Superficial Velocity, m/s	0.138	0.146	0.150
GHSV, Nm <sup>3</sup> /h kgCat	3.31	3.32	3.33
Mass Velocity, kg/h m <sup>2</sup>	121781	101485	104444
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	826	820	819
STY - kg -CH <sub>2</sub> -/(h kgCat)	.502	.503	.505
STY - kg -CH <sub>2</sub> -/(h m <sup>3</sup> )	125	124	124
Heat Flux, kW/m <sup>2</sup>	NA	18.912	18.912



Table 4.15

DIMENSIONS	SLURRY FISCHER-TROPSCH BAFFLED HIGH CONVERSION		
	4 Reactors	5 Reactors	Max Capacity
Cooling Tubes	External	Internal	Internal
Diameter, m	4.8	4.8	4.8
Straight Length of Bed, m	12.42	12.10	13.30
Xsect, m <sup>2</sup>	18.10	18.10	18.10
Head Vol, m <sup>3</sup>	28.95	28.95	28.95
Head Volume Effectiveness - %	15.00	15.00	15.00
Tube OD, mm	NA	38.1	38.1
Tube ID, mm	NA	34	34
Tube Length, m	NA	11.60	12.80
No. of tubes	NA	2926	2893
Tube Area (OD), m <sup>2</sup> /tube	NA	1.389	1.532
Tube Xsect (OD), m <sup>2</sup> /tube	NA	0.001140	0.001140
Tube Area (ID), m <sup>2</sup> /tube	NA	0.000908	0.000908
Net Xsect of Reactor, m <sup>2</sup>	18.10	14.76	14.80
Total Cooling Surface, m <sup>2</sup> (OD)	NA	4063.6	4433.0
Reaction Volume, m <sup>3</sup> (Effective)	229.09	182.95	201.19
Reaction Volume, m <sup>3</sup> (Total)	253.70	207.56	225.80
CONDITIONS - PER REACTOR			
Feed Gas Temp., °C	149	149	149
Operating Temp, °C	257	257	257
Operating Pressure, atm	28.3	28.3	28.3
Slurry Concentration, wt%	35	35	35
Gas Holdup, %	23.3	23.0	24.1
Liquid Density, kg/m <sup>3</sup>	675	675	675
Particle Density, kg/m <sup>3</sup>	3000	3000	3000
Slurry Density, kg/m <sup>3</sup>	926.2	926.2	926.2
Catalyst Loading, kg/m <sup>3</sup>	248.7	249.6	246.1
Catalyst Weight, kg (Effective)	56963.6	45669.0	49503.1
Catalyst Weight, kg (Total)	63082.9	51812.3	55558.5
FF - kgm <sup>3</sup> /h	5954.6	4763.7	5196.8
TF - kgm <sup>3</sup> /h	5954.6	4763.7	5196.8
TF - m <sup>3</sup> /h	9155.8	7324.8	7990.6
TF - Nm <sup>3</sup> /h	133466	106774	116481
R/FF Ratio	0	0	0
MW of TF	20.90	20.90	20.90
MW of Effluent	38.04	38.04	38.04
Syngas in TF - %	90.8	90.8	90.8
Syngas Conversion/Pass - %	95.5	95.5	95.5
-CH <sub>2</sub> -Production, MTPD	579.4	463.5	505.6
Heat Duty, MW	96.1	76.9	83.8
Inlet Superficial Velocity, m/s	0.141	0.138	0.150
GHSV, Nm <sup>3</sup> /h kgCat	2.343	2.338	2.353
Mass Velocity, kg/h m <sup>2</sup>	124450	99562	108613
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	583	584	579
STY - kg -CH <sub>2</sub> -/(h kgCat)	.424	.423	.426
STY - kg -CH <sub>2</sub> -/(h m <sup>3</sup> )	105	106	105
Heat Flux, kW/m <sup>2</sup>	NA	18.912	18.912

#### 4.7 Superficial Velocity and Catalyst Concentration

As discussed above, Bechtel has chosen to design the slurry reactors in all cases for 35wt% slurry concentration and up to 0.15 m/s superficial inlet velocity. This represents current liquid phase methanol design practice, although it is understood that Air Products is designing the reactor for the Great Plains Clean Coal 3 Demonstration Project for a superficial velocity of 0.25 m/s (personal communication). On the other hand, Bechtel's design conditions are well beyond anything that has been demonstrated to date in Fischer-Tropsch pilot plant operations. For this reason an alternative design has been prepared for more conventional Fischer-Tropsch design conditions of 0.7 m/s and 20 wt% slurry.

The results of this effort are shown in Tables 4.16 and 4.17. Basically, as superficial velocity is decreased with no change in other conditions, the reactor capacity decreases but the reactor can become shorter. Mass transfer becomes more limiting but the decrease in GHSV is slight since surface kinetics predominate. Decreasing the slurry concentration, as well, decreases the rate of reaction since the amount of surface is reduced. This brings the relative contribution of mass transfer back to the original level, the allowable GHSV is reduced and the reactor stays about the same in height. Halving the superficial velocity and halving the slurry concentration would double the number of untubed reactors for the same capacity without changing their dimensions. This can be seen by comparing the first columns of Figure 4.6 and Figure 4.17. The number of reactors has increased from 5 to 10. The bed length is slightly shortened since the slurry concentration has not quite been halved, decreasing from 35 wt% to 20 wt%.

Because the heat removal requirement has not been changed, the number of internal tubes required per reactor is reduced and the space available for reaction is increased. As shown in the middle columns of Figures 4.6 and 4.17, the number of reactors of the internal tube design increases from 6 to 11 and the reactors can be about one meter shorter in height.

Air Products uses the higher superficial velocity in the Great Plains once-through methanol design to reduce the diameter of the reactor, increasing the height. This is beneficial from a cost standpoint since the wall thickness of the shell and heads is reduced.

Table 4.16

	A	B	C	D	E
1	CASE	ALTERNATIVE DESIGN - LOW VELOCITY LOW CONCENTRATION			5/25/90
2	uGo - cm/s		7.5		
3	alpha		-0.5658		
4	l		2.2317		
5	U		2.5604		
6	alpha'		-0.623348182		
7	T - oC		257		
8	Wt.% Slurry		20		
9	Vol.% Solids		5.132521834		
10	dR - cm		480		
11	L - cm		1123		
12	dp - micron		26		
13	rhoS - g/cm <sup>3</sup>		3.1		
14	muL - poise		0.02474214		
15	rhoL - g/cm <sup>3</sup>		0.670866		
16	sigmaL - dyne/cm		16.5		
17	DA - cm <sup>2</sup> /s		0.00053911		
18	muSlurry - poise		0.029706009		
19	rhoSlurry - g/cm <sup>3</sup>		0.795540884		
20	kLa Correction Factor		0.808602596		
21	REACTOR MODEL	MODEL 1	MODEL 2	MODEL 3	
22	epsilonG - Bukur's Model	0.154595362	0.160202376	0.160967831	
23	kLa - s <sup>-1</sup> (uncorr) for H	0.630505221	0.6557049	0.659152012	
24	kLa - s <sup>-1</sup> (corr) for H	0.509828159	0.530204685	0.532992028	
25	kH - (s <sup>2</sup> kgCat/m <sup>3</sup> ) <sup>-1</sup>		0.000507903	3.3e <sup>9</sup> *exp(-130/RT)	
26	kH - s <sup>-1</sup>		0.052563367	With pressure correction	
27	kH*epsilonL - s <sup>-1</sup>	0.044437314	0.044142591	0.044102356	
28	He - (kPa cm <sup>3</sup> )/mol		20064929.63		
29	RTL/(uGo*He) - s <sup>-1</sup>		32.80264484		
30	kA - s <sup>-1</sup>	0.040874626		0.040731992	
31	Stanton No. - target	1.344065819		1.339375638	
32	H2 Conversion	0.879178047		0.704955101	
33	Stanton No. - result	1.344064032		1.339372189	
34	Average uG - cm/s	5.44487236		5.852128198	
35	Stanton No. - reaction		1.45152513		
36	StantonM - target		17.43453233		
37	H2 Conversion		0.726174448		
38	n		0.500283759		
39	Y		0.726174449		
40	StantonM - result		17.43279638		
41	Average uG - cm/s		5.802526792		
42	Pressure - kPa		2600		
43	Reactor Xsect - m <sup>2</sup>		18.09557368		
44	Reactor Vol. - m <sup>3</sup>		203.2132925		
45	Feed Rate - m <sup>3</sup> /h		4885.004895		
46	Feed Rate - Nm <sup>3</sup> /h		64561.33350		
47	SV - Nm <sup>3</sup> /(m <sup>3</sup> h)		317.7023156		
48	H2+CO Conversion	0.968600278	0.800034503	0.776656912	
49	CO Conversion	1.008669367	0.833130374	0.808785897	
50	STY - Nm <sup>3</sup> /(h*m <sup>3</sup> )	307.7285513	254.1728143	246.7456993	
51	STY - Nm <sup>3</sup> /(kgCat h)	2.287746207	1.902225313	1.848325805	
52	GHSV - Nm <sup>3</sup> /(kgCat h)	2.361909509	2.377679094	2.379848267	
53	Catalyst - kg	27334.38066	27153.08965	27128.34028	
54	Catalyst Loading kg/m <sup>3</sup>	134.5107907	133.6186689	133.4968788	
55	Reaction Enthalpy - kJ/gmol -CH2-		214.6	214.6	214.6
56	kgmol/h of H2+CO Conv (-3° -CH2-)	2789.958315	2304.421098	2237.084231	
57	Heat Release - kW	55437.50504	45789.70068	44451.69223	
58	Heat Release - kW/m <sup>3</sup>	272.8045216	225.3282751	218.7440186	
59	Heat Release - Btu/(h ft <sup>3</sup> )	26378.51195	21786.20026	21149.5916	
60	Mass Transfer Resistance - %	8.017333992	7.686696884	7.642139131	
61	DL - cm <sup>2</sup> /s	24760.23883	25269.47681	25338.39994	

Table 4.17

SLURRY FISCHER-TROPSCH ALTERNATIVE DESIGN			
DIMENSIONS	10 Reactors	11 Reactors	Max Capacity
Cooling Tube Design	External	Internal	Internal
Diameter, m	4.8	4.8	4.8
Straight Length of Bed, m	10.97	10.95	12.07
Xsect, m <sup>2</sup>	18.10	18.10	18.10
Head Vol, m <sup>3</sup>	28.95	28.95	28.95
Head Volume Effectiveness - %	15.00	15.00	15.00
Tube OD, mm	NA	38.1	38.1
Tube ID, mm	NA	34	34
Tube Length, m	NA	10.95	12.07
No. of tubes	NA	1444	1431
Tube Area (OD), m <sup>2</sup> /tube	NA	1.311	1.445
Tube Xsect (OD), m <sup>2</sup> /tube	NA	0.001140	0.001140
Tube Area (ID), m <sup>2</sup> /tube	NA	0.000908	0.000908
Net Xsect of Reactor, m <sup>2</sup>	18.10	16.45	16.46
Total Cooling Surface, m <sup>2</sup> (OD)	NA	1893.4	2066.8
Reaction Volume, m <sup>3</sup> (Effective)	202.93	184.48	203.06
Reaction Volume, m <sup>3</sup> (Total)	227.54	209.09	227.67
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%	20	20	20
Gas Holdup, %	15.3	15.3	16
Liquid Density, kg/m <sup>3</sup>	675	675	675
Particle Density, kg/m <sup>3</sup>	3000	3000	3000
Slurry Density, kg/m <sup>3</sup>	798.8	798.8	798.8
Catalyst Loading, kg/m <sup>3</sup>	135.3	135.3	134.2
Catalyst Weight, kg (Effective)	27460.6	24963.7	27250.4
Catalyst Weight, kg (Total)	30790.8	28293.9	30553.0
FF - kgmp/h	2304.2	2094.7	2286.5
TF - kgmp/h	2913.4	2648.5	2891.1
TF - m <sup>3</sup> /h	4479.7	4072.4	4445.4
TF - Nm <sup>3</sup> /h	65301	59364	64801
R/FF Ratio	0.2644	0.2644	0.2644
MW of TF	20.90	20.90	20.90
MW of Effluent	38.04	38.04	38.04
Syngas in TF - %	90.8	90.8	90.8
Syngas Conversion/Pass - %	80	80	80
-CH <sub>2</sub> -Production, MTPD	237.5	215.9	235.6
Heat Duty, MW	39.4	35.8	39.1
Inlet Superficial Velocity, m/s	0.069	0.069	0.075
GHSV, Nm <sup>3</sup> /h kgCat	2.378	2.378	2.378
Mass Velocity, kg/h m <sup>2</sup>	60890	55354	60424
Space Velocity, Nm <sup>3</sup> /h m <sup>3</sup>	322	322	319
STY - kg -CH <sub>2</sub> -/(h kgCat)	.360	.360	.360
STY - kg -CH <sub>2</sub> -/(h m <sup>3</sup> )	49	49	48
Heat Flux, kW/m <sup>2</sup>	NA	18.912	18.912

## 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 Appendices 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 H<sub>2</sub>/CO Ratio

The slurry F-T reactor used in this study operates below 0.67 H<sub>2</sub>/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. *Unless the design pressure can be reduced, however, further test work is not 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.

## 6.0 CAPITAL AND OPERATING COST COMPARISONS

Capital and operating costs differentials have been determined for the slurry and fixed-bed reactor Fischer-Tropsch processing systems described in Section 4.3. The cost estimates are for those specific units which are affected by the choice of reactors. Backup in terms of process flow diagrams, equipment lists, material balances, overall steam and water balance diagrams and utility summaries are given in Appendix F. Capital costs have also been compared for the slurry and fixed-bed methanol synthesis sections described in Section 4.1. Backup is provided in Appendix E. Appendix E also contains Lurgi material on their Octamix™ process.

For those plant sections where detailed information is provided, costs were estimated for each item of major equipment and an overall direct cost was built up by using Bechtel historical factors for installation labor, bulks and subcontracts. Cost of pertinent Fischer-Tropsch upgrading units and utility plants were read off of cost-capacity curves. To these direct costs were added the contractor's indirect costs (distributable field costs which are not identified with any particular process or utility unit) to give the total field cost. An allowance of 25% was then made for contractor's home office engineering, fee and contingency to give the total plant investment. Owner's costs, working capital, startup costs and initial catalyst and chemicals are not included. Import duties on equipment which might be purchased overseas are also not included. Costs are for mid-1990 and represent a typical U. S. Gulf Coast location, with labor at \$16/manhour. These estimates should be accurate to within  $\pm 25\%$ .

The alternative cases described in Subsections 4.5, 4.6 and 4.7 have not been costed, nor have the mixed alcohol designs covered in Section 4.2. A preliminary estimate is provided of the cost savings effected by doubling superficial velocity and slurry concentration for the slurry reactor over what has been demonstrated experimentally for the Fischer-Tropsch process.

Because the Fischer-Tropsch cases are of the greatest interest, these will be discussed first.

### 6.1 Fischer-Tropsch Comparison

As described in Section 4.3, there are key processing differences between the slurry reactor case and the fixed-bed reactor case. The slurry reactors are operated on low  $H_2/CO$  ratio gas as produced in the Shell gasifiers without shifting whereas the fixed-bed reactors are operated on 2 to 1 ratio gas which requires shifting and  $CO_2$  removal. The slurry reactor thus starts with a distinct advantage in terms of gas preparation. This is partially balanced by a large downstream  $CO_2$  removal requirement. Nevertheless, it would be expected that, if the reactors are competitive in cost, the overall slurry reactor processing scheme would show a cost advantage.

In the following subsections, the design of the F-T reactors is reviewed and reactor drawings and costs are provided for both cases. The slurry reactor benefits from operating at a higher temperature level and a higher conversion level. Overall reactor dimensions are similar but only 6 reactors are required as compared to 8 fixed-bed reactors. Differential capital investments and operating costs for the two processing systems are then provided. Finally, some implications of changes in the reactor design parameters are discussed.

It is emphasized that these capital costs are for those selected process units which differ depending on which reactor is used, so only the differential costs are truly meaningful. Reference should be made to the block flow diagrams given in Figures 4.2 and 4.3 to see which units are covered and not covered by the estimate. Using previous Bechtel and MITRE studies, however, it is possible to put these differentials in perspective relative to the overall cost of a coal-to-liquids processing scheme.

#### 6.1.1 Reactor Costs

The reactor design bases provided in Tables 4.6 and 4.8 were reviewed by Bechtel process, mechanical and materials experts who provided the process sizing criteria, material selection and vessel design basis. The resulting designs are shown in Figure 6.1, for the slurry reactors, and Figure 6.2, for the tubular-fixed-bed reactors.

These designs are preliminary. There will be specific site-related mechanical design criteria, for example, that need to be considered. There are also cost optimization factors to consider such as whether to design to Section VIII Division 1 or Division 2 of the ASME code. The former, used for this design, is more conservative but the latter requires a greater number of inspections, increasing the cost of manufacture.

Reactor costs were estimated by Bechtel based on cost quotations from related jobs and studies such as the California Fuel Methanol Cost Study. Confirmation was sought by obtaining quotations from Deggendorfer Werft und Eisenbau GmbH through their U. S. representative, the Ferrostaal Corporation. Agreement was good when all factors were taken into consideration. There is considerable variation, however, depending on the tightness of the market for equipment and on currency exchange rates.

The delivered cost of the reactors shown in Figures 6.1 and 6.2 is estimated at \$2.85 MM and \$4.3 MM, respectively. This cost includes shipping charges at \$1000/ton but does not include any import duty since alternative U.S. sources are available. The lower cost for the slurry reactor reflects its lower overall weight which results from the simplification of the bottom head and the reduction in the weight of heat exchange tubes. Six slurry reactors are required as compared to eight fixed-bed reactors so the total cost of reactors is \$17.1 MM versus \$34.4 MM. The slurry reactor requires a number of auxiliary pieces of equipment such as cyclones, hydroclones, filters, centrifuges and a catalyst makeup and pretreatment system. Some of these can be common to a large number of reactors. When all such equipment is taken into consideration the delivered cost of the reactor systems rises to \$23.3 MM and \$35.4 MM, respectively.

#### 6.1.2 Capital Investment

As shown in Table 6.1, a cost savings of \$91.4 MM is estimated for a 20,000 BPSD coal-based Fischer-Tropsch plant using slurry reactors versus a comparable one using fixed-bed reactors. Some 85% of this savings is identified with the process plants and 15% with the utility plants. Judging from MITRE's study reported in WP89W00144-1 (February 1990), a complete facility of this size starting from coal and producing finished products would cost in the neighborhood of \$1.08 billion (this estimate factors MITRE's total plant investment of \$3.6 billion for an 80,000 BPSD plant by a 0.9 capacity exponent and adds 4% for escalation). Thus the projected cost savings are on the order of 8.5% of the total plant investment.



### 6.1.3 Operating Costs

Comparative operating costs are shown in Table 6.2 and are summarized below:

	Slurry Reactor	Fixed-Bed Reactor
<u>Variable Costs</u>	<u>\$MM/yr</u>	<u>\$MM/yr</u>
Fuel Gas	12.44	17.58
Raw Water	0.25	0.30
Catalysts and Chemicals	14.04	8.20
Total Variable Costs	26.73	26.08
 <u>Fixed Costs</u> <sup>7</sup>		
Maintenance @3% of Investment/yr.	10.66	13.27
<b>Total Selected Operating Costs</b>	<b>37.39</b>	<b>39.35</b>
<b>Operating Cost Differential</b>		<b>1.96</b>

The largest single operating cost items are the fuel gas costs, the F-T catalyst replacement costs and maintenance. The fuel gas requirements are due to an imbalance in power and heating demands as compared to what could be supplied by heat recovery, including that from the gasifier. It was difficult to find a good use for the low pressure steam generated in the F-T reactors in the fixed-bed case. These initial results indicate that it is not necessary to achieve as high a synthesis gas utilization to liquid products as was done in this study, if this would result in a cost reduction.

In calculating the F-T catalyst makeup requirement the slurry reactor case assumes a 60 day catalyst life, following MITRE's lead. For the fixed-bed reactors a one year life is assumed since anything less than this would be impractical and inconsistent with a 90% on-stream factor. It is understood that Sasol dumps the ARGE catalyst more frequently than this but indications are that Shell expects a reasonable catalyst life in their Middle Distillate Process. If a one year equivalent life could also be demonstrated for the slurry reactor the operating cost differential would rise to \$9.06 MM/year.

In the slurry reactor case, 16.1 MW of power are available for export. If a market exists at, say, 2.5 cents per kWh, this would represent an additional annual revenue of \$3.17 MM for that case. There are also small differences in the relative distribution of products between cases as shown in Appendix F. No particular significance can be assigned to these differences, however, since no attempt was made to identify true differences in yield between cases. As mentioned in Section 4, the recovery or disposal of oxygenates is a problem requiring further study in both cases and the assumption of equal oxygenate yields may be an oversimplification.

### 6.1.4 Discussion

The development of the capital cost estimates is documented in Table 6.3 where total costs for each type of equipment and bulks are itemized for both cases. The F-T reactor system costs given in Subsection 6.1.1 represent 25% of the identified major equipment costs in the slurry reactor case and 29% in the fixed-bed reactor case.

An alternative case has been developed in which the number of slurry reactors is increased from 6 to 11. Reactor system costs are now comparable to the fixed-bed case. This

---

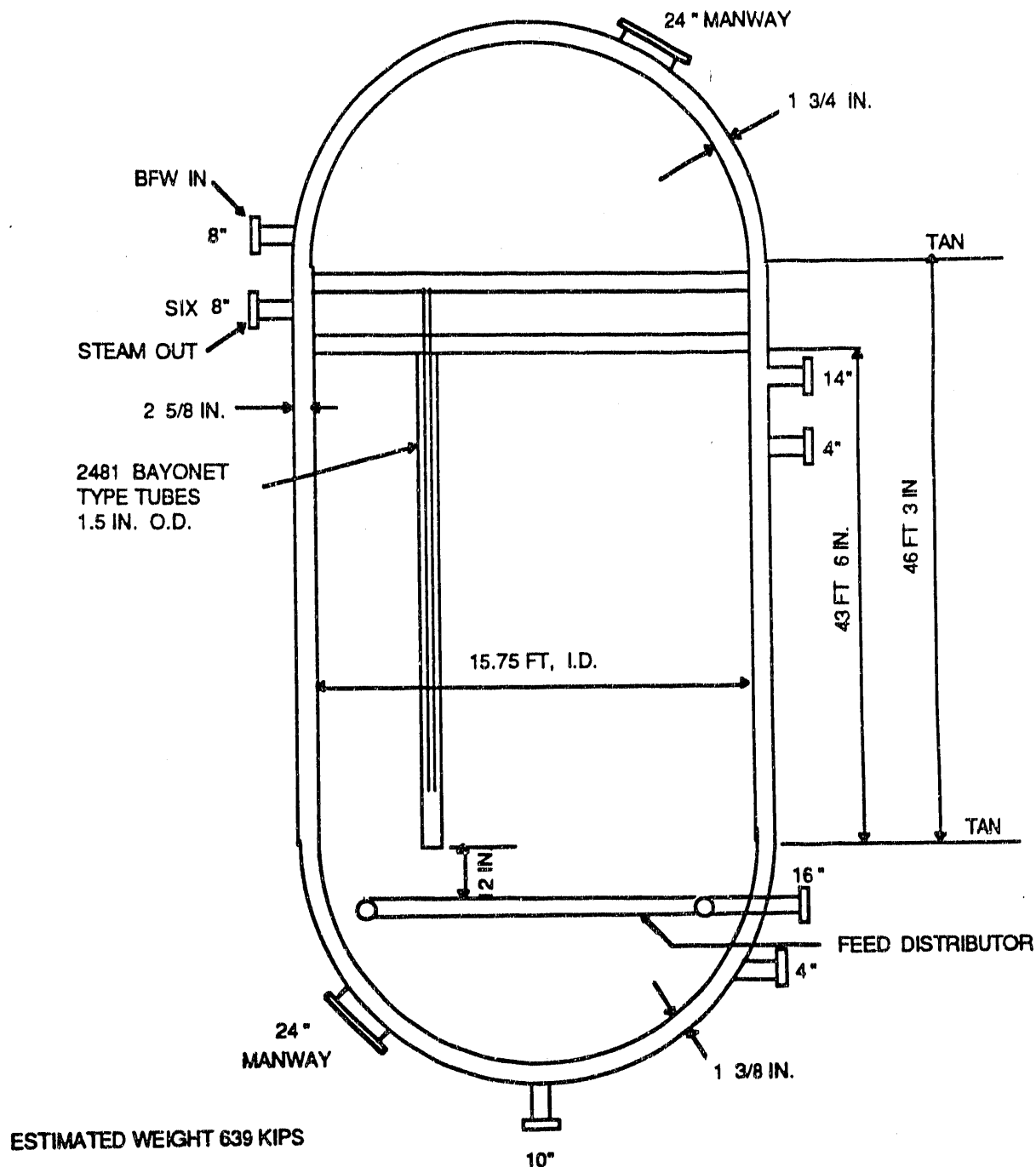
<sup>7</sup> Other fixed costs are deemed not to vary between cases.

increases the cost of the F-T synthesis section from \$49 MM to \$77 MM and increases total plant investment from \$372 MM to \$411 MM, cutting the differential in favor of the slurry case from \$91 MM to \$52 MM. Obviously, it is important to demonstrate that the reactor design conditions assumed for this study can be achieved.

The present estimate compares roughly as might be expected with MITRE's figures where a comparison can be made. MITRE's "plant construction cost" corresponds in scope to Bechtel's "total field cost" but is for a plant four times as large. MITRE's cost for Sulfur Removal, Shift, Fischer-Tropsch Synthesis, Autothermal Reforming and F-T Catalyst Preparation is \$877 MM. Scaling down by the 0.9 or 1.0 capacity exponent and allowing 4% escalation, this corresponds to a range from \$228 to \$262 MM. Bechtel's cost for COS Hydrolysis, Acid Gas Removal, SynGas Compression, F-T synthesis and the F-T gas plant is \$195 MM, at the field cost level, but in the alternate case with 11 reactors this is increased to \$226 MM. MITRE would have used 14 or 15 reactors of roughly comparable dimensions, but running at lower pressure, for the same capacity.

Increased pressure improves the capacity of either the fixed-bed or slurry reactor. Because of the superficial velocity limitation, doubling pressure doubles the capacity of a given diameter slurry reactor (neglecting the area occupied by the cooling tubes). It also doubles the reactor wall thickness (excluding corrosion allowance). The fixed-bed reactor is more complicated but a good rule of thumb is that capacity increases as the square root of pressure, which keeps pressure drop constant. In this case, however, only the wall thickness of the heads and tube sheet are affected. For this reason, increasing pressure is expected to be more cost beneficial when using fixed-bed reactors. While the effect of pressure needs to be examined for both cases, the catalyst activity and selectivity data available to do so are extremely limited.

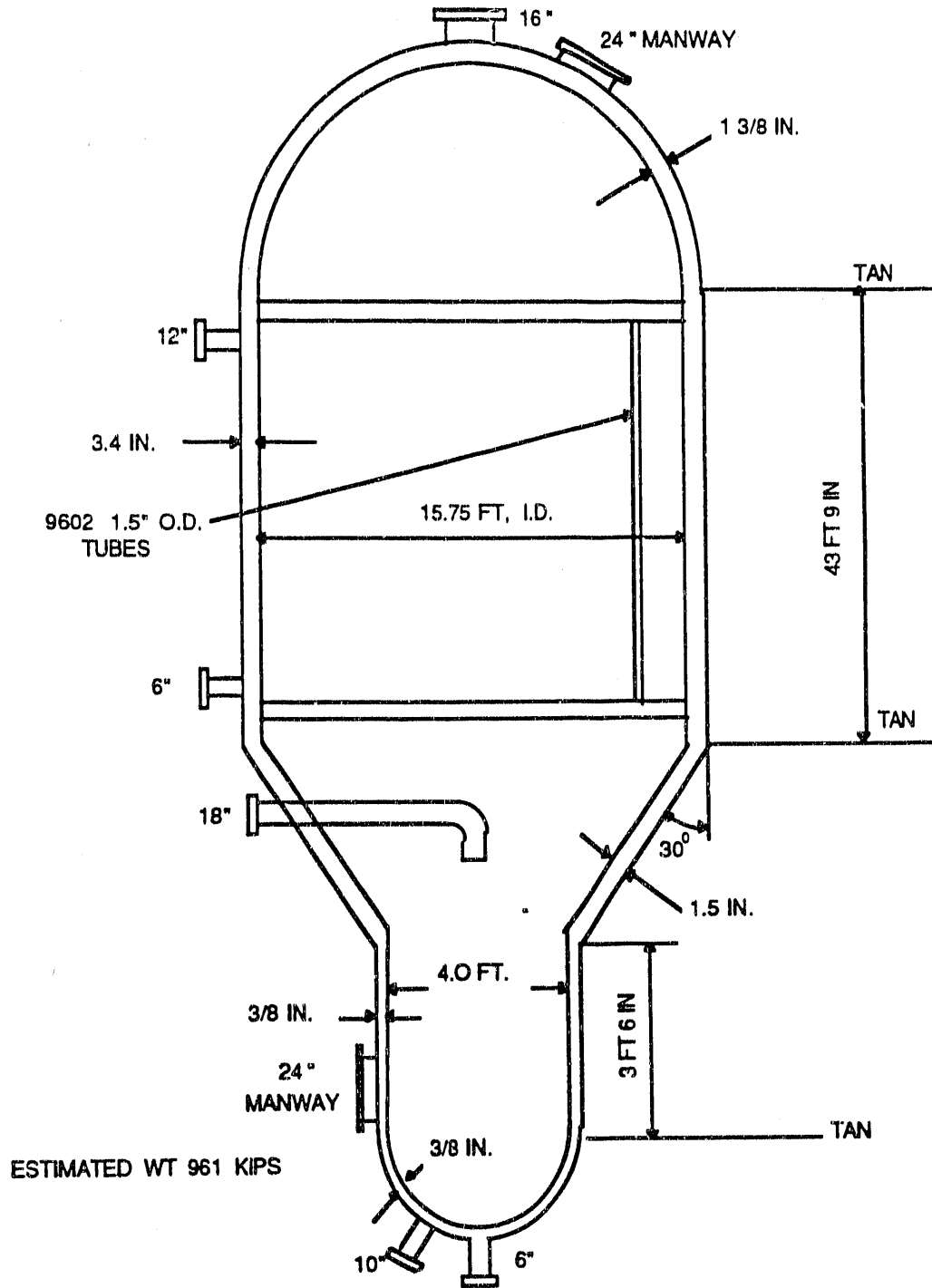
FIGURE 6.1  
 SLURRY REACTOR DESIGN STUDIES  
 FISCHER-TROPSCH PLANT  
 SLURRY REACTOR



NOTES:

- (1) DESIGN CONDITIONS- TUBESIDE 580 PSIG, 550 F ; SHELLSIDE 460 PSIG 550 F
- (2) METALLURGY: SHELL - SA516 GR 70 WITH 1/8" C.A. ; TUBES C.S. CHROMIZED; TUBESHEET A516 GR70 WITH 1/8" C. A
- (3) ALL NOZZLES ARE 400 LB CLASS

Figure 6.2  
 SLURRY REACTOR DESIGN STUDIES  
 FISCHER-TROPSCH PLANT  
 FIXED BED FISCHER-TROPSCH REACTOR



NOTES:

- (1) DESIGN CONDITIONS- TUBESIDE 580 PSIG, 550 F ; SHELLSIDE 600 PSIG 550 F
- (2) METALLURGY: SHELL - SA516 GR 70 WITH 1/8" C.A. ; TUBES C.S. CHROMIZED; TUBESHEET A516 GR 70 WITH 1/8" CA
- (3) ALL NOZZLES ARE 300LB CLASS

Table 6.1

Capital Cost Comparison  
Fischer-Tropsch Cases - Selected Units  
\$Millions

	Slurry Reactor		Fixed-Bed Reactor	
<u>Process Plants:</u>				
<u>From Equipment Lists</u>				
Shift Conversion	NA		22.4	
COS Hydrolysis	15.3		NA	
Acid Gas Removal	43.3		65.7	
SynGas Compression	7.2		11.6	
F-T Synthesis	49.0		82.1	
F-T Gas Plant	11.3		32.4	
CO2 Removal	47.6		14.3	
<b>Subtotal from Lists</b>	<b>173.8</b>		<b>228.4</b>	
<u>From Cost-Capacity Curves</u>				
		<u>BPSD</u>		<u>BPSD</u>
Catalytic Polymerization	4.6	1249	5.9	1674
HGO Hydrotreater	0.5	356	0.4	249
Gasoline Alkylation	5.7	1409	7.5	2136
<b>Subtotal from Curves</b>	<b>10.8</b>		<b>13.8</b>	
<b>Subtotal Onsites</b>	<b>184.6</b>		<b>242.2</b>	
<u>Offsites:</u>				
		<u>Capacity</u>		<u>Capacity</u>
Power Generation	20.4	61.4 MW	16.5	42.2 MW
Cooling Water	20.0	221 Mgpm	18.9	209 Mgpm
Waste Water Treatment	15.8	1900 gpm	18.3	3200 gpm
Raw Water Treatment	12.6	6640 gpm	14.2	7788 gpm
Sour Water Stripping	9.9	461 gpm	17.4	1036 gpm
<b>Subtotal Offsites</b>	<b>78.7</b>		<b>85.2</b>	
<b>Total Direct Cost</b>	<b>263.3</b>		<b>327.4</b>	
Contractor's Indirects	34.3		43.3	
<b>Total Field Cost</b>	<b>297.6</b>		<b>370.7</b>	
Eng'ng + Cont. @ 25%	74.4		92.7	
<b>Total Project Cost</b>	<b>372.0</b>		<b>463.4</b>	
<b>Cost Differential</b>		<b>91.4</b>		

Table 6.2  
Fischer-Tropsch Operating Costs  
Selected Cost Items  
90% On-Stream Factor

<u>Variable Costs</u>	<u>Unit Cost</u>	<u>Slurry Reactor</u>		<u>Fixed-Bed Reactor</u>	
		<u>Quantity/hr</u>	<u>\$MM/yr</u>	<u>Quantity/hr</u>	<u>\$MM/yr</u>
Fuel Gas	\$2.50/MMBtu	631 MMBtu	12.44	892 MMBtu	17.58
Raw Water	\$0.08/MGal	398 MGal	0.25	467 MGal	0.30
<b>Catalysts</b>					
COS Hydr.	\$377/CF	18.5 CF	2.30	NA	
CO Shift	\$242.5/CF	NA		8.9 CF	0.71
F-T	\$2.23/Lb.	11.8 Mlb. (60 day life)	8.69	5.3 Mlb. (1 year life)	3.90
<b>Subtotal Catalysts</b>			<b>10.99</b>		<b>4.61</b>
<b>Chemicals</b>					
Selexol	\$2.00/lb.	98.3 lb.	0.07	NA	
Rectisol	\$0.06/lb.	NA		5506 lb.	0.11
MEA	\$0.56/lb.	4277 lb.	0.79	645 lb.	0.12
<b>Offsites Chemicals (unit cost is cost per gpm treated)</b>					
<b>Water Trtg.</b>			<b>0.90</b>		<b>2.10</b>
Raw	\$10/yr	6638 gpm		7788 gpm	
Demin.	\$1086/yr	657 gpm		1743 gpm	
BFW	\$1518/yr	84 gpm		84 gpm	
Cooling Twr.	\$907/yr	1304 gpm	1.25	1273 gpm	1.22
Effl. Trtg.	\$43/yr	866 gpm	0.04	859 gpm	0.04
<b>Subtotal Chemicals</b>			<b>3.05</b>		<b>3.59</b>
<b>Total Variable Costs</b>			<b>26.73</b>		<b>26.08</b>
<b>Fixed Costs @3% of Investment/yr.</b>			<b>10.66</b>		<b>13.27</b>
<b>Total Selected Operating Costs</b>			<b>37.39</b>		<b>39.35</b>
<b>Total with 1 yr F-T life</b>			<b>30.29</b>		

Table 6.3

Fischer-Tropsch Equipment Cost Summary  
(Including Installation Labor)

	All Plants	
	Slurry Reactor \$MM	Fixed-Bed Reactor \$MM
Major Equipment		
Pressure Vessels	40.32	54.16
Tanks	1.31	0.55
Exchangers	30.08	43.15
Fired Heaters	0.50	0.90
Pumps and Drivers	2.11	1.96
Compressors	18.83	24.65
Package Equipment	2.57	
<b>Total Major Equipment</b>	<b>95.71</b>	<b>125.38</b>
<b>Bulks</b>	<b>78.15</b>	<b>103.05</b>
<b>Total Direct Cost</b>	<b>173.87</b>	<b>228.43</b>

## 6.2 Methanol and Mixed Alcohols

The block flow diagram for both types of reactors is given in Figure 4.1. As described in Section 4.1, only the methanol synthesis loop differs between cases. Methanol production is identical at 1488 tonnes per day (1640 short tons per day). The process flow diagram and equipment list for the methanol cases can be found in Appendix E.

In order to achieve capacity, the slurry reactor is operated at a pressure of 10,000 kPa and a recycle to fresh feed ratio of 2.2. The fixed-bed reactor operates at 5600 kPa. While the fixed-bed design is for a recycle to fresh feed ratio of 3 to 1, Lurgi has advised that a 4 to 1 ratio is required but that the pressure balance can remain as shown. This is not reflected in the equipment lists but adjustments have been made to the final cost estimate which allow for the resulting change in capacity of the recycle compressor and exchangers.

Methanol presents an entirely different situation than Fischer-Tropsch since conversion per pass is limited by equilibrium. To achieve high ultimate conversions to methanol a recycle operation is required. High pressure is needed to achieve capacity in a slurry reactor and this is a serious disadvantage since the vessel walls become very thick and feed gas compression is required. Recycle operation, however, suits the fixed-bed design very well. With a stoichiometric feed gas, operation at the pressure level available from a Texaco gasifier is possible and has actually been demonstrated at the Tennessee-Eastman facility.

The design of the slurry methanol reactor is provided in Figure 6.3, but the design of the tubular fixed-bed reactor is proprietary to Lurgi. Overall reactor dimensions are 4.8 m I.D. by 7.5 m T-T height for the fixed-bed reactor and 4.8 m I.D. by 16.25 m T-T height for the slurry reactor. The slurry reactor shell is designed for 11000 kPa (1600 psig), whereas the fixed-bed shell is designed for a maximum steam pressure of 4700 kPa (675 psig). Delivered cost of the fixed-bed reactor is estimated at \$4.6 MM, that of the slurry reactor, at \$7.9 MM. This includes shipping at \$1000/ton. The slurry reactor synthesis loop requires a feed gas compressor and auxiliary slurry handling equipment such as holding tanks, a cyclone, filters, pumps and a catalyst prereduction system. All in all the slurry reactor system is projected to cost \$41 MM and the fixed-bed system \$23 MM. The breakdown on costs is given in Table 6.4.

Several comments are necessary on this result. The slurry reactor has not been proposed seriously for recycle type methanol operations but rather has been aimed at coproduction of methanol and power via a once-through operation, at low conversion, on gas without H<sub>2</sub>/CO ratio adjustment. Pressure can be on the order of 5600 kPa with little reduction in capacity since there is no recycle. In addition, it is understood that Air Products feels that superficial velocity can be increased up to 0.25 m/s. All these factors will reduce the cost.

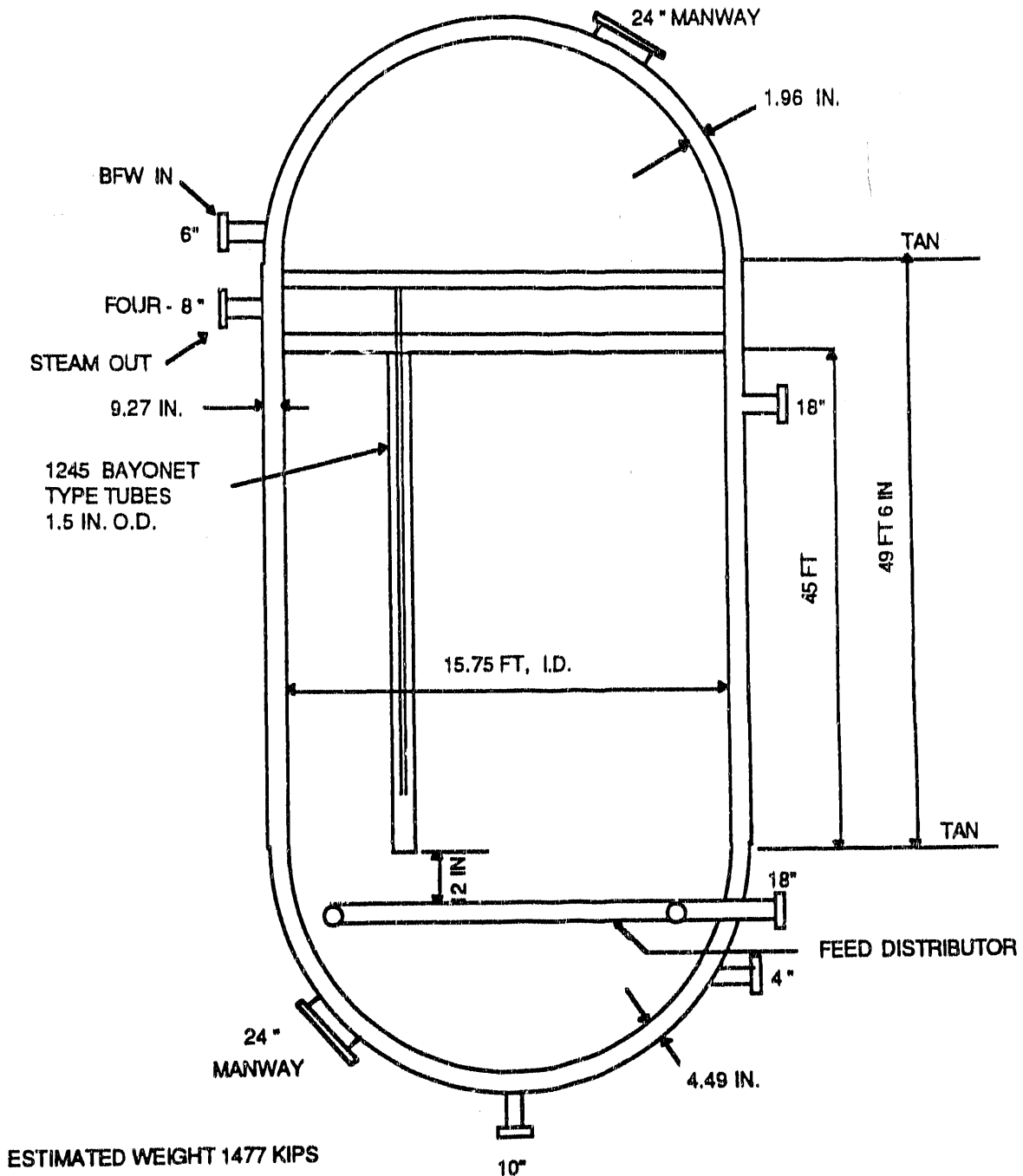
It would be of interest to compare the fixed-bed and slurry reactors for once-through methanol operation if appropriate data can be obtained from the licensors of the technology. While it is conceivable that the fixed-bed reactor could be operated under such conditions there is no publicly available data on which to base a design.

The fixed-bed reactor is operated under low H<sub>2</sub>/CO ratio conditions in Lurgi's Octamix™ process and the design of such a system is provided in Appendix E. This proposed new technology is a low space velocity, recycle operation intentionally producing mixed alcohols as a superior automotive fuel. As described in Section 4.2, the economic potential of the slurry reactor for this type of operation depends on whether design conditions can be altered in the direction of higher temperature and higher space velocity as shown in Table 4.2. It would also be essential for an economically competitive design to be able to run at a



lower operating pressure than the 99 atmospheres specified by Lurgi, because of the effect of pressure on the shell thickness of a slurry reactor. Bechtel's conclusion is that the mixed alcohols application does not appear worth pursuing further.

Figure 6.3  
 SLURRY REACTOR DESIGN STUDIES  
 METHANOL PLANT  
 SLURRY REACTOR



NOTES:

- (1) DESIGN CONDITIONS- TUBESIDE 675 PSIG, 550 F ; SHELLSIDE 1600 PSIG 550 F
- (2) METALLURGY: SHELLSIDE - 304SS CLAD SA220; TUBES SA669, TUBESHEET SA204C +309SS OVERLAY ;  
 TOP HEAD- A516GR 70 W 1/8" CA

Table 6.4

Methanol Synthesis Section  
Equipment Cost Summary  
(Including Installation Labor)

	Slurry Reactor	Fixed-Bed Reactor
	\$MM	\$MM
Major Equipment		
Pressure Vessels	8.81	5.05
Tanks	0.09	0.24
Exchangers	0.71	1.68
Pumps and Drivers	0.28	0.04
Compressor	5.86	2.26
Package Equipment	0.43	
<b>Total Major Equipment</b>	<b>16.18</b>	<b>9.02</b>
 Bulks	 13.24	 7.39
<b>Total Direct Cost</b>	<b>29.42</b>	<b>16.41</b>
Contractor's Indirects	3.43	1.94
<b>Total Field Cost</b>	<b>32.85</b>	<b>18.35</b>
Eng'ng + Cont. @ 25%	8.21	4.59
<b>Total Project Cost</b>	<b>41.06</b>	<b>22.94</b>
Cost Differential		18.12

### Table of Nomenclature

a	gas-liquid interfacial area, $m^{-1}$
Bo	Bodenstein Number = $d_R^2 \cdot \rho_L \cdot g / \sigma_L$
c	heat capacity of the fluid, Btu/(lb·°F)
C	pressure drop coefficient in ft·hr <sup>2</sup> /in <sup>2</sup>
C'Cat	catalyst concentration, kg/m <sup>3</sup>
CHG	hydrogen concentration in gas phase, kg mole/m <sup>3</sup>
C*HL	hydrogen concentration, liquid, in equilibrium with gas, kg mole/m <sup>3</sup>
CHL	hydrogen concentration in the liquid phase, kg mole/m <sup>3</sup>
d	effective particle diameter, ft
d <sub>R</sub>	I.D. of reactor, cm
D	internal tube diameter (fixed-bed), ft
D <sub>A</sub>	diffusivity of component A, m <sup>2</sup> /s
D <sub>L</sub>	Axial dispersion coefficient, cm <sup>2</sup> /s
D <sub>H</sub>	diffusivity of hydrogen, m <sup>2</sup> /s
f	friction factor dependent on the modified Reynolds Number, dG/μ
Fr <sub>G</sub>	Froude Number = $u_G^2 / (g \cdot d_R)$
g	gravitational acceleration in consistent units
G	superficial mass velocity, lb/(h·ft <sup>2</sup> ).
GHSV	Gas hourly space velocity, Nm <sup>3</sup> (H <sub>2</sub> +CO)/[h · m <sup>3</sup> reactor volume], (reactor volume is expanded slurry height times cross section area)
h	heat transfer coefficient, Btu/(h·ft <sup>2</sup> ·°F) or W/(m <sup>2</sup> ·s)
H	solubility coefficient of hydrogen = CHG/C*HL
He	Henry's law constant, kPa·cm <sup>3</sup> /mol
I	Inlet ratio of CO/H <sub>2</sub>
k	thermal conductivity, Btu/(h·ft <sup>2</sup> ·°F/ft) or equivalent SI units
k <sub>A</sub>	overall reaction rate constant defined by $1/K_A = 1/k_L a + 1/k_r \epsilon_L$
k <sub>r</sub>	rate constant in volume/(unit volume · time) for H <sub>2</sub> , $k_r = k_H = k'_H \cdot (\text{kgCat}/m^3)$
k <sub>L</sub>	liquid side mass transfer coefficient, m/s
k <sub>H</sub>	effective reaction rate constant for hydrogen consumption, s <sup>-1</sup> (note that to agree with space velocity in Nm <sup>3</sup> /[s·kgCat], $k_H = k'_H \cdot C'Cat$ )
k <sub>H</sub> '	rate constant for hydrogen in volume/(mass catalyst · time), m <sup>3</sup> /[kg·s]
L	Length of expanded slurry bed or of fixed-bed, m or ft
P	pressure, kPa
r	rate of hydrogen consumption, $r = k_H \cdot CHL$ , kg moles/[m <sup>3</sup> ·s]
St	Stanton Number = $-K_A/SV$
SV	Space velocity in actual m <sup>3</sup> inlet gas/[s·m <sup>3</sup> ]
T	temperature, °K
u <sub>G</sub>	superficial gas velocity, cm/s or m/s
u <sub>Go</sub>	inlet superficial gas velocity
U	Usage ratio of CO/H <sub>2</sub>
X <sub>H</sub>	hydrogen fractional conversion per pass (If U = I, X <sub>H</sub> = X <sub>CO</sub> )
α	contraction factor, $\alpha = [m^3/s(X_{H_2+CO}=1) - m^3/s(\text{inlet})] / [m^3/s(\text{inlet})]$

$\alpha^*$  contraction factor modified for H<sub>2</sub> conversion,  $\alpha^* = \alpha \cdot (1+U)/(1+D)$   
 $\Delta P$  pressure drop, psi or equivalent SI units  
 $\epsilon_G$  fractional gas hold-up  
 $\epsilon_L$  fractional liquid hold-up  
 $\mu_L$  liquid viscosity, poise or lb/(h·ft)  
 $\rho_L$  liquid density, g/cm<sup>3</sup> or lb/ft<sup>3</sup>  
 $\sigma_L$  surface tension, N/m

# APPENDIX A

## SLURRY REACTOR DESIGN STUDIES

### A. Akgerman Reports

#### Contents

<u>Effect of H/CO Ratio on Fischer-Tropsch Synthesis Reaction (Slurry vs Fixed-Bed)</u>		
<u>"The Boudouard Reaction"</u>	5 pages	
<u>Design of Slurry Reactors</u>	24 pages	Page
A. Suspension of the Solids		1
B. Design Model		2
C. Design Equations - Parametric Analysis		4
D. Design Equations - Model Development		11
E. Solids Dispersion		13
F. Calculation of the Transport Parameters		
1. Axial Dispersion Coefficient		18
2. The Mass Transfer Coefficient, $k_L a$		19
<u>Effects of Solids on <math>K_L a - k_L a</math></u>	5 pages	
<u>Model Solutions for Slurry Reactors</u>	5 pages	
Model 1		1
Model 2		4
<u>Effectiveness Factors in Fixed-Bed Fischer-Tropsch</u>	1 page	

## Effect of H/CO Ratio on Fischer-Tropsch Synthesis Reaction (Slurry vs Fixed-Bed) "The Boudouard Reaction"

The Boudouard Reaction is the carbon formation from CO, and is given by:



This carbon formation is associated with catalyst particle swelling and formation of graphite nuclei within the catalyst crystallites that create stresses which disintegrate the particle which eventually leads to bed plugging, maldistribution of the feed, and hot spots. In Fischer-Tropsch synthesis on fixed-bed, gas phase reactors, as the H/CO ratio<sup>8</sup> goes down and the temperature increases, the selectivity to the Boudouard reaction increases. For this reason, fixed bed Fischer-Tropsch synthesis reactor is run at sufficiently low temperatures and with high H/CO ratios, SASOL reportedly uses H/CO ratios of about 6 [Dry 1980; Dry et. al. (1976); Stern et. al. (1983)].

Dry has correlated the rate of coke formation with  $(P_{\text{CO}}/P_{\text{H}}^3)$  (Dry et al., 1976) and with  $(P_{\text{CO}}/P_{\text{H}}^2)$  (Dry, 1980) where  $P_i$  are the partial pressures. So the rate of coke formation,  $r_c$  is given by:

$$r_c = k \cdot (P_{\text{CO}}/P_{\text{H}}^3) \quad \text{or} \quad k' \cdot (P_{\text{CO}}/P_{\text{H}}^2)$$

Thus when the H/CO ratio decreases from 2 to 1, the coke formation rate increases from  $0.25 k'$  to  $k'$ . Dry (1980) shows the temperature dependency of  $k'$ , at a temperature  $T_1$ ,  $k'= 1.0$  and at  $T_2$ ,  $k'= 2.0$ . The temperatures are not specified in that study.

For a fixed bed reactor operating in the gas phase, the rate of coke formation should be applied integrally over the whole length of catalyst bed to derive the overall carbon deposition rate. As conversion by the F-T reaction increases down the reactor, H/CO ratio decreases resulting in higher rates of coke formation as we go down the reactor. However, higher temperatures are experienced at the inlet which also increases the rate of coke

---

<sup>8</sup> In this writeup, H<sub>2</sub> is abbreviated as H.

formation. Dry (1980) indicates that the rate of coke formation is approximately constant over the whole bed. However, he studied H/CO ratios of 4-6, which are much higher than the desired ratio of 0.7-1.

When the process is carried in a slurry reactor, the effective H/CO ratio the catalyst sees is the concentration in the liquid phase which is controlled by the vapor-liquid equilibrium and the mass transfer rates.

If the reaction is kinetics-controlled, i.e., the reaction rate is slow enough so that the concentration in the liquid phase is uniform, then the effective H/CO ratio the catalyst particle sees is the ratio of solubilities of hydrogen and CO in the liquid phase. If we assume Henry's Law,

$$P_i = H_i \cdot C_i$$

then the solubility ratio  $C_H/C_{CO}$  is given by,

$$C_H/C_{CO} = (P_H/H_H) \cdot (H_{CO}/P_{CO}) = (P_H/P_{CO}) \cdot (H_{CO}/H_H)$$

The data on the Henry's Law constants are somewhat scattered:

Stern et al. (1983) give  $H_{CO}/H_H = 0.75$  based on Peter and Weinert's classic work (Peter & Weinert 1955).

Air Products Report gives  $H_{CO} = 0.91$  for methanol synthesis in liquid Freezene-100.

Matsumoto and Satterfield (1984) report:

$$\begin{aligned} H_{CO}/H_H &= 0.91 \text{ for octacosane at } 250 \text{ }^\circ\text{C} \\ &= 1.08 \text{ for phanthene at } 250 \text{ }^\circ\text{C} \end{aligned}$$

Deckwer, et.al.give  $H_{CO}/H_H = 1.60$  at  $250 \text{ }^\circ\text{C}$

Based on these values, for  $P_H/P_{CO} = 0.7$ ,

$$C_H/C_{CO} = 0.5 - 1.12$$



Therefore, if we have reaction control, the effective H/CO concentration the particle sees would not be much different from a gas phase reaction.

At the other extreme, if the reaction is mass transfer controlled, then the mass flux would be:

$$J_i = -\mathcal{D}_i \cdot (dC_i / dx) = -\mathcal{D}_i \cdot (\Delta C_i / \delta) = D_i \cdot C_i$$

What the catalyst sees would be the flux ratio,  $J_H/J_{CO}$

$$\therefore J_H/J_{CO} = (D_H/D_{CO}) \cdot (C_H/C_{CO}) = (D_H/D_{CO}) \cdot (H_{CO}/H_H) \cdot (P_H/P_{CO})$$

We have measured the diffusion coefficient of hydrogen and CO in octacosane, and in F-T wax.  $D_H/D_{CO}$  is about 3.0 at F-T conditions. Hence, for  $P_H/P_{CO} = 0.7$  the flux ratio (Akgerman 1988):

$$J_H/J_{CO} = 1.5 - 3.36$$

depending on the values of the Henry's Law Constants. Thus the catalyst sees a higher concentration ratio than the gas phase.

If the process is gas-liquid mass transfer controlled, then the H/CO ratio the catalyst sees would be the ratio of mass transfer coefficients:

$(k_{La H}) / (k_{La CO})$	$\propto$	$D^{0.376}$	Hughmark, 1962
	$\propto$	$D^{0.6}$	Akita & Yoshida, 1973
	$\propto$	$D^{0.667}$	Calderbank & Moo Young, 1961

where D is the ratio  $D_H/D_{CO}$ .

Using a value of  $D_H/D_{CO} = 3.0$ ,

$$(k_{La H}) / (k_{La CO}) = 1.5 - 2.0$$

depending on the mass transfer coefficient calculation.

Thus, for mass transfer control, the H/CO ratio the catalyst particle sees is significantly higher than the ratio in the gas phase.

The above analysis is valid for Fischer-Tropsch or methanol synthesis. However, the Boudouard reaction is active on an iron catalyst with iron carbide sites. Therefore, it is important for the F-T reaction only. There is no reference to the Boudouard reaction on methanol synthesis catalyst. The choice of slurry reactor there is based on superior heat transfer characteristics and higher conversion per pass due to shift of kinetic equilibrium.

### References:

- Akgerman, A., Final Report, DE-AC22-84PC70032, 1988
- Akita, K., F. Yoshida, Ind. Eng. Chem., Process Des. Dev., 12, 76 (1973)
- Calderbank, P.H., M. B. Moo Young, Chem Eng. Sci., 16, 39 (1961)
- Dry, M.E., Hydrocarbon Processing, February 1980, pp. 92-94
- Dry, M. E., Ind. Eng. Chem. Proc. Res. Dev., 15, 282 (1976)
- Hughmark, G. A., Ind. Eng. Chem., Proc. Des. Dev., 6, 218 (1967)
- Matsumoto, D. K., C. N. Satterfield, Ind. Eng. Chem. Process Des. Dev., 24, 1297 (1985)
- Stern, D., A. T. Bell, H. Heineman, Chem. Eng. Sci., 38, 597 (1983)
- von Wedel, W., S. Ledakowicz, W. D. Deckwer, Chem Eng. Sci., 43, 2169 (1988)

## DESIGN OF SLURRY REACTORS

### A. Suspension of the Solids

Reference: Roy, N. K., D. K. Guha, M. N. Rao. "Suspension of Solids in a Bubbling Liquid; Critical Gas Flow Rates for Complete Suspension", Chem. Eng. Sci., 19, 215 (1964).

Roy et al. derived a correlation, using dimensional analysis, for critical solid hold up, i.e. the maximum amount that can be kept in complete suspension for a given slurry reactor.

$$H_s = 6.84 \times 10^{-4} C_\mu N_{Re} N_B^{-0.23} \left( \frac{u_t}{u_B} \right)^{-0.18} \left( \gamma^1 \right)^{-3.0}$$

for  $R_e < 500$

$$H_s = 1.072 \times 10^{-1} C_\mu N_{Re}^{0.2} N_B^{-0.23} \left( \frac{u_t}{u_B} \right)^{-0.18} \left( \gamma^1 \right)^{-3.0}$$

for  $R_e > 600$

$H_s$  - Critical Solids hold-up (weight portion of solids)

$C_\mu = 1 - 5.892 \times 10^{-1} \log \mu_L + 1.026 \times 10^{-1} (\log \mu_L)^2$  where  $\mu_L$  is the liquid viscosity in cP.

$N_{Re}$  - gas phase Reynolds number based on superficial velocity  $\frac{d_T \rho_g u_g}{\mu_g}$

$d_T$  - column diameter

$\rho_g$  - gas density

$u_g$  - gas superficial velocity based on empty cross section area

$\mu_g$  - gas viscosity

$N_B = \frac{\sigma_L^e}{u_g \mu_L}$

$\sigma_L$  - surface tension of liquid

$\epsilon_g$  - gas holdup

$u_B$  - bubble velocity,  $u_g/\epsilon_g$

$u_t$  - Stoke's free settling velocity =  $\frac{gd_p^2 (\rho_s - \rho_L)}{18 \mu_L}$

$d_p$  - particle diameter

$\rho_s$  - solid density

$\rho_L$  - liquid density

$\gamma^l$  - wettability factor, taken unity for most catalysts.

I have used

$u_g = 0.41 - 0.5$  ft/s

$\gamma' = 1.0$

$\mu_L = 2$  cP

$\rho_g = 7 \times 10^{-3}$  g/cm<sup>3</sup>

$\sigma_L = 16.5$  dynes/cm

$\rho_s = 1.7$

$\rho_L = 0.8$

and the dimension of the La Porte reactor, this gives a solids loading (max) of 65%. So up to 45% solids should be easy to suspend.

#### B. Design Model

Both the F-T synthesis and the MeOH synthesis in slurry reactor involve gas phase reactants dissolving in the liquid, diffusing to the catalyst particle and reaction on the catalyst surface. Since the catalyst particles are small,  $\sim 50\mu$ , internal diffusion effects would probably be negligible; an effectiveness factor of unity. However, this assumption can be relaxed if needed.

The Thiele modulus for a 1st order reaction is

$$\theta = L \sqrt{\frac{k}{D_{\text{eff}}}}$$

Deckwer et al. (Chem. Eng. Sci., 36, 765 (1981)) give an overall first order rate constant of  $0.02 - 0.4 \text{ s}^{-1}$  (based on synthesis gas consumption) for Fischer-Tropsch. The constant is  $0.01 - 0.2 \text{ s}^{-1}$  for hydrogen consumption.  $D_{\text{H}_2\text{-slurry}} \approx 54 \times 10^{-5} \text{ cm}^2/\text{s}$   $L = 50 \text{ }\mu\text{m}/6 = 50 \times 10^{-4} \text{ cm}/6$  for spherical particles

$$\therefore \theta = \frac{50 \times 10^{-4}}{6} \sqrt{\frac{0.2}{54 \times 10^{-5}}} \approx 0.016$$

which corresponds to an effectiveness factor of unity. For  $k = 0.01 \text{ s}^{-1}$ ,  $\theta = 0.004$ ; thus the internal diffusion effects are probably negligible. For methanol synthesis, there is no simple 1st order pseudo rate expression. However, one can use the Weisz Modulus

$$\Phi = \phi^2 \eta = \frac{R \cdot L^2}{C_s \cdot D_{\text{eff}}}$$

Where  $R$  is the rate,  $C_s$  is the surface concentration. If  $\Phi < 0.015$ , pore diffusion effects are negligible. There is a rate expression given by v. Wedel et al. von Wedel, W., S. Ledakowicz, W. D. Deckwer, Chem. Eng. Sci. 43, 2169 (1988). Which correlates data from 7 sources.

$$R = 1.98 \times 10^7 \exp(-56343/RT) P_{\text{H}_2}^{0.4} P_{\text{CO}}^{0.18} - 2.15 \times 10^{10}$$

$$\exp(-85930/RT) P_{\text{meOH}}^{0.13}$$

if we take the maximum value of the rate, at the reactor entrance, then the second term can be neglected. At a total pressure of 1000 psia (6.895 MPa), 250C (523K) and H/CO ratio of 0.7,

Rate = 91.18 kmol/kg h

Using  $L = R/3$ , 25  $\mu\text{m}/3$

$$C_s = \text{Hydrogen solubility at these conditions} = \frac{100 \text{ kmol}}{\text{m}^3}$$

$$D_{\text{eff}} = 50 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$\text{gives } \Phi = 7 \times 10^{-4}$$

If we use the rate expression given by Air Products,  $R = 89.55 \text{ mol/kg h}$  which will give a similar  $\Phi$ . (Note: I have interpreted the "mol" in rate expression as "kmol", if they are taken as "g mol" then  $\Phi$  is even smaller). So for all practical purposes, we can safely assume that the internal diffusion effects are negligible for 50  $\mu\text{m}$  particles both for the Fischer Tropsch and the methanol synthesis reaction.

#### C. Design Equations - Parametric Analysis

References:

Chaudhari, R. V., P. A. Ramachandran, AIChEJ, 26, 177 (1980).

Ramachandran, P. A., R. V. Chaudhari, Ind. and Eng. Chem., Process Des. Dev., 18, 703 (1979).

Ozturk, S. S., Y. T. Shah, W. D. Deckwer, Chem. Eng. J., 37, 177 (1988).

Schumpe, A., Y. Serpemen, W. D. Deckwer, Ger. Chem. Eng., 2, 234 (1979).

Deckwer, W. D., Y. Serpemen, M. Ralek, B. Schmidt, Ind. & Eng. Chem. Process Des. Dev., 21, 231 (1982).

Deckwer, W. D., in "Chemical Reactor Design and Technology", H. I. de Lasa, Editor, Martinus Nijhoff Pub., NATO ASI Series E - No. 110, pp. 411-461, 1986.

In the following analysis, I have first developed a simple model to estimate the effects of various parameters, which is then extended to a more realistic model.

The simple model assumes plug flow in the gas phase and perfectly mixed liquid phase. This would be a realistic model at high gas velocities and at low column height/diameter ratios. Our analysis is based on material balance equations for a single component, although they have to be written for each reactant.

Gas phase:

$$-u_g \frac{dP_A}{dz} = k_g a (P_A - P_{Ai})$$

$u_g$ : gas velocity

$P_A$ : partial pressure

$P_{Ai}$ : interface concentration

$k_g a$ : gas side mass transfer coeff.  $\times$  area,

But by Henry's Law  $P_{Ai} = H_A C_{Ai}$  and through steady state assumption

$$k_g a (P_A - P_{Ai}) = k_L a (C_{Ai} - C_A)$$

where  $k_L a$  is the liquid side resistance,  $C_A$  is the liquid concentration and  $C_{Ai}$  interface concentration at the liquid side.

If the equations are solved eliminating  $C_{Ai}$  and  $P_{Ai}$

$$-u_g \frac{dP_A}{dz} = \frac{1}{\frac{1}{H_A k_{gA}} + \frac{1}{k_{LA}}} \left( \frac{P_A}{H_A} - C_A \right) = (K_{LA})_A \left( \frac{P_A}{H_A} - C_A \right)$$

where  $(K_{LA})_A$  is the overall resistance.

If we assume that the liquid phase is perfectly mixed, then  $C_A \neq f(z)$  and the above equation can be integrated with the inlet condition at  $z = 0$   $P_A = P_A^0$  yielding

$$\frac{P_A - H_A C_A}{P_A^0 - H_A C_A} = \exp(-\alpha_A z) \quad \text{where} \quad \alpha_A = \frac{(K_{LA})_A}{u_g H_A}$$

The partial pressure at the column exit, at  $z = L$  is  $P_A^l$ ,

$$\therefore P_A^l = P_A^0 \exp(-\alpha_A L) + H_A C_A (1 - \exp(-\alpha_A L))$$

The average rate of absorption is then given by

$$R_A = \frac{P_A^0 - P_A^l}{\bar{t}} \quad \text{where } \bar{t} \text{ is the residence time}$$

and  $\bar{t} = \frac{V}{Q_g}$        $Q_g$  : gas flow rate  
 $V$  : total slurry volume

$$\therefore R_A = \frac{Q_g H_A}{V} \left[ 1 - \exp(-\alpha_A L) \right] \left[ \frac{P_A^0}{H_A} - C_A \right]$$

This absorption rate is the mass transfer rate from the bulk of the gas to the bulk of the liquid. This rate should equal to the rate of mass transfer to the surface of the catalyst particle.



$$\therefore R_A = (k_s a_p)_A (C_A - C_{AS})$$

$$= \frac{Q H_A}{V} (1 - \exp(-\alpha_A L)) \left[ \frac{P_A^0}{H_A} - C_A \right]$$

Eliminating  $C_A$  between these equations yields

$$R_A = \frac{1}{\frac{Q H_A}{V} (1 - \exp(-\alpha_A L)) + \frac{1}{(k_s a_p)_A}} \left[ \frac{P_A^0}{H_A} - C_{AS} \right]$$

Now the total driving force is the difference between the inlet concentration and the surface concentration.

We can write 
$$R_A = (\text{M.T.R.})_A \left[ \frac{P_A^0}{H_A} - C_{AS} \right]$$

where the mass transfer resistance for A is given by

$$(\text{M.T.R.})_A = \left[ \frac{1}{\frac{Q H_A}{V} (1 - \exp(-\alpha_A L))} + \frac{1}{(k_s a_p)_A} \right]^{-1}$$

If we examine this equation

a. If gases are sparingly soluble  $H_A \gg 1.0$

$$\therefore \frac{1}{H_A k_g} \ll \frac{1}{k_L a}$$

and then  $(K_L a)_A = (k_L a)_A$  and  $\alpha_A \ll 1$

then  $\exp(-\alpha_A L) = 1 - \alpha_A L$

and

$$\frac{Q_G H_A}{V} (1 - \exp(-\alpha_A L)) = \frac{Q_G H_A \alpha_A L}{V} = \frac{Q_G H_A}{V} \cdot \frac{k_L a}{u_{G A}} \cdot L$$

$$u_G = Q_G / \text{Area} \quad V = \text{Area} \times L$$

$$\therefore \frac{Q_G H_A}{V} (1 - \exp(-\alpha_A L)) \approx k_L a$$

$$\text{and } (M.T.R)_A = \left[ \frac{1}{(k_L a)_A} + \frac{1}{(k_{s p})_A} \right]^{-1}$$

This indicates that varying the gas phase concentration will not affect the M.T.R

b. If the gases are highly soluble

$$H_A \ll 1.0$$

$$\therefore \exp(-\alpha_A L) \rightarrow 0$$

$$\text{and } \frac{H_A Q_G}{V} (1 - \exp(-\alpha_A L)) \approx \frac{Q_G H_A}{V}$$

$$\text{and } (M.T.R)_A = \left[ \frac{V}{Q_G H_A} + \frac{1}{(k_{s p})_A} \right]^{-1}$$

$$\approx (k_{s p})_A \text{ for most cases}$$

Indicating gas to liquid resistance has no significance. If there is a component B, the second reactant, we have similar equations

$$R_B = \nu R_A = (M.T.R)_B \left( \frac{P_B^0}{H_B} - C_{Bs} \right)$$

with

$$(M.T.R)_B = \left[ \frac{1}{\frac{H_B Q_E}{V} (1 - \exp(-\alpha_B L))} + \frac{1}{(k_{sp})_B} \right]^{-1}$$

First Order Reaction

$$r_A = k_r C_{AS} \cdot W$$

$k_r$  = rate constant in  $t^{-1}$   
 $w_r$  = catalyst mass/unit volume  
 $r_A$  = rxn rate.

Since  $R_A = r_A$

$$(M.T.R)_A \left( \frac{P_A^o}{H_A} - C_{AS} \right) = w k_r C_{AS}$$

eliminate  $C_{AS}$

$$R_A = r_A = \frac{P_A^o}{H_A} \left[ \frac{1}{(M.T.R)_A} + \frac{1}{w k_r} \right]^{-1} = K \frac{P_A^o}{H_A}$$

where K is the overall rate constant

$$K = \left[ \frac{1}{\frac{H_A Q_E}{V} (1 - \exp(-\alpha_A L))} + \frac{1}{(k_{sp})_A} + \frac{1}{w k_r} \right]^{-1}$$

Let's analyze K

For Fischer-Tropsch and Methanol Synthesis reaction the literature indicates that the

$$\frac{H_A Q_E}{V} (1 - \exp(-\alpha_A L)) = (k_L a)_A$$

$$\therefore K = \left[ \frac{1}{k_L a} + \frac{1}{k_{sp}} + \frac{1}{w k_r} \right]^{-1}$$

where  $k_r$  is a pseudo first order rate constant.

For Fischer-Tropsch and MeOH synthesis the physicochemical properties of the liquid phase is about the same.

$k_L a$  : Although there are many correlations, all the data in the literature indicate that  $k_L a = 0.1 - 0.2 \text{ s}^{-1}$  the maximum value reported being  $k_L a = 0.4 \text{ s}^{-1}$ .

$k_s a_p$  : We use the correlation by Sanger & Deckwer (Sanger, P., W. D. Deckwer, Chem. Eng. J., 22, 179 (1981)).

$$\text{Sh} = 2.0 + 0.545 \text{ Sc}^{1/3} \left( \frac{\epsilon d_p^4}{\nu^3} \right)^{0.264} \quad \text{Sh: } \frac{k_s d_p}{D}$$

$$\text{with } \epsilon = u_g \cdot g \quad \text{Sc: } \frac{\nu}{D}$$

Using  $D = 50 \times 10^{-5} \text{ cm}^2/\text{s}$  for  $\text{H}_2$ ,  $20 \times 10^{-5} \text{ cm}^2/\text{s}$  for  $\text{CO}$

$$\mu = 2 \text{ cp}$$

$$\rho_L = 0.8 \text{ g/cm}^3$$

$$d_p = 50 \text{ } \mu\text{m}$$

$$u = 0.5 \text{ ft/s} = 15 \text{ cm/s}$$

$$g = 980 \text{ cm/s}^2$$

$$(\text{Sh})_{\text{H}_2} = 3.74$$

$$k_s = 0.374 \text{ cm/s}$$

$$(\text{Sh})_{\text{CO}} = 4.37$$

$$k_s = 0.175 \text{ cm/s}$$

The liquid-solid interphase area  $a_p$  is

$$a_p = \frac{6 \epsilon_p}{d_p}$$

For 35% loading, 50 $\mu$ m particles  $a_p = 420 \text{ cm}^{-1}$

$$\therefore k_s a_p = 157 \text{ for H}_2 \\ 74 \text{ for CO.}$$

$wk_r$  : The reported values of  $wk_r$  vary in the literature. For Fischer Tropsch Reaction, it is in the range 0.02 - 0.4  $\text{s}^{-1}$  as mentioned on p. 3 of this report

$$\therefore K = \left[ \frac{1}{0.1 - 0.2} + \frac{1}{74 - 157} + \frac{1}{0.02 - 0.4} \right]^{-1}$$

Obviously,  $k_s a_p \gg k_L a$  and  $wk_r$  and hence the liquid solid mass transfer resistance can be neglected in analysis.  $k_L a$  is a strong function of solids suspension, solid loading, gas holdup, etc., and its value may decrease by an order of magnitude making it the controlling resistance. However, the reactor design should include both the gas-liquid mass transfer and the reaction rate terms. Liquid-solid mass transfer and diffusion into solid particle may be neglected based on the analysis presented in previous pages. Relative magnitude of these resistances will not change if a more complicated rate and hydrodynamic model is employed.

#### D. Design Equations - Model Development

##### Assumption

1. Plug flow in the gas phase - justified in terms of the high gas velocities.
2. Axial Dispersion in the liquid phase

3. Isothermal
4. Non-uniform catalyst distribution → use of sedimentation dispersion model.
5. Constant pressure → implies the influence of hydrostatic head on gas expansion and fluid properties is negligible.
6. Change in gas flow rate due to gas consumption and change in number of moles.
7. Change in gas holdup along the reactor.

A. GAS PHASE

$$-\frac{d}{dz} (u_g p_A) - (k_L a)_A \left[ \frac{P_A}{H_A} - C_A \right] = 0$$

$$-\frac{d}{dz} (u_g p_B) - (k_L a)_B \left[ \frac{P_B}{H_B} - C_B \right] = 0$$

B. LIQUID PHASE

$$\epsilon_L^D \frac{d^2 C_A}{dz^2} + (k_L a)_A \left( \frac{P_A}{H_A} - C_A \right) - \underbrace{u_L \frac{dC_A}{dz}}_{\text{is 0 if liquid batch}} - \underbrace{\epsilon_L R_A}_{\text{rxn rate term}} = 0$$

$$\epsilon_L^D \frac{d^2 C_B}{dz^2} + (k_L a)_B \left( \frac{P_B}{H_B} - C_B \right) - \underbrace{u_L \frac{dC_B}{dz}}_{\text{coefficient}} - \underbrace{\epsilon_L \nu R_A}_{\text{stoichiometric}} = 0$$

The variable gas velocity is given by

$$u_G = u_{G0} (1 + \alpha x_{A+B})$$

$$\alpha \text{ is the contraction factor} = \frac{Q_G \text{ at } x_{A+B} - 1 - Q_G \text{ at } x_{A+B} = 0}{Q_G \text{ at } x_{A+B} = 0}$$

$x_{A+B}$  is the total synthesis gas conversion  $x_{H+CO}$

$Q_g$  = volumetric flow rate of gas

$u_{Go}$  = inlet superficial gas velocity

$x_{A+B}$  is related to  $x_A$  or  $x_B$ , conversion of A or B, through the usage ratio and inlet molar ratio.

$$x_{A+B} = \frac{1+U_B}{1+I_B} x_A = \frac{1+U_A}{1+I_A} x_B$$

$$U_B = \text{usage ratio} = \frac{\text{change in \# of moles of B}}{\text{change in \# of moles of A}}, \quad U_A = \frac{1}{U_B}$$

$I_B$  = inlet B/A molar ratio ( $I_A$  = A/B ratio)

$$x_A = \text{conversion of A} = \frac{u_{Go} y_{Ao} - u_G y_A}{u_{Go} y_{Ao}}$$

$y_{Ao}$  and  $y_A$  are A mole fraction at the inlet and at  $z$ , in the gas phase

$$\therefore x_A = 1 - \frac{u_G y_A}{u_{Go} y_{Ao}} = 1 - \bar{u}_G \bar{y}_A$$

where  $\bar{u}_G$  and  $\bar{y}_A$  are dimensionless gas velocity and mole fraction

These equations can be put in dimensionless form for dimensionless profiles

(See Deckwer et al., Ind. & Eng. Chem., Process Des. Dev. 21, 231 (1982).)

#### E. Solids Dispersion

An important phenomenon in bubble column slurry reactors is the suspension and axial dispersion of solids. For bubble column slurry

operation two suspension states may exist; namely complete suspension in which all particles are in suspension and homogeneous suspension in which particle concentration is uniform throughout the reactor. We have already presented the criteria of Roy *et al.* (1964) for determining the maximum amount of solids that can be kept in complete suspension for a given operating condition and have shown that for Fischer-Tropsch and Methanol Synthesis reactors, theoretically up to 60% can be suspended.

In bubble column slurry reactors there is a solids distribution with height.

Reference: Kato, Y., A. Nishiwaki, T. Fukuda, S. Touka, J. Chem. Eng., Japan, 5, 112 (1972).

The solids distribution effect is more significant in columns with large  $L/d_t$  ratios. The effect of this profile on reaction rate is obvious, if the catalyst particles are not well dispersed, the reactor space time yields will suffer.

Normally, for catalytic reactors, the reaction rate is expressed in terms of

$$R = \frac{\text{moles product}}{\text{unit weight catalyst} \times \text{time}}$$

If there is uniform catalyst loading, this quantity R multiplied by the total density of the catalyst in weight/volume, yields the reactor size for a specified conversion. If the catalyst dispersion is not uniform; i.e., there is a catalyst concentration profile in the reactor; then, in the model equations, instead of R, one must use  $R \cdot C_{\text{cat}}$  where  $C_{\text{cat}}$  is the catalyst concentration in weight/volume, and



integrate the equation over the reactor length. For slurry bubble columns this concentration can be calculated from the dispersion/sedimentation model. For batch suspension, this model yields

$$D_c \frac{d^2 C_{cat}}{dz^2} + u_{cs} \frac{dC_{cat}}{dz} = 0$$

$D_c$  - dispersion coefficient for the catalyst particles

$u_{cs}$  - settling velocity of catalyst particles

For Batch Slurry: The solution of this equation, with the appropriate boundary conditions yields

$$C_{cat}(z) = (C_{cat})_{avg} \frac{u_{cs} L \exp\left[-\frac{u_{cs} z}{D_c}\right]}{1 - \exp\left[-\frac{u_{cs} L}{D_c}\right]}$$

where  $(C_{cat})_{avg}$  is the mean catalyst concentration.

If the liquid is also flowing, the equation then becomes

$$D_c \frac{d^2 C_{cat}}{dz^2} + \left[ u_{cs} - \frac{u_L}{1 - \epsilon_g} \right] \frac{dC_{cat}}{dz} = 0$$

(Reference: Ozturk, S. S., Y. T. Shah, W. D. Deckwer, Chem. Eng. J., 37, 177 (1988)).

the solution then becomes

$$C_{cat} = (C_{cat})_{feed} \frac{\exp\left[\left(\frac{u_{cs} L}{D_c} - \frac{u_L L}{D_c(1 - \epsilon_g)}\right)(1 - z)\right] - \frac{u_L L}{D_c(1 - \epsilon_g)}}{\frac{L}{D_c} \left[ u_{cs} - \frac{u_L}{1 - \epsilon_g} \right]}$$

In these equations, the two parameters are  $D_c$  and  $u_{cs}$ .

1. Calculation of  $D_c$  (Kato, et al. 1972)

$$\frac{u_G d_R}{D_c} = \frac{13 Fr}{1 + 8Fr^{0.85}}$$

$u_G$  - gas superficial velocity

$d_R$  - reactor column diameter

$$Fr = \text{Froude number, } = \frac{u_G}{(g d_R)^{0.5}}$$

2. Calculation of the settling velocity in a particle swarm,

$$u_{cs} = 1.2 u_{st} \left( \frac{u_G}{u_{st}} \right)^{0.25} \left( \frac{1 - \epsilon_s^*}{1 - \epsilon_{s1}^*} \right)^{2.5}$$

$u_{st}$  - terminal settling velocity according to Stoke's Law

$\epsilon_s^*$  - volume fraction of solids in the bubble free suspension

$\epsilon_{s1}^*$  - the value of  $\epsilon_s^*$  at  $0.1 \text{ g/cm}^3$  solids conc.

3. To calculate  $u_{st}$

$$Re = \frac{u_{st} d_p}{\nu}$$

$d_p$  - particle diameter

$\nu$  - kinematic viscosity of the liquid

$$Re = \frac{Ar}{18} \quad \text{if } Re \leq 0.5$$

$$Re = \left( \frac{Ar}{13.9} \right)^{0.7} \quad \text{if } Re > 0.5$$

where Ar is the Archimedes number given by

$$Ar = \frac{\rho_L (\rho_{cat} - \rho_L) g d_p^3}{\mu_L^2}$$

$\rho_L$  - liquid density

$\rho_{cat}$  - catalyst density (particle density)

$\mu_L$  - fluid viscosity

With the knowledge of  $D_c$  and  $u_{cs}$ , the solids (catalyst) concentration profile in a suspension reactor can be calculated for various operating conditions ( $u_G$ ,  $u_L$ ,  $d_R$ , etc.). This information is important for process optimization and yield estimation.

Validity of the sedimentation dispersion model was confirmed by several investigators. At low Froude numbers and for large particle diameters Kato et al. (1972) observed significant deviation from the equation

$$\frac{u_{GR} d_p}{D_c} = \frac{13 Fr}{1 + 8 Fr^{0.85}}$$

which can be accounted for by incorporating the particle Reynolds number in the correlation. However, this should not be necessary for F-T Synthesis' and Methanol Synthesis Reaction. So, for these cases

$$\frac{u_{GR} d_p}{D_c} = \frac{13 Fr (1 + 0.009 Re_p Fr^{-0.8})}{1 + 8 Fr^{0.85}}$$

Thus, in the equations presented on page 12, the  $R_A$  terms should be multiplied by  $C_{cat}$  to get the real profiles.

F. Calculation of the Transport Parameters

As we have shown already, of the mass transfer coefficients, we only need  $k_L A$  since  $k_{s,p} a \gg k_L a$ . In addition we need the gas and the liquid holdup, the axial dispersion coefficient  $D_L$  and the relevant parameters in the correlations.

1. Axial Dispersion Coefficient:

Ref: Y. T. Shah and W. D. Deckwer, Scale-up Aspects of Fluid-Fluid Reactions, in "Scale-up in Chemical Process Industries",

R. Kabel and A. J. Bisio, Editors, Wiley, New York, 1986.

For non-flowing liquid phase (batch slurry with gas flow) they give

$$\frac{u_G L}{D_L \epsilon_L} = 2.83 \left( \frac{u_G^2}{g d_R} \right)^{0.34}$$

$u_G$  - mean linear gas velocity

$D_L$  - axial dispersion coefficient

$L$  - column length

$\epsilon_L$  - liquid holdup =  $1 - \epsilon_G$

$g$  - acceleration of gravity,  $980 \text{ cm/s}^2$

$d_R$  - column diameter.

Another correlation is

$$D_L = 3.676 u_G^{0.32} d_R^{1.34} \text{ cm}^2/\text{s}$$

in this equation  $u_G$  is in  $\text{cm/s}$   $d_R$  in  $\text{cm}$ .

## 2. The Mass Transfer Coefficient, $k_L a$

Some authors (for example Alvarez-Cuenca et al., 1980) have reported the dependence of  $k_L a$  on the liquid flow rate. However, it has been shown by Barckhart and Deckwer (1976) that this effect results from using the NTU method for the data evaluation, which assumes plug flow for both phases in a bubble column.

There are numerous correlations in the literature to determine  $k_L a$ . Most widely accepted ones are given below.

a. Akita and Yoshida, 1973

Ref: Akita, K., F. Yoshida, Ind. Eng. Chem., Process Des. Dev., 12, 76(1973).

$$\frac{(k_L a)_A d_R^2}{D_A} = 0.6 \left( \frac{\nu_L}{D_A} \right)^{0.5} \left( \frac{g d_R^2 \rho_L}{\sigma_L} \right)^{0.62} \left( \frac{g d_R^3}{\nu_L^2} \right)^{0.31} \left( \epsilon_G \right)^{1.1}$$

$d_R$  = column diameter

$D_A$  = diffusion coefficient of A in the liquid

$\nu_L$  = kinetic viscosity of the liquid

$\rho_L$  = liquid density

$g$  = gravitational constant

$\sigma_L$  = surface tension

$\epsilon_G$  = gas hold up.

---

Alvarez-Cuenca, M., G. C. J. Baker, M. A. Bergougnou, Chem. Eng. Sci., 35, 1121 (1980)

Burekhardt, R., W. D. Deckwer, Verfahrenstechnik (Mainz), 10, 429 (1976).

b. Calderbank and Moo-Young (1961)

Ref: Calderbank, P. M., M. B. Moo-Young, Chem. Eng. Sci., 16, 39  
(1961)

$$k_L = 0.42 \left[ \frac{(\rho_L - \rho_G) \mu_L g}{\rho_L^2} \right]^{1/3} \left[ \frac{D_A \rho_L}{\mu_L} \right]^{1/2}$$

$\rho_G$  - gas density

$\rho_L$  - liquid density

$\mu_L$  - liquid viscosity

$D_A$  - diffusion coefficient

$g$  - gravitational constant

To use this equation, one needs the interface area "a" to calculate  $k_L a$ .

Calderbank, in Trans. Instr. Chem. Eng., 36, 443 (1958) gives "a" as

$$a = 1.44 \frac{\left( \frac{P}{V_L} \right)^{0.4} \rho_L^{0.2}}{\sigma_L^{0.6}} \left( \frac{u_g}{u_t} \right)$$

$P$  - power consumption in agitation,  $V_L$  - slurry volume

$u_g$  - gas superficial velocity,  $u_t$  - terminal bubble velocity.

limitations of the correlation for "a" are given in the original reference.

There are other ways of interpreting the gas-liquid interface area,

$$a = 6 \frac{\epsilon_G}{d_m}$$

$\epsilon_G$  = gas holdup

$d_m$  = volume/surface mean bubble diameter.

(or also sauter mean diameter)

Deckwer, et al., Ind. and Eng. Chem., Process Des. Dev., 21, 231 (1982)

$$\text{give } a = 4.5 u_g^{1.1}$$

Akita and Yoshida, Ind. Eng. Chem., Process Des. Dev., 13, 84 (1974),  
give

$$ad_R = \frac{1}{3} \left[ \frac{gd_R^2 \rho_L}{\sigma_L} \right]^{0.5} \left[ \frac{gd_R^3}{\nu_L^2} \right] \left[ \epsilon_G \right]^{1.13}$$

C. Kawagoe, et al. Correlation

Kawagoe, M., K. Nakao, T. Otake, J. Chem. Eng. Japan, 8, 254 (1975).

$$\frac{k_L d_m}{D_A} = 0.975 \left[ \frac{\mu_L}{D_A \rho_L} \right]^{1/2} \left[ \frac{g d_m^3 \rho_L^2}{\mu_L^2} \right]^{1/4}$$

This correlation, again needs  $a$ , the interface area and an expression for the mean bubble diameter.

D. Deckwer, et al., 1983

Deckwer, W. D., K. Nguyen-tein, B. G. Kelkar, Y. T. Shah, AIChE J., 29, 915 (1983).

$$k_L a = 0.157 u_g^{0.82}$$

where  $u_g$  is in m/s

The first two correlations, Akita and Yoshida and Calderbank and Moo

Young are the ones used the most. It has been pointed out that the correlation of Akita and Yoshida applies well to the cases where gas is sparged by less effective spargers, i.e., either single or multi orifice distributors. Therefore, the Akita-Yoshida correlation can be recommended for a conservative estimation of  $k_L a$ . Only Margartz and Pilhofer (Chem. Eng. Sci., 36 1069 (1981)) report even lower  $k_L a$  values, i.e. about 50% of those predicted from Akita & Yoshida Correlation. If efficient gas spargers like porous plates and two component nozzles are used  $k_L a$  values, considerably higher than those calculated from the correlation of Akita and Yoshida can be obtained.

In slurry bubble columns  $k_L a$  is affected by the presence of solids. The degree of influence depends on the particle concentration, size, the liquid-solid density difference, geometric shape, and operating condition.

At high liquid velocities ( $u_L = 0.093$  m/s) and low gas velocities, the  $k_L a$  values are slightly higher than those without the presence of solids. Such a small increase in  $k_L a$  is reported by various investigators at low particle concentration, typically less than 15%, for particle sizes in the 50 - 300 micron range.

References:

1. Nguyen-Tien, K., W. D. Deckwer, Chem. Eng. Sci., 17, 693 (1962).
2. Joosten, G. E. H., J. G. H. Schilder, J. J. Jansen, Chem. Eng. Sci., 32, 563 (1977).
3. Slessor, C. G. M., W. T. Allen, A. R. Cummings, U. Pavlowsky, J. Shields, Chem. Reaction Eng., Proc. 4th European Symposium, Brussels, 41, 1968.



4. Tamhaukar, S. S., R. V. Chaudhari, Ind. Eng. Chem., Fundam 18, 406 (1979).

With rising gas velocities and decreasing liquid velocities the  $k_L a$  values are lower than those obtained without the dispersed solid phase. At high solid concentration, a steep decrease in  $k_L a$  takes place which is caused by a decrease in "a".

Ref. - Kato, Y., A. Nishiwaki, T. Kago, T. Fukuda, S. Tarraha, Int. Chem. Eng., 13, 582 (1973).

Joosten, et al. has shown that as solids are added to the bubble column  $k_L a$  first increases slightly and then starts to decrease rapidly by addition of more solids. The point (or solids conc.) where the decrease starts depends on the solid type and particle size. The curves of  $k_L a$  v.s. volume fraction of solids, therefore, do not coincide for various solids and particle sizes. They explain the sharp reduction in  $k_L a$  by reduction in the interface area "a". They had observed that the gas holdup at high solids concentration (greater than 15%) is lower and gas bubbles are larger, apparently bubble coalescence takes place at a higher frequency.

Joosten et al. as well as Deckwer and co-workers claim that presence of solid particles in the range  $50 < dp < 200$  microns and at loadings less than 15%, the effect of solids on  $k_L a$  is negligible.

However, we know that even then, the process of mass transfer can be enhanced if the particles are very reactive or if the volumetric absorption capacity of the particles with respect to A (the absorbing species) is much larger than the solubility of A in the liquid.

Recently, new data reported (Sada, et al., Chem. Eng. Sci., 38

2047 (1983)), indicates 50% drop in  $k_L a / k_L a^0$  with 10% solids loading of 2 micron particles ( $k_L a^0$  is the mass transfer in absence of solids).

An equation predicting the drop in  $k_L a$  is still missing.

## Effects of Solids on $K_L a \approx k_L a$

---

It is shown in the literature that  $k_L a$  decreases with loading of solid catalyst in the slurry, especially in the loading range above 15%. References are provided in the previous report.

From a fundamental point of view,  $k_L$  is a property related to a solute diffusing from the interface into the liquid phase. Hence, theoretically  $k_L$  should be independent of solute loading. Surface renewal theory gives  $k_L \propto \sqrt{D_A}$ .

The solids loading, however, will change the interphase area "a" since they will affect both the bubble size and the bubble coalescence.

If we start with the Akita-Yoshida correlation

$$\frac{(k_L a) d_R^2}{D_A} = 0.6 \left( \frac{v_L}{D_A} \right)^{0.5} \left( \frac{g d_R^2 \rho_L}{\sigma_L} \right)^{0.62} \left( \frac{g d_R^3}{v_L^2} \right)^{0.31} (\epsilon_G)^{1.1}$$

and calculate  $(k_L a) / (k_L a)^0$  where  $(k_L a)^0$  is the mass transfer coefficient in the absence of solids, we get

$$\frac{k_L a}{(k_L a)^0} = \left( \frac{v_L}{v_L^0} \right)^{0.5} \left[ \left( \frac{\rho_L}{\rho_L^0} \right) \left( \frac{\sigma_L}{\sigma_L^0} \right) \right]^{0.62} \left( \frac{v_L}{v_L^0} \right)^{0.62} \left( \frac{\epsilon_G}{\epsilon_G^0} \right)^{1.1}$$

since  $v_L = \frac{\mu_L}{\rho_L}$ ; and  $d_R, D_A, g$  are constants and if we assume  $\sigma_L \approx \sigma_L^0$  in absence

of data on the effect of solids on surface tension, one obtains a correction factor CF such that CF multiplied by  $(k_L a)^0$  from Akita-Yoshida Equation yields the  $k_L a$  for the slurry. Thus

$$\text{C.F.} = \frac{k_L a}{(k_L a)^0} = \left( \frac{\mu_L}{\mu_L^0} \right)^{0.12} \left( \frac{\rho_L}{\rho_L^0} \right)^{0.74} \left( \frac{\epsilon_G}{\epsilon_G^0} \right)^{1.1}$$

In this equation,  $\rho_L$  is the density of the slurry.

$\rho_L = \epsilon_s \rho_s + (1 - \epsilon_s) \rho_L^0$  where  $\rho_s$  is the density of solids,  $\epsilon_s$  is the volume fraction of solids, and  $\rho_L^0$  is the density of pure liquid.

$$\therefore \frac{\rho_L}{\rho_L^0} = \epsilon_s \frac{\rho_s}{\rho_L^0} + (1 - \epsilon_s)$$

One of the better equations for predicting  $\epsilon_G$  in presence of solids is proposed by Zheng, et al. Reference: Zheng, L., B. Yao, Y. Feng, *Chem. Eng. Sci.*, 43, 2195 (1988).

They give

$$\epsilon_G = 0.114 Fr^{0.35} Ar^{0.11} \left(1 + \frac{u_L}{u_G}\right)^{-0.48} (1 - \epsilon_s)^{1.74}$$

$$\text{where: } Fr = \frac{u_G}{\sqrt{gd_R}} \qquad Ar = \frac{gd_p^3 \rho_L (\rho_s - \rho_L)}{\mu_L^2}$$

$$\text{Then: } \left(\frac{\epsilon_G}{\epsilon_G^0}\right) = (1 - \epsilon_s)^{1.74}$$

So the correction factor becomes

$$\text{C.F.} = \frac{k_L a}{(k_L a)^0} = \left(\frac{\mu_L^0}{\mu_L}\right)^{0.12} \left(\epsilon_s \frac{\rho_s}{\rho_L^0} + (1 - \epsilon_s)\right)^{0.74} (1 - \epsilon_s)^{1.914}$$

In the above analysis it is assumed that the Froude and Archimedes numbers are the same for the liquid and the slurry in the limit as  $\epsilon_s \rightarrow 0$ .

The above correlation seems to work for the data in the literature in the particle range ~50 microns. The correlation fails for larger and/or smaller particles due to the significant contribution from the Archimedes number. However, for other diameter particles

$$\frac{(k_L a)_1}{(k_L a)_2} = \frac{(d_{p1}^3)^{0.11}}{(d_{p2}^3)^{0.11}} = \left(\frac{d_{p1}}{d_{p2}}\right)^{0.33} \quad \text{where 1 is for } 50 \mu\text{m, 2 is for other sizes}$$

if everything else is the same.

I have applied the above correlation to Joosten's data and Sada et.al.'s data. The results are as follows:

Joosten et.al., *Chem. Eng. Sci.*, 32, 563 (1977).

Sada et.al., *Chem. Eng. Sci.*, 38, 2047 (1983).

Thus, the equation is:

$$\frac{(k_L a)}{(k_L a)^0} = \left(\frac{\mu_L^0}{\mu_{SL}}\right)^{0.12} \left(\epsilon_s \frac{\rho_s}{\rho_L^0} + (1 - \epsilon_s)\right)^{0.74} (1 - \epsilon_s)^{1.914} \left(\frac{d_p}{50}\right)^{0.31}$$

$\mu_{SL}$  - slurry viscosity;  $d_p$  - particle diameter in microns

Dispersed Solid	Size	Solids Loading	( $k_L a$ ) Measured	( $k_L a$ ) Calculated	
Polypropylene	53 – 105 $\mu$	30%	0.08 s <sup>-1</sup>	0.079 s <sup>-1</sup>	Data from Joosten et.al.
		35%	0.04	0.066	"
		40%	–	0.054	"
Polypropylene	250 $\mu$	30%	0.16	0.12	"
		35%	0.13	0.10	"
		40%	0.06	0.08	"
Glass Beads	53 $\mu$	9%	0.20	0.18	"
		30%	0.16	0.12	"
		35%	0.11	0.10	"
		40%	0.06	0.08	"
Glass Beads	88 $\mu$	30%	0.16	0.13	"
		35%	0.14	0.12	"
		40%	0.10	0.09	"
Sugar	74 – 105 $\mu$	30%	0.13	0.11	"
		35%	0.06	0.075	"
		40%	0.04	0.06	"
and from Sada et.al. Mg(OH) <sub>2</sub>	2 $\mu$	5%	$k_L a / (k_L a)^0$ measured 0.6	– calculated 0.4	

Although the correlation is quite simple to use, and somewhat empirical, it seems to work. The  $(k_L a)^0$  from Joosten et.al., is 0.2 s<sup>-1</sup> in the absence of solids. So the agreement is acceptable.

When I apply the technique to F-T and/or MeOH synthesis, the following results are obtained:

Data:  $\mu_{SL} / \mu_L$  (the liquid viscosity increases with solid content, we assumed the values measured by Joosten et.al. since his liquid, kerosene, is similar to the F-T wax and/or MeOH fluid at reaction conditions  $\Rightarrow \rho_L = 0.8 \text{ g/cm}^3$ ,  $\mu_L = 1 - 2 \text{ cp}$ .)

$$\therefore 25\% \text{ loading } \frac{\mu_{SL}}{\mu_L} = 6.5$$

$$30\% \text{ loading } = 10$$

$$35\% \text{ loading } = 15$$

$$40\% \text{ loading } = 20$$

Skeletal density is taken as 5.5, as specified in Air Products Report p. III-19 – Skeletal density of iron catalyst and it is consistent with values for iron ore reported in Perry's. Particle density  $\rho_s$  is taken as 3.3 g/cm<sup>3</sup> based on an assumed porosity of 40% (gas filled).

$$\rho_L = 0.8 \text{ g/cm}^3, \quad d_p = 26 \mu$$

Then:

$$\frac{k_{La}}{(k_{La})^0} = \left( \frac{\mu^0}{\mu} \right)^{0.12} \left( \epsilon_s \frac{\rho_s}{\rho_L} + (1 - \epsilon_s) \right)^{0.74} (1 - \epsilon_s)^{1.914} \left( \frac{26}{50} \right)^{0.33}$$

Loading Volume %	$\left[ \frac{k_{La}}{k_{La}^0} \right]$ Calculated
25%	0.56
30%	0.50
35%	0.44
40%	0.37

Calculation of  $(k_{La})^0$ , Akita Yoshida Correlation

$$\frac{(k_{La})^0 d_R^2}{D_A} = 0.6 \left( \frac{\mu_L}{D_A \rho_L} \right)^{0.5} \left( \frac{g d_R^2 \rho_L}{\sigma_L} \right)^{0.62} \left( \frac{g d_R^3 \rho_L}{\mu_L^2} \right)^{0.31} (\epsilon_G)^{1.1}$$

$$\mu_L = 2_{cp} \Rightarrow \text{Fig. III B-1, page III-22 of Air Products Report}$$

$$\rho_L = 0.8 \text{ g/cm}^3$$

$$\sigma_L = 16.5 \text{ dyne/cm at } 250\text{C, Air Products Rpt. p. III-7}$$

$$\left. \begin{array}{l} D_A \text{ for H}_2 = 54 \times 10^{-5} \text{ cm}^2/\text{s} \\ D_A \text{ for CO} = 20 \times 10^{-5} \text{ cm}^2/\text{s} \end{array} \right\} \text{from our measurements}$$

$$g = 980 \text{ cm/s}^2$$

$$\therefore (k_{La})^0_{\text{H}_2} = 2.01 d_R^{0.17} \epsilon_G^{1.1}$$

$$(k_{La})^0_{\text{CO}} = 1.27 d_R^{0.17} \epsilon_G^{1.1}$$

where  $d_R$  is the tube diameter in cm.,  $\epsilon_G$  is the gas hold up.

Akita-Yoshida correlation for  $\epsilon_G$  is:

$$\frac{\epsilon_G}{(1 - \epsilon_G)^4} = 0.2 \left( \frac{g d_R^2 \rho_L}{\sigma_L} \right)^{1/8} \left( \frac{g d_R^3 \rho_L^2}{\mu_L^2} \right)^{1/12} \frac{u_g}{\sqrt{g d_R}}$$

$$\frac{\epsilon_G}{(1 - \epsilon_G)^4} = 0.034 u_G \text{ for the system defined above (note that the } d_R \text{ terms cancels.)}$$

for  $u_G = 15 \text{ cm/s} \approx 0.5 \text{ ft/s}$

$$\epsilon_G \approx 0.20$$

$$\therefore (k_L a)_H^0 = 0.342 d_R^{0.17}$$

$$(k_L a)_{CO}^0 = 0.216 d_R^{0.17}$$

Thus for the reactor

Volume %	$(k_L a)_H$	$(k_L a)_{CO}$
25% loading	$0.192 d_R^{0.17}$	$0.121 d_R^{0.17}$
30% loading	$0.171 d_R^{0.17}$	$0.108 d_R^{0.17}$
35% loading	$0.150 d_R^{0.17}$	$0.095 d_R^{0.17}$
40% loading	$0.127 d_R^{0.17}$	$0.080 d_R^{0.17}$

These will be the  $(k_L a)$  values as a function of  $d_R$ . I would like to note that as  $d_R$  ranges from 1 cm to 10 m (1000 cm),  $d_R^{0.17}$  varies only from 1 to 3.23.

# Model Solutions for Slurry Reactors

---

## A. ASSUMPTIONS

1. Gas phase in plug flow
2. Liquid phase not mixed and in PF (Model 1) or perfectly mixed (Model 2)
3. Only gas/liquid mass transfer and the reaction terms are important, liquid/solid mass transfer resistance is negligible
4. Intraparticle diffusion is negligible (small particles,  $\eta = 1.0$ )
5. First order reaction rate;  $r = k_r \epsilon_L C_H$
6. Constant usage ratio (moles of CO consumed per mole H is constant), the stoichiometry is  $H_2 + \gamma CO \rightarrow \text{products}$
7. Liquid phase batch
8. Assume catalyst uniformly dispersed

## MODEL 1

Gas phase plug flow, liquid phase not well agitated so that the concentration in the liquid phase varies along the reactor as well.

$$-\frac{d(u_G P_H)}{dx} = k_L a \left( \frac{P_H}{H_H} - C_H \right)$$

$$P_H = RT C_{GH} \text{ where } C_{GH} \text{ is the gas phase concentration}$$

$$\frac{C_{GH}}{H_{GH}} = C_H^* \text{ the interphase concentration}$$

$$P_H = y_H P \Rightarrow \text{ideal gas}$$

$$\therefore -\frac{d(u_G P_H)}{dx} = k_L a RT \left( C_H^* - \frac{C_H}{RT} \right) = k_r \epsilon_L C_H$$

$$\text{For the liquid phase } k_L a RT \left( C_H^* - \frac{C_H}{RT} \right) = k_r \epsilon_L C_H$$

$$\therefore C_H = \frac{k_L a RT C_H^*}{k_r \epsilon_L + k_L a}$$



Substitute back and simplify

$$- \frac{d(u_G y_H)}{dx} = \frac{(k_L a) k_r \epsilon_L RT}{(k_r \epsilon_L + k_L a) P} C_H^*$$

$$\text{let } \frac{1}{K_H} = \frac{1}{k_L a} + \frac{1}{k_r \epsilon_L}, \quad C_H^* = \frac{y_H P}{H_H}, \quad z = \frac{x}{L}$$

$$\therefore - \frac{d(u_G y_H)}{dz} = \frac{K_H RT L}{H_H} y_H$$

$$\text{define conversion } X_H = \frac{u_{GO} y_{HO} - u_G y_H}{u_{GO} y_{HO}}$$

$$\text{then } u_G y_H = u_{GO} y_{HO} (1 - X_H)$$

Overall conversion (H and CO combined)

$$X_{H+CO} = X_H \frac{1+U}{1+I} \quad \text{where } U = \frac{\text{change in \# of moles of CO}}{\text{change in \# of moles of H}}$$

$$\text{inlet ratio } I = \frac{n_{CO}^0}{n_H^0}, \quad \text{ratio of inlet molar flow rates}$$

$$u_G = u_{GO} (1 + \alpha X_{CO+H}) \quad \text{where } \alpha \text{ is contraction factor defined as}$$

$$\alpha = \frac{Q (\text{at } X_{H+CO} = 1) - Q_0}{Q_0}, \quad Q \text{ is the volumetric flow rate}$$

$$\text{then } d(u_G y_H) = - u_{GO} y_{HO} dX_H$$

$$\frac{y_H}{u_G} = \frac{u_{GO} y_{HO} (1 - X_H)}{u_G} = \frac{y_{HO} (1 - X_H)}{(1 + \alpha X_H \frac{1+U}{1+I})}$$

$$\text{let } \alpha^* = \alpha \frac{1+U}{1+I}$$

$$\text{then } u_G^0 y_H^0 \frac{dX_H}{dz} = \frac{K_H RT L}{H_H} y_H^0 \frac{(1 - X_H)}{(1 + \alpha^* X_H)}$$

$$\frac{(1 + \alpha^* X_H)}{(1 - X_H)} \frac{dX_H}{dz} = \frac{K_H RT L}{H_H u_G^0}$$

integrate from 0 to  $X_H$  on  $dX_H$   
and 0 to 1 on  $dz$

$$(1 + \alpha^*) \ln(1 - X_H) + \alpha^* X_M = -St$$

when the Stanton No  $St = \frac{K_H RTL}{u_G^0 H_H}$

Reference: Deckwer, W. D., Serpemen Y., Ralek M., Schmidt, B. *Chem. Eng. Sci.*, 36, 765 (1981).

$$K_H = \frac{(k_L a) (k_r \epsilon_L)}{(k_L a) + (k_r \epsilon_L)}$$

Most studies indicate  $\alpha \approx -0.5$

$k_r = k_w W$  where  $k_w$  is the rate constant in

units  $\frac{\text{volume}}{\text{mass catalyst} \times \text{time}}$  and  $W$  is

catalyst loading in  $\frac{\text{mass}}{\text{unit volume}}$

At this stage we may take into consideration the change in  $\epsilon_G$  and  $u_G$  in calculating  $(k_L a)$  from Akita-Yoshida correlation.

$$\frac{\epsilon_G}{(1 - \epsilon_G)^4} \approx 0.034 u_G \quad (\text{p. 3 of previous report})$$

$$\text{and } (k_L a) \propto \epsilon_G^{1.1}$$

$$\text{so } u_G = u_{G0} (1 + \alpha X_{CO+H})$$

Solution of this equation,  $X_H$  vs.  $St$  will give the conversion profile. In the Stanton number  $k_L a$  and  $L$  are variables.

**MODEL 2**

Gas phase in plug flow, liquid phase perfectly mixed.

Gas phase – using concentration instead of partial pressure.

$$- \frac{d(u_G C_{HG})}{dx} = k_L a (C_{HL}^* - C_{HL})$$

Liquid Phase

$$A_c \int_0^L k_L a (C_{HL}^* - C_{HL}) dx = V k_r \epsilon_L C_{HL}, \quad V \text{ is the volume of the slurry}$$

Based on previous definition

$$C_{HG} = C_{HG}^0 \left( \frac{1 - X_H}{1 + \alpha^* X_H} \right)$$

$$u_G = u_G^0 (1 + \alpha^* X_H)$$

Alternatively, we can use overall hydrogen balance

$$u_G^0 A_c C_{HG}^0 X_H = k_r \epsilon_L C_{HL} V$$

Substituting these back into the first equation and integrating as before, we get:

$$\frac{L(k_L a)}{u_G^0 H_H} = - \frac{1}{1 + \alpha^* n} \left( \alpha^* X_H + (1 + \alpha^* Y) \ln \left( 1 - \frac{X_H}{Y} \right) \right)$$

$$\text{where } n = \frac{H_H C_{HL}}{C_{HG}^0} \quad Y = \frac{1 - n}{1 + \alpha^* n}$$

Rearranging the overall hydrogen balance

$$\frac{A_c X_H u_G^0}{(k_r \epsilon_L) V} = \frac{X_H u_G^0}{(k_r \epsilon_L) L} = \frac{C_{HL}}{C_{HG}^0}$$

Multiply by  $X_H$

$$\frac{X_H u_G^0 H_H}{k_r \epsilon_L L} = \frac{H_H C_{HL}}{C_{HG}^0} = n$$

$\therefore$  We have an implicit relationship between  $X_H$  and  $\frac{L(k_L a)}{u_G^0 H_H}$

Reference: Bukur, D., Chem, Eng. Sci, 38, 441 (1988).

The *liquid phase mixing* and *volume contraction* ( $\alpha$ ) have a very significant effect on the reactor performance, particularly at high conversion. For example, if 90% hydrogen conversion is desired, the required reactor heights calculated from these two models are:

1. 8.3 m      Model 1       $\alpha = -0.5$
2. 17 m      Model 1       $\alpha = 0$
3. 23.3 m    Model 2       $\alpha = -0.5$
4. 63.1 m    Model 2       $\alpha = 0$

Thus axial mixing,  $D_z$ , and volume contraction factor,  $\alpha$ , are very important. PF model, Model 1, assumes  $D_z = 0$  and PM model, Model 2, assumes  $D_z = \infty$ .

The above numbers are from Bukur's paper. When we have a non first order reaction rate expression and axial mixing term  $D_z$ , the numbers calculated will be somewhat in the middle.

## Effectiveness Factors in Fixed-Bed Fischer Tropsch

It is generally agreed that in F-T synthesis in the gas phase, the catalyst pores will be wax filled.

Excellent reference is Huff and Satterfield, Ind. Eng. Chem., Process Des. Dev., 24, 986 (1985).

If we assume liquid filled pores, Avg. MWt of wax  $\approx$  400, then 1/8" - 1/16" diameter particles with 1st order rate constant  $0.01 - 0.4 \text{ s}^{-1}$ , then from

$$\theta = \frac{R}{3} \sqrt{k/D} \quad \text{with } D \approx 50 \times 10^{-5} \text{ cm}^2/\text{s}$$

we get  $\theta = 0.11 - 1.44$

and  $\eta = 1.0 - 0.62$

Similarly for CO,  $\eta = 1.0 - 0.42$

So the diffusion effect will not be very large.

# APPENDIX B

## SLURRY REACTOR DESIGN STUDIES

### J. M. Smith Reports

#### Contents

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

	Page
I. Available Models	1
II. Mass Transfer, Heat Transfer and Mixing Effects	2
III. Difference Between Models	
A. Stoichiometry and CO/H <sub>2</sub> Feed Ratio	3
B. Contraction of Gas Velocity	5
IV. Gas Holdup	5
V. Kinetics	7
VI. Solution of Model Equations	
A. Deckwer Model	8
B. Stern Model	9
VII. Design Quantities	9
Literature Cited	12

Summary of Literature on Methanol Production from Synthesis Gas  
13 pages

	Page
I. Background on Methanol Processes	1
II. Reaction Kinetics	2
III. Reactor Design	
A. Fixed-Bed	5
B. Liquid-Phase Processes	6
IV. Comparison of Fixed-Bed and Slurry Processes	8
V. Miscellaneous Comments	
A. Catalyst deactivation	10
B. Improved Catalysts	10
C. Future Catalysis Research	11
Literature Cited	12

Letter Concerning Pressure Effect on F-T Kinetics      2 pages

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

This review is not a complete survey of all aspects of liquid-phase (slurry) Fischer-Tropsch (FT) processes. Instead, the intent is a critical analysis of available procedures for design of bubble-column type slurry reactors for processing syngas ( $\text{CO} + \text{H}_2$ ). The desired results from a model are the conversion and productivity [(product produced) / (amount of catalyst (time))] as a function of reactor length and include the influence of pressure, temperature, superficial gas velocity, reactor diameter, and catalyst loading (mass of catalyst/volume of liquid). The effects of these operating and design conditions are important for scaleup and economic optimization.

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

I. Available Models

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

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

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

## II. Mass Transfer, Heat Transfer and Mixing Effects

All three models neglect mass transfer resistance between the bulk liquid and outer surface of the catalyst particles and intraparticle diffusion resistance. These transport processes are rapid with respect to other steps in the overall reactions since the catalyst particles are small ( $\sim 50\mu\text{m}$ ). Deckwer et al (4) included both these effects through an overall effectiveness factor  $\eta_s$  but in applying the equations  $\eta_s$  is taken equal to 1.0. This leaves gas bubble-to-liquid mass transfer, intrinsic kinetics and axial dispersion to be considered. These concepts about modeling bubble reactors are reasonable and the three significant rate steps are accounted for in all three models. However, the Kuo (6) model only includes axial dispersion in the liquid phase. The plug-flow assumption for the gas probably would not introduce much error because the solubilities of CO and H<sub>2</sub> in the waxy-oil liquid are relatively low (6,12) and the gas velocity would be high ( $\sim 10\text{-}15\text{cm/s}$ ) in commercial scale reactors. All three models account for the change in gas velocity, due to reaction, as the gas moves up the reactor.

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



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

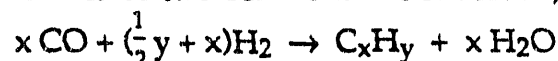
### III. Difference Between Models

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

#### A. Stoichiometry and CO/H<sub>2</sub> Feed Ratio

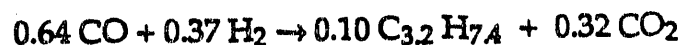
The Deckwer model does not consider variations in hydrocarbon product chain length (the chain growth probability,  $\alpha$ ) or product composition (fraction of product that is paraffinic,  $\gamma$ ). Rather, a constant value throughout the reactor is chosen for the ratio of CO to H<sub>2</sub> consumed by the reaction (the usage factor, U). Also, the feed ratio (I) of CO to H<sub>2</sub> is restricted to a narrow range of about 1.5 to 1.8 so that it is safe to assume a rate equation first order in hydrogen and zero order in CO. Thirdly, the water-gas-shift (WGS) reaction is assumed to be fast and irreversible so that water is not a final product. These three restrictions mean that the design model requires only mass balances for hydrogen, one for the gas phase and one for the liquid phase. However, these second-order ordinary differential equations are coupled so that they must be solved simultaneously, and with an energy balance if a temperature distribution is to be calculated.

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



and water is a product. With this more general treatment of stoichiometry and WGS reaction, the model includes coupled, mass-balance equations for CO, H<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> and C<sub>x</sub>H<sub>y</sub> in both gas and liquid phases. Because finite kinetics of the WGS reaction are included, the usage factor U can vary along the reactor length.

The complex stoichiometry evaluation of Stern turns out to be close to the simpler approach of Deckwer when the WGS shift reaction is irreversible and fast. For example, Stern chooses  $\alpha = 0.69$  and  $\gamma = 0.25$  and  $\beta = 0$  [ $\beta =$  water/CO<sub>2</sub> in the product] to compare with the Deckwer et al (13) experimental data in a 3.8cm reactor. For this case the Stern equations for the stoichiometry lead to the overall reaction



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

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

### B. Contraction of Gas Velocity

Since the volume of gas decreases with reactor length due to reaction, the superficial gas velocity also decreases. This decrease depends upon the conversion of  $\text{CO} + \text{H}_2$ , and hence upon the stoichiometry and feed ratio. For the simple case of Deckwer (4) where a constant usage factor is used, the contraction of gas velocity is linearly related to the conversion of hydrogen. This relation and the relation between velocity and gas-phase mol fraction of  $\text{H}_2$  are derived by Deckwer (4).

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

### IV. Gas Holdup

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

$$\epsilon_g (\text{holdup}) = 0.053u_g^{1.1} \quad (1)$$

where  $u_g$  is the superficial gas velocity. This slightly greater than linear proportionality was obtained from experimental measurements at  $250^\circ\text{C}$  in waxy liquid (14).

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

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

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

$$\left( \frac{\epsilon_g}{1 - \epsilon_g} \right) = 0.115 \left[ \frac{u_g^3 \rho_L}{g (\mu/\rho)_L (\rho_L - \rho_g)} \right]^{0.23} \quad (2)$$

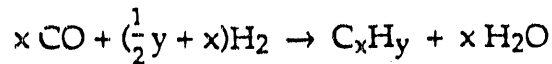
where  $\rho$  = density,  $\mu$  = viscosity and subscripts L and g designated liquid and gas and all units are cgs.

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

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

### V. Kinetics

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



proposed in reference (22) is

$$r_{\text{H}_2 + \text{CO}} = \frac{k_F C_{\text{H}_2}^2 C_{\text{CO}}}{a C_{\text{CO}} C_{\text{H}_2} + C_{\text{H}_2\text{O}}} \quad (3)$$

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

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

$$r_s = k_s \left[ C_{\text{CO}} C_{\text{H}_2\text{O}} - \frac{1}{K} C_{\text{CO}_2} C_{\text{H}_2} \right] \quad (4)$$

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

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

expression for the rate of combined H<sub>2</sub> + CO consumption for a feed and usage ratio of 1.5

$$r_{\text{H}_2 + \text{CO}} = A W_{\text{Fe}} C_{\text{H}} \exp\left(-\frac{E}{RT}\right) \epsilon_L \quad (5)$$

where

- $r$  = moles/(cm<sup>3</sup> reactor volume) (s)
- $A$  = [(s) (wt. % catalyst in slurry)]<sup>-1</sup> = 1.12 × 10<sup>5</sup>
- $W_{\text{Fe}}$  = wt. % catalyst in slurry
- $C_{\text{H}}$  = liquid phase H<sub>2</sub> concentration, moles/cm<sup>3</sup>
- $\epsilon_L$  = liquid holdup
- $E$  = 70,000 kJ/mol
- $U$  = usage ratio

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

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

## VI. Solution of Model Equations

### A. Deckwer Model (4)

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

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

### B. Stern Model

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

### VII. Design Quantities

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

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

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

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

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

---

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



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

### Literature Cited

1. Kölbel, Herbert and Ralek, Milos, "The Fischer-Tropsch Syntheses in the Liquid Phase", Catal. Rev. - Sci. Eng., 21 225-274 (1980).
2. Saxena, S.C., Rosen, M., Smith, D.N. and Ruether, J.A., "Mathematical Modeling of Fischer-Tropsch Slurry Bubble Column Reactors", Chem. Eng. Commun. 40, 97-151 (1986).
3. Schlinder, H.D., Chm. COLIRN Panel Assessment, "Coal Liquefaction - A Research and Development Needs Assessment, Chap. 5 Review of Indirect Liquefaction" (by Wender, Irving and Klier, Kamil), Final Report, Vol. II, p. 5-1 to 5-132, March 1989, DOE Contract DE-AC01-87ER30110.
4. Deckwer, Wolf-Dieter, Serpemen, Yalein, Ralek, Milos and Schmidt, Bruno, Ind. Eng. Chem. Process Des. Dev. 21, 231 (1982).
5. Kuo, J.C.W., "Slurry Fischer-Tropsch/Mobil Two-Stage Process of Converting Syngas to High Octane Gasoline" Final Report DOE/PC/30022-10, DOE Contract DE-AC-80PC30022, June 1983.
6. Stern, David, Bell, Alexis, T. and Heinemann, Heinz, Chem. Eng. Sci. 40, 1665 (1985).
7. Calderbank, P.H., Evans, F., Farley R., Jepson, G. and Poll, A., Catalysis in Practice, Sympos. 67, Instn. Chem. Engrs. (1983).
8. Calderbank, P.H. and Moo-Young, M.B., Chem. Eng. Sci. 16, 39 (1961).
9. Satterfield, C.N. and Huff, G.A., Chem. Eng. Sci. 35, 195 (1980) and 36, 790 (1981).
10. Bukur, D.B., Chem. Eng. Sci. 38, 441 (1983).
11. Bukur, D.B. and Gupte, K.M., Chem. Eng. Sci. 38, 1363 (1983).
12. Chang, Hungteh and Smith, J.M., AIChE Journal 29, 699 (1983).

## Summary of Literature on Methanol

### Production from Synthesis Gas

#### I. Background on Methanol Processes

Prior to about 1960 methanol from hydrogen and carbon monoxide was produced in high pressure (>10 MPa) fixed-bed reactors using metals and oxides of Cu, Zn, and Cr<sub>2</sub>O<sub>3</sub> (1-4). In the 1960 decade new, extremely selective Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> catalysts were developed by Imperial Chemical Industries (ICI) and Lurgi. These catalysts gave high rates of production at lower pressures (5-10 MPa) and at 220° to 280°C. A detailed history of methanol production is available including a description of new processes in the development stage (5).

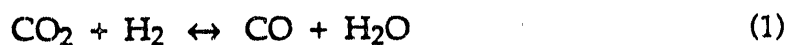
The maximum conversion of CO or CO<sub>2</sub> to methanol is limited by equilibrium. Since the reactions are exothermic, higher maximum conversions are obtained at lower temperatures. In fixed-bed reactors it is difficult to prevent some temperature rise so that much of the effort in reactor design has been directed toward efficient removal of the heat of reaction. The temperature control problem also is partially responsible for the development work on the liquid-phase process. Fine catalyst particles are suspended in an inert liquid and the synthesis gas flows upward through the slurry. The relatively good mixing and heat capacity of the slurry prevents large temperature gradients. The reaction heat is removed either by internal heat transfer surface or by circulating the slurry through an external exchanger.

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

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

## II. Reaction Kinetics

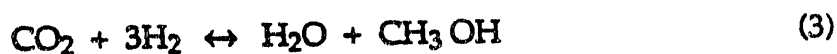
As noted by Bart and Sneed (6), methanol synthesis involves five reactants and products,  $H_2$ ,  $CO$ ,  $H_2O$ ,  $CO_2$  and  $CH_3OH$ . Usually carbon dioxide and often steam are present in the gas feed. Hence, the water-gas-shift (WGS) reaction



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



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



Both reactions (2) and (3) are exothermic ( $\Delta H_2$  is about  $-100\text{kJ/mol}$  and  $\Delta H_3$  about  $-61\text{kJ/mol}$ ) at process temperatures. When synthesis gas is produced either by reforming of natural gas or by coal gasification  $H_2O$  and  $CO_2$  are present unless efficient upstream separation is installed.

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

Sneeden (6) list seven separate rate expressions written in terms of partial pressures in the gas phase. These expressions would be applicable for slurry processes only if gas and liquid compositions are in equilibrium and solubilities (Henry's law constants) are introduced. Reference (6) provides an abbreviated assembly of all the studies on methanol kinetics for the  $\text{Al}_2\text{O}_3$ -based catalysts. Graaf (8, 9) has proposed somewhat different but equally complex rate equations that are applicable for the  $\text{Al}_2\text{O}_3$ -based catalysts (employed in the ICI process).

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

$$r = \frac{k \left[ f_{\text{CO}} f_{\text{H}_2}^{3/2} - f_{\text{CH}_3\text{OH}} / f_{\text{H}_2}^{1/2} \right]}{\left( 1 + K_1 f_{\text{CO}} + K_2 f_{\text{CO}_2} \right) \left( f_{\text{H}_2}^{1/2} + K_3 f_{\text{H}_2\text{O}} \right)} \quad (4)$$

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

Simpler rate expressions have been proposed. For example Andrew (10) suggested from data on the commercial (ICI)  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst:

$$r \text{ (for } \text{CH}_3\text{OH)} = k p_{\text{H}_2}^{0.7} p_{\text{CO}}^{0.4} \phi(\text{CO}_2) \quad (5)$$

where  $\phi(\text{CO}_2)$  is an unspecified function of  $\text{CO}_2$  pressure.

Apparently, the activity of the catalyst depends significantly in its oxidation states and this in turn depends on the  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  content of the gas. This complex situation means that catalyst activity of the same catalyst can vary within a reactor as the gas composition changes.

Berty and colleagues (11) have proposed for the  $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$  catalyst rate equations that follow stoichiometry. Their expressions for reactions (2) and (1) are

$$r_{\text{CH}_3\text{OH}} = r_2 = k_2 \left[ C_{\text{H}_2} - \frac{C_{\text{CH}_3\text{OH}}}{K_2 C_{\text{H}_2} C_{\text{CO}}} \right] \quad (6)$$

$$r_1 = k_1 \left[ C_{\text{H}_2} = \frac{C_{\text{CO}} C_{\text{H}_2\text{O}}}{K_1 C_{\text{CO}_2}} \right] \quad (7)$$

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

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

$$r = k P_{\text{CO}}^{1/3} P_{\text{H}_2}^{2/3} \left[ 1 - \frac{P_{\text{CH}_3\text{OH}}}{K P_{\text{CO}} P_{\text{H}_2}^2} \right] \quad (8)$$

Since no terms for  $\text{CO}_2$  or  $\text{H}_2\text{O}$  are included, this expression should be applicable only when neither of these two species are present. Then  $K$  is proportional to the equilibrium constant for reaction (2). Also, gas and liquid phase concentrations are apparently assumed to be in equilibrium since the equation is expressed in partial pressures for the liquid-phase processes, Henry's law constants are incorporated in  $k$  and  $K$ .

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

### III. Reactor Design

#### A. Fixed Bed

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

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

rule is that external mass transfer resistance is negligible with respect to intraparticle diffusion, while the external (bulk fluid-to-particle) temperature difference is more important than the intraparticle temperature gradient. Öztürk, et al (14) in their modeling of the fixed-bed process, include both external and intraparticle temperature and concentration gradients. Of these four transport effects only intraparticle mass transfer was significant at the conditions studied. The Öztürk approach (which utilized Equations (6) and (7) for the intrinsic rate) is a general one for representing mass and energy transport effects in a non-isothermal, adiabatic, fixed-bed reactor. Their model is for a catalyst bed without intercooling (Lurgi type) except that the bed is considered to be adiabatic rather than exposed to a constant surroundings temperature. Alternately, the model could be applied to an individual segment of an ICI reactor which operates close to adiabatically. While the Öztürk, et al results are given for a Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> catalyst, the same procedure could be applied to any catalyst with appropriate changes in the rate equations.

#### B. Liquid-Phase Process

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

---

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



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

A simple model assuming plug flow of gas and well-mixed batch liquid, as presented by Bukur (16) for F-T reactors, might be applied to methanol production. This would require that the heat of reaction be removed internally and that the rate of accumulation of methanol (and CO and CO<sub>2</sub>) in the liquid is negligible with respect to the reaction rate.

The results (12,17) obtained for the Laporte PDU demonstration-size reactor provide useful experimental data on the performance of the liquid-phase process. Data are available for the effects of catalyst loading (10-50 wt%), feed composition [55% H<sub>2</sub>, 19 CO, 5 CO<sub>2</sub> and 35% H<sub>2</sub>, 51 CO, 13 CO<sub>2</sub> and 1% inerts], catalyst deactivation, gas holdup, type of slurry liquid, and method of heat transfer, on methanol production rate. It was shown that internal heat transfer could be used satisfactorily so that continuous circulation of slurry through an external heat exchanger could be eliminated. With internal heat

removal, constant productivity could be achieved with periodic withdrawal (daily, for example) of a small volume of slurry, combined with addition of an equal volume of slurry with fresh catalyst. Catalyst life tests showed a deactivation rate of less than 0.2% per day. A uniform decrease of 0.2% per day at constant temperature corresponds to a drop to 11% of original activity in three years. However, the rate of decrease could diminish with time, and also the temperature could be increased to approach constant activity. Maximum space time yields above 1.0 kg CH<sub>3</sub> OH per kg catalyst per hour were obtained.

The authors of reference (17) conclude that the technology of the liquid-phase process is now reasonably well established. Once field tests are satisfactorily completed on removal of catalyst poisons (prime poisons are iron and nickel carbonyls, H<sub>2</sub> S, COS and HCl), it was proposed to go to the next step toward commercialization—a 500 ton/day methanol unit.

#### IV. Comparison of Fixed-Bed and Slurry Processes

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

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

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

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

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

### I. Miscellaneous Comments

#### A. Catalyst Deactivation

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

#### B. Improved Catalysts

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

---

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

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

### C. Future Catalysis Research

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

### Literature Cited

1. Parart, M., French Patent 540,343, August 1921.
2. Lormand, C. Ind. Eng. Chem. 17, 430 (1925).
3. Frolich, P.K., Fenske, M.R. and Quiggle, D., Ind. Eng. Chem. 20, 694 (1928).
4. Frolich, P.K., Fenske, M.R., Taylor, P.S. and Southwich, C.A., Ind. Eng. Chem. 20, 1327 (1928).
5. Klier, Kamil, Chapter 5, Sec. 3, in "Coal Liquefaction--A Research and Development Needs Assessment" by Schlinder, H.D. Chm. Panel Assessment, Final Rept. Vol. II, March 1989, DOE Contract DE-AC01-87ER30110.
6. Bart, J.C.J. and Sneed, R.P.A., Catalysis Today 2, 1-24 (1987).
7. Chemierohstoff, aus Kohle, Herausgeber Jurgen Falbe, Chapter 9, p. 300-322, Georg Thieme Verlag, Stuttgart (1977). Chapter 8 on Fischer-Tropsch processing includes information on liquid-phase reactors that is applicable to methanol production.
8. Graaf, G.H., Ph.D. Thesis, Chapter 7, Rijksuniversitat, Groningen, Netherlands 1988. Kinetics results for fixed-bed operation are to be published: Graaf, G.H., Stamhuis, E.J. and Beenackers, A.A.C.M., "Kinetics of Low-Pressure Methanol Synthesis," Chemical Engineering Science.
9. Graaf, G.H., Winkelman, J.G.M. and Beenackers, Chemical Engineering Science 43 2161 (1988).
10. Andrew, W.P.S., Plenary Lecture (paper #13) Post Congress Symposium, 7th Internat'l Cong. on Catalysis, Osaka, July 1980.
11. Berty, J.M., Lee, S., Sivagnanam, K. and Szeifert, F., Inst. Chem. Eng., Symp. Series 87 (1981).

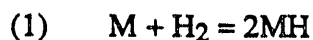
12. "Liquid Phase Methanol Process Development Unit, Laporte PDU Research and Engineering Support Studies," Final Report, DOE Contract DE-AC22-85PC80007, Feb. 1988.
13. Supp, Emil, Hydrocarbon Processing, p. 71, March 1981.
14. Öztürk, S.S., Shah V.T. and Deckwer, W.-D., The Chemical Engineering Journal 37, 177 (1988).
15. Stern, David, Bell, A.T. and Heinemann, Heinz. Chem. Eng. Sci. 40, 1665 (1985).
16. Bukur, Dragomir, B., Chem. Eng. Sci., 38, 441 (1983).
17. Studer, D.W., Henderson, J.L., Hsiung, T.H. and Brown, D.M., "Status Report on the Liquid-Phase Methanol Project," (Electric Power Research Institute (EPRI) Conference on Fuel Science and Conversion, Palo Alto, CA May 18-19, 1989.
18. Lee, S., Berty, J.M., Green, H.L., Desirazu, S., Ko, M. Parameswaran, V., and Sawant, A., Quarterly Report to Electric Power Research Institute (EPRI), Jan. 7, 1984.
19. Serwin, M.B. and Frank, M.B., Hydrocarbon Processing, p. 122, November, 1986.
20. Oldshue, J.V. and Ruston, J.H., Chemical Eng. Progress 48, 297 (1952).
21. Joshi, J.B., Pandit, A.B., and Sharma, M.M., Chem. Eng. Sci. 37, 813 (1982).
22. Vedage, G.A., Himelfarb, P.B., Simmons, G.W., and Klier, K., ACS Symposium Series 279, 295 (1985).
23. Klier, K., Young, C.W., and Nunan, J.G., Ind. Eng. Chem. Fund. 25, 36 (1986).

March 16, 1990

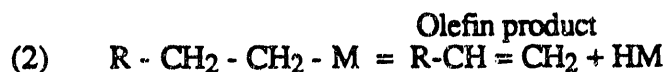
Mr. Joseph M. Fox III  
Bechtel Group Inc.  
P.O. Box 3965  
San Francisco, CA 94119-3965

Dear Joe:

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



The paper by G. Henrici-Olive and S. Olive [Angew. Chemie International Ed. 15, 136 (1976)] seems to be a logical explanation of how hydrocarbons are produced from the metal hydride. The carbon atoms (from CO) are introduced into the chains attached to the catalyst (M). Then growth is determined by a "chain transfer" mechanism. That is a chain, R-CH<sub>2</sub>-CH<sub>2</sub>-M, leaves the catalyst and a new chain is started at the same site (M) according to the reaction:



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

While these latter steps [after reaction (1)] may be affected by pressure, the effect of pressure on rate and conversion is primarily determined by reaction (1). This production of metal hydride is an activated adsorption process, and its rate increases with pressure (hydrogen pressure) on any one site. Also, as the pressure increases more of the sites in the catalyst are utilized for adsorption. The overall result is that the rate of reaction appears as a first-order process. This then means that as the pressure increases at low pressure, with a constant T and volumetric gas flow rate through the reactor, the conversion remains the same, but the space-time-yield increases linearly with hydrogen pressure (see Deckwer paper, Fig. 4). This result has been verified up to 400-600 psia with experimental data [Industrial and Engineering Chemistry 46, 2278 (1954); 44, 391 (1952)].

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



J. M. Fox  
March 16, 1990  
Page 2

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

$$\text{rate} = \frac{k p_{\text{H}_2}}{1 + K p_{\text{H}_2}}$$

over a very wide pressure range.

Up to the critical or threshold pressure,  $K p_{\text{H}_2} \ll 1$ , but at high pressures 1 and  $K p_{\text{H}_2}$  are about the same, and at very high pressures  $K p_{\text{H}_2} \gg 1$  so that the rate =  $k/K$  and no longer increases with pressure.

Sincerely,

Joe Smith

**APPENDIX C**  
**SLURRY REACTOR DESIGN STUDIES**  
**REVIEW OF FIXED-BED AND SLURRY**  
**REACTOR KINETICS**

Contents

	Page
Fused Magnetite Catalyst - Slurry vs Fixed-Bed	1
Cobalt Fixed-Bed Kinetics	1
CSTR Model for Fischer-Tropsch	3

## APPENDIX C

### REVIEW OF FIXED-BED AND SLURRY REACTOR REACTION KINETICS

When trying to match observed conversions with slurry reactor model predictions (Section 2.4.3) it was found that a new expression for the kinetic constant had to be developed. It was also necessary to get an insight into the differences, if any, between slurry reactor and fixed-bed kinetics, to examine any differences between iron and cobalt catalysts and to look at pressure effects. This review is by no means complete, but some observations were made that could be useful to future investigators.

Fused Magnetite Catalyst - Slurry vs Fixed-Bed - Data of Satterfield, et al (IEC Fund. 24, 450, 1985)

This data was of interest since it consisted of a direct comparison of the same catalyst in a fixed-bed reactor and in a well-mixed slurry reactor. The authors concluded that "...the catalyst activity in the fixed-bed appears to have been moderately greater than in the slurry reactor." They could not ascribe the difference to the higher inlet pressure in the fixed-bed reactor but thought the fixed-bed catalyst might have been reduced in a more optimal manner. Catalyst activity, expressed in  $\mu\text{mols of CO} + \text{H}_2 \text{ converted}/[\text{min} \cdot \text{g of cat} \cdot \text{atm of H}_2]$ , varied from 100 to 190 over the temperature range 233 to 250 °C in the fixed-bed measurements. Over approximately the same range, they observed values of 78 and 130 in the slurry reactor.

It was of interest to see whether this same data could be fit to the simplified models discussed earlier in this report. Figure C-1 shows the result of plotting the fixed-bed CO conversion data in the form indicated by the plug-flow model (Model 1). A temperature correction was applied by multiplying  $\text{GHSV}^{-1}$  by an exponential activation energy term. An activation energy of 80 kJ/gmol brought the data onto one curve. Values of  $\alpha$  of 0.0 and -0.5 were tested and, somewhat unexpectedly, a value of 0.0 gave the best straight line. The fixed-bed data were obtained on a fine catalyst diluted with inert material and placed in a reactor tube surrounded by a fluidized sand bath. GHSV is expressed in  $\text{Nm}^3/(\text{h} \cdot \text{kgCat})$ .

The slurry reactor data were obtained in a small, stirred autoclave so that mass transfer resistance could be minimized. A CSTR model (Model 3) should be most applicable under these circumstances and one was developed for this project. It is presented at the end of Appendix C. Figure C-2 shows the best straight-line fit to the CO conversion data using this model, which was obtained using an activation energy of 135 kJ/gmol and an  $\alpha$  of -0.6. It is not known why the activation energy was higher than in the fixed-bed case, but activation energies of this magnitude have been reported for the Fischer-Tropsch reaction where mass transfer effects are known to be insignificant.

Cobalt Fixed-Bed Kinetics - Data of Singleton and Rogier (Hyd. Proc., p 71 -74, May 1983) - Data of Post, et al (AIChEJournal, 35, 1107-1114, 1988)

The fixed-bed data of Singleton and Rogier are of interest because they represent a new cobalt type catalyst, developed by Gulf before their merger with Chevron, and because a pressure effect is presented. Increased pressure is shown to increase "catalyst activity" but

the effect diminishes with increasing pressure. The authors present a table of CO conversion data taken at low pressure in a 1" diameter, single tube, pilot plant in which space velocity is given per gram of catalyst. They also present 250 psig data which are apparently on a volumetric space velocity basis and can be related to their low pressure data and their reported pressure effect if a catalyst bulk density of roughly 500 kg/m<sup>3</sup> is assumed. The Gulf technology described in this paper was later sold to Shell.

Post, et al, present a review of diffusional effects in fixed-bed F-T catalysts which quantifies the effects of particle size and pore diameter. The catalyst is a Zirconium promoted cobalt catalyst developed by Shell, presumably to be used in their new plant in Malaysia. Some data are given for iron catalysts but not enough to quantify differences. Space velocity and STY are given per m<sup>3</sup> of catalyst, rather than per kg of catalyst, and on this basis there does not appear to be much difference between catalysts at comparable particle size.

Figure C-3 presents a correlation of the Shell data on H<sub>2</sub> conversion and Gulf data on CO conversion using a Model 1 (plug flow) type plot. The value of  $\alpha$  used is that reported by Post, et al. To compare Figures C-1 and C-3, multiply the ordinate in C-3 by the expected catalyst density in kg/m<sup>3</sup>. If, for example, this density is 500, then a coordinate value of 2 on Figure C-3 corresponds to a coordinate value of 4 on Figure C-1. On this basis, conversions are roughly comparable. Figure C-1 mixes H<sub>2</sub> and CO Conversions, which is unfortunate, but can't be helped. It can be stated, however, that with 2.0 H<sub>2</sub>/CO ratio feed gas and a catalyst with low water gas shift activity, the two conversions should be of comparable magnitude.

The ARGE design point (precipitated iron catalyst) and the design point selected for this study are also indicated in Figure C-1. It would be of value to have a better definition of space velocity requirement and the pressure effect for various catalysts, but it is felt that the design point represents a reasonable consensus of the above information for a "generic" catalyst..

Table C-1 compares the various kinetic curve fits developed in this report over the temperature range of interest. Columns 2 and 3 represent Figures C-1 and C-2, respectively. Column 4 is the Gulf correlation line from Figure C-3, assuming a catalyst bulk density of 532 kg/m<sup>3</sup>, and column 5 is the ARGE design point. Column 6 represents the equation developed to fit the Rheinprussen laboratory data<sup>9</sup> in Section 2 and is expressed in terms of hydrogen conversion:

$$k'_H = k_H / (\text{kgCat}/\text{m}^3) = 3.3 \cdot 10^9 \cdot e^{(-130,000/RT)}$$

The slurry concentration and gas holdup correspond to estimated Rheinprussen laboratory conditions.

---

<sup>9</sup> The comparable expression given by Deckwer was expressed in terms of wt% Fe:

$$k'_H = k_H / \text{wt \% Fe} = 112,000 \cdot e^{(-70,000/RT)}$$

## CSTR MODEL FOR FISCHER-TROPSCH

### Model 3

**Assumptions:** Basically the same assumptions as for Model 1 and Model 2, except that both gas phase and liquid phase are fully mixed so that the concentrations in the reactor - both phases at steady state - are those corresponding to the product gas composition. Other assumptions:

1. Only gas/liquid mass transfer and the reaction terms are important, liquid/solid mass transfer is negligible.
  2. Intraparticle diffusion is negligible.
  3. First order reaction rate,  $r = k_r \epsilon_L \cdot C_H$ .
  4. Constant usage ratio,  $U$ , (moles of CO consumed per mole of H<sub>2</sub> consumed).
  5. Stoichiometry handled by means of a contraction factor,  $\alpha$ , which is constant.
  6. Liquid phase batch (liquid flow can be neglected).
  7. Catalyst is uniformly dispersed.
  8. Reaction rate expressed in terms of catalyst loading:  
 $k_r = k_H = k'_H \cdot (\text{kgCat}/\text{m}^3)$  where  $k'_H = 3.3 \cdot 10^9 \cdot e^{(-130,000/RT)} \cdot (P/1100)^{0.5}$ ,  $T$  in °K,  $P$  in kPa,  $k_r$  in sec<sup>-1</sup> (Section 2.4.3).
  9.  $k_L a$  and  $\epsilon_G$  are established at an average value of superficial velocity  $u_G$ .
  10. The correction to  $k_L a$  for solids content, previously derived, applies.
- $$Q^0 \cdot C^{0HG} - Q \cdot C_{HG} = k_L a \cdot (C^*_{HL} - C_{HL}) \cdot V_L = k_r \epsilon_L \cdot C_{HL} \cdot V_L$$

$$H_e/RT = H_H = C_{HG}/C^*_{HL}, \text{ where } H_e \text{ is Henry's law constant.}$$

By definition of the contraction terms,  $\alpha$  and  $\alpha^* = \alpha \cdot (1 + U)/(1 + I)$  :

$$Q = Q^0 \cdot (1 + \alpha^* \cdot X_H)$$

$$Q^0 \cdot C^{0HG} \cdot X_H = Q^0 \cdot C^{0HG} - Q \cdot C_{HG} = Q^0 \cdot C^{0HG} - Q^0 \cdot (1 + \alpha^* \cdot X_H) \cdot C_{HG}$$

$$C_{HG} = C^{0HG} \cdot (1 - X_H) / (1 + \alpha^* \cdot X_H)$$

$$k_L a \cdot (C_{HG}/H_H - C_{HL}) = k_r \epsilon_L \cdot C_{HL}$$

$$C_{HL} = k_L a \cdot C_{HG}/H_H / (k_r \epsilon_L + k_L a)$$

$$(Q^0/V_L) \cdot C^{0HG} \cdot X_H = ((k_r \cdot \epsilon_L \cdot k_{La}) / (k_r \cdot \epsilon_L + k_{La})) \cdot C_{HG} / H_H$$

$$\text{Let } K_{La} = (k_r \cdot \epsilon_L \cdot k_{La}) / (k_r \cdot \epsilon_L + k_{La})$$

$$(Q^0/V_L) \cdot C^{0HG} \cdot X_H = (K_{La}/H_H) \cdot C_{HG} = (K_{La}/H_H) \cdot C^{0HG} \cdot (1 - X_H) / (1 + \alpha^* \cdot X_H)$$

$$X_H \cdot (1 + \alpha^* \cdot X_H) / (1 - X_H) = (K_{La}/H_H) \cdot V_L / Q^0 = K_{La} \cdot R \cdot T \cdot L / (H_e \cdot u_G^0) = \text{Stanton No.}$$

For  $\alpha^* = -0.5$

$X_H$	Stanton No.
0.95	9.975
0.90	4.95
0.80	2.40

For  $\alpha^* = 0.0$

$X_H$	Stanton No.
0.95	19.0
0.90	9.0
0.80	4.0

Figure C-1

Fused-Magnetite Fixed-Bed Kinetics  
 $f(\text{Conv}) = (1 + \alpha) \ln(1 - X) + \alpha X$

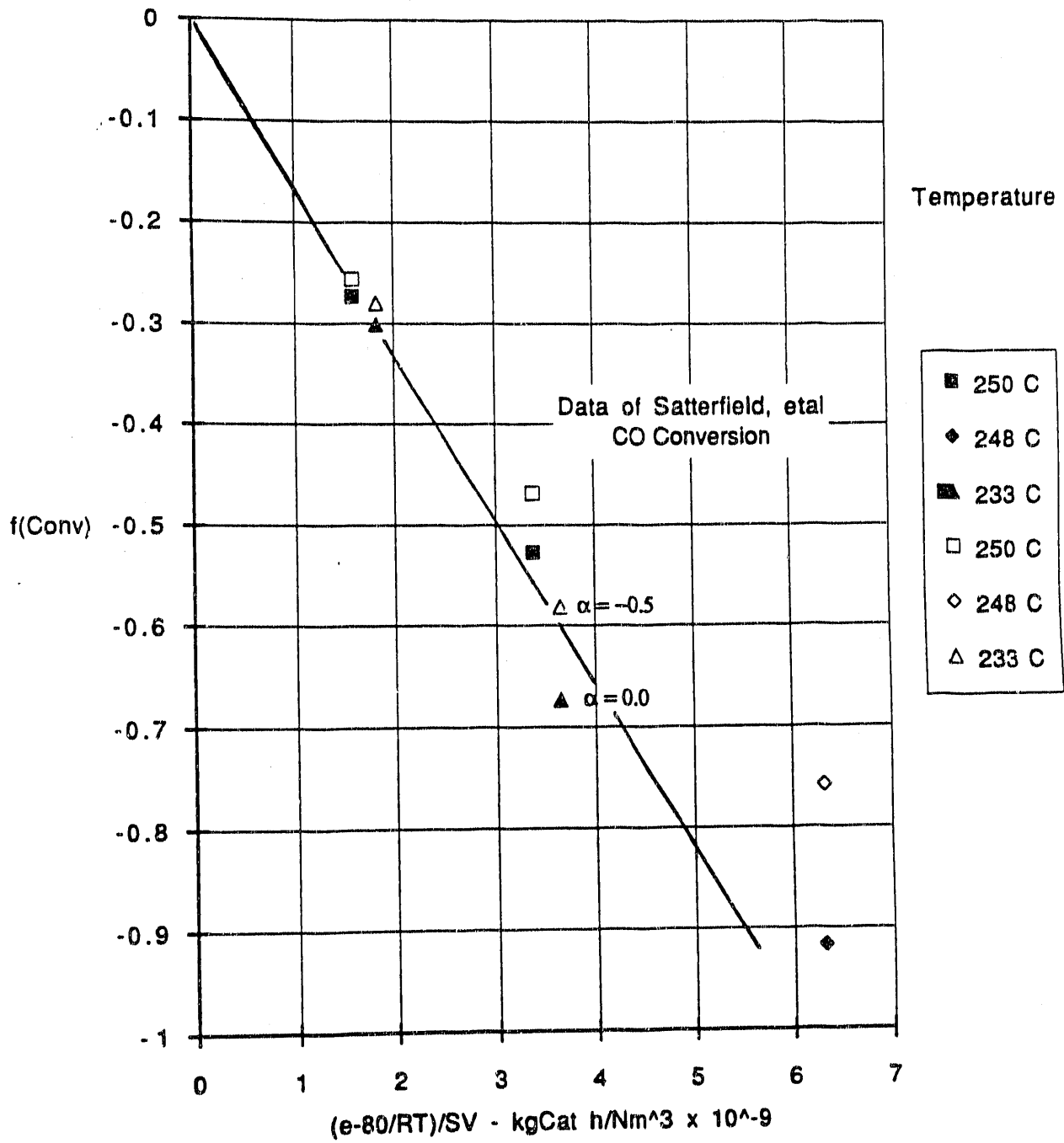


Figure C-2

Fused-Magnetite Slurry CSTR Kinetics  
 $f(\text{Conv}) = X(1 - \alpha X)/(1 - X)$

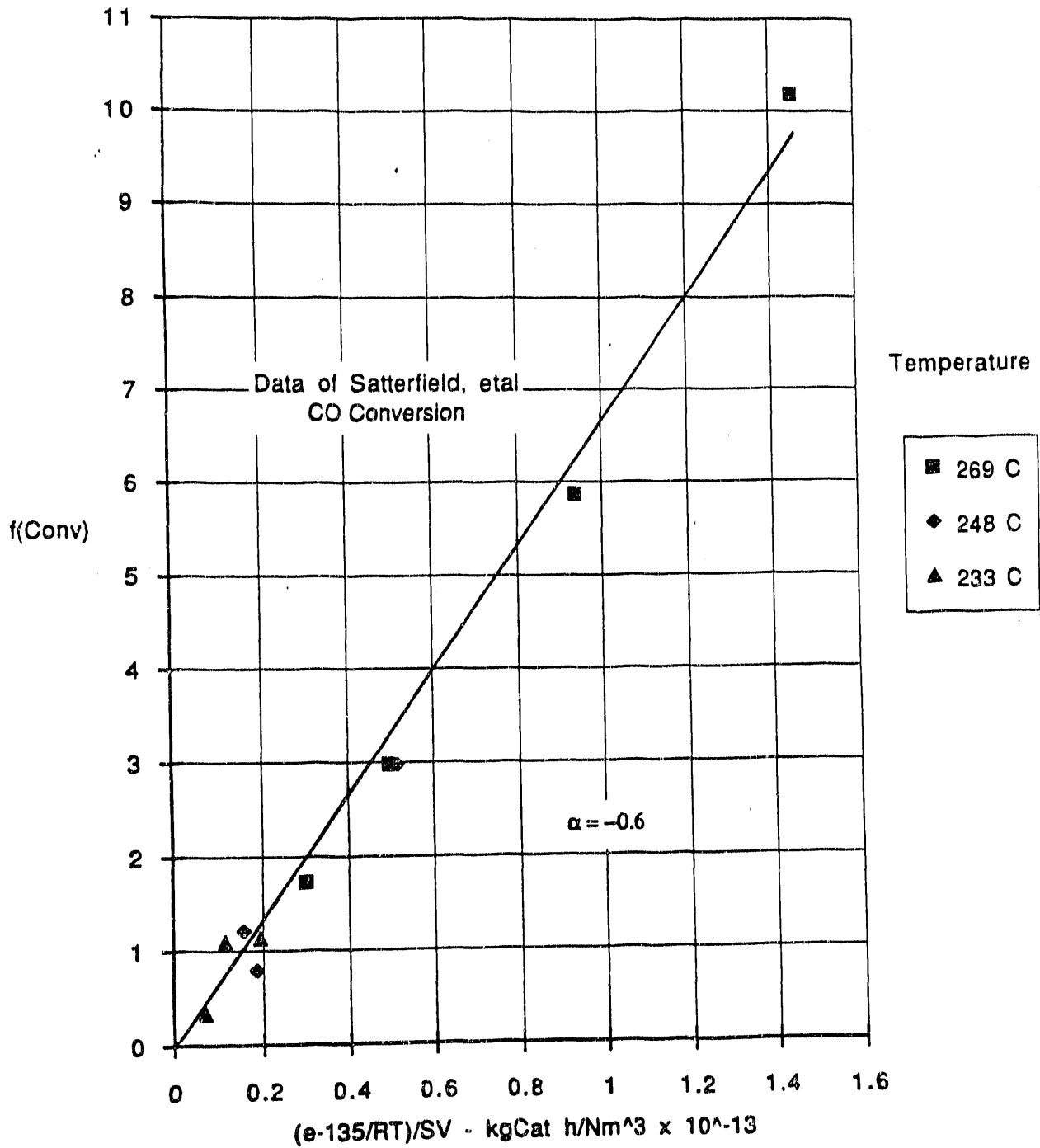




Figure C-3

**Cobalt Fixed-Bed Fischer-Tropsch Kinetics**  
 $f(\text{Conv}) = (1 + \alpha) \ln(1 - X) + \alpha X$

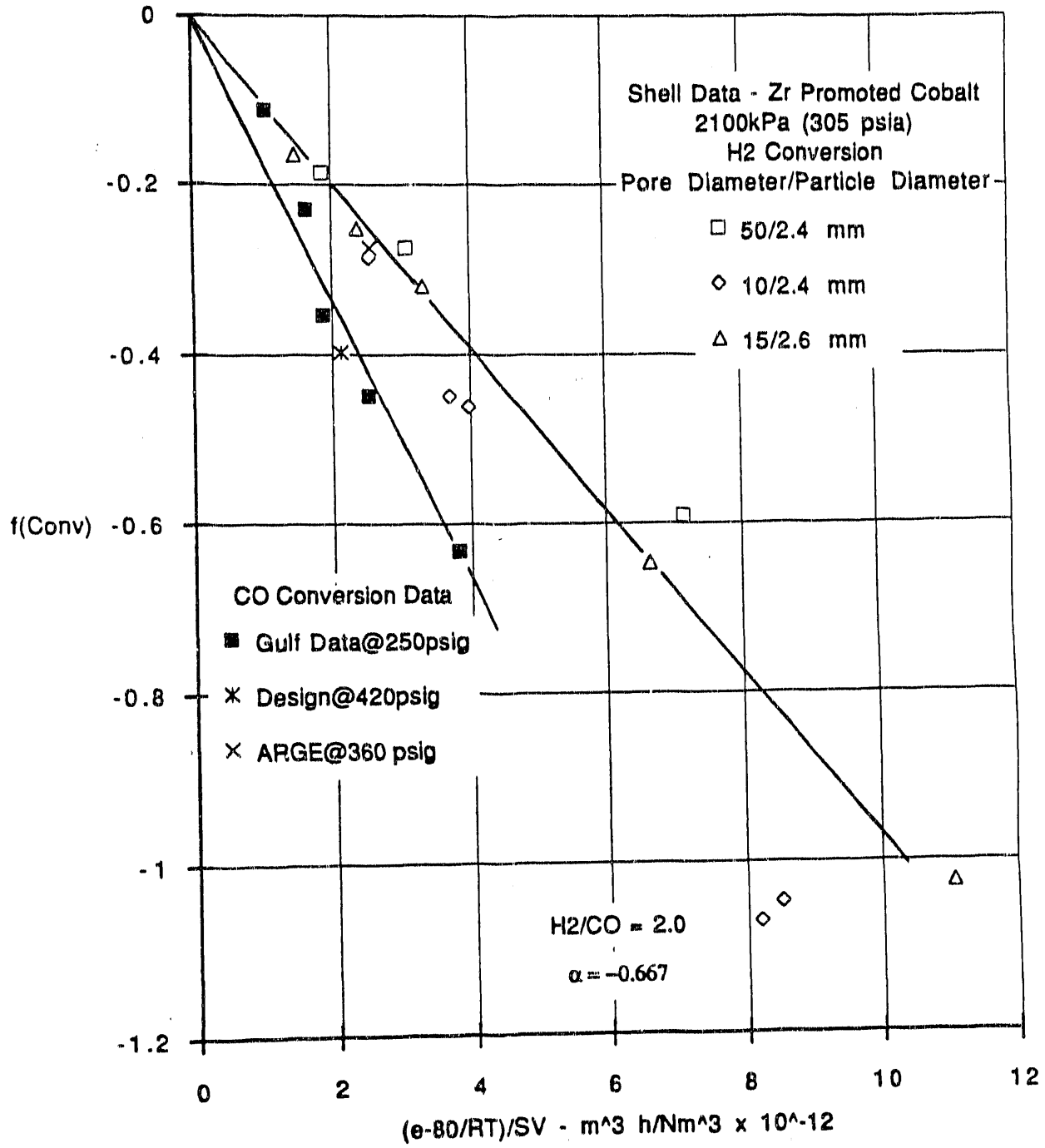


Table C-1

1	2	3	4	5	6	7	
1	CO Conversion Data				H2 Conversion		
2	Fe Fixed-Bed	Fe Slurry	Co Fixed-Bed	ARGE	Slurry Model	4/18/90	
3	Source	Satterfield, et al. (1983)	Singleton (1983)	ECT Ed.2, Vol.4	Used for Design		
4	Pressure-atm	8.88	7.8	18	25.5	10.86	
5	T - oC	Rate Constant in Nm3 H2+CO Conv/(h KgCat) (same as NL/(h gCat))				Comments	
6	200	0.23398579	0.08250512	0.438723357	0.273470893	0.056214709	Divide by 0.7
7	210	0.35653921	0.16794022	0.668511022	0.416705204	0.114333656	to convert to
8	220	0.53407779	0.33212859	1.001395849	0.624203413	0.225938446	Nm3/(h kgFe)
9	230	0.78727001	0.63926718	1.476131273	0.920121827	0.434554363	
10	240	1.14307034	1.1994213	2.143256879	1.335963454	0.814749051	Mult. by 3.6/7
11	250	1.63617258	2.19689992	3.067823597	1.912276709	1.49129862	to convert to
12	260	2.31068508	3.93356363	4.332534525	2.700613187	2.668418441	cm3/(s gFe)
13	270	3.22203906	6.89357292	6.041323239	3.765758152	3.716685987	
14	Preexponential	1.8x10 <sup>18</sup>	6.69x10 <sup>13</sup>	3.0x10 <sup>18</sup>	1.87x10 <sup>18</sup>		
15	Act. Energy kJ/m	80	135	80	80		
16							
17	T - oC	Rate Constant in millimols H2+CO Conv/(m KgCat atm)					
18	200	35.4361994	14.2251521	32.77848444	14.42253315	6.96130652	Nm3/(h kgCat)
19	210	53.9964182	29.9554775	49.94668686	21.97654222	14.15842297	times
20	220	80.8839156	57.2640791	74.81762189	32.91975363	27.97891892	22.4*60/atm.
21	230	119.228852	110.219496	110.2866878	48.52614265	53.81271545	
22	240	173.113368	206.798685	160.1298656	70.45714086	100.8938411	
23	250	247.791705	378.779344	229.207327	100.8512239	184.6738524	
24	260	349.943888	678.206886	323.6980961	142.4271623	330.4416073	
25	270	487.964753	1188.55803	451.3673969	198.6016546	460.2530371	
26							
27	T - oC	Rate Constant in Nm3/(h m3)					
28	200	198.887922	8.19837714	233.4008261	232.4502589	5.585948853	Nm3/(h kgCat)
29	210	303.05833	16.5610914	355.6478639	354.1994234	11.27478655	times
30	220	453.866118	32.5012641	532.7425918	530.5729008	22.10976484	Catalyst Density
31	230	669.17951	62.0737804	785.3018372	782.1035527	42.19586595	kg/m3
32	240	971.609785	115.558248	1140.212659	1135.568936	78.49699935	line 33 or
33	250	1390.7467	209.997441	1632.082153	1625.435202	142.5503689	E40 thru E47
34	260	1964.08232	373.022565	2304.908367	2295.521209	253.0479697	
35	270	2738.7332	650.588117	3213.983963	3200.894429	350.7661073	
36	Bulk Density	850		532	850		
37	Fract Voids	0.37		0.37	0.37		Slurry Model Used for Design
38	Part. Dens.	1349.20635	3100	844.4444444	1349.206349		(no mass transfer resistance)
39	% Slurry		15	Rheinprussen Lab	Unit Condition	Preexponential	3300000000
40	Gas Holdup		0.1664			Act. Energy	130
41	T - oC		Liq Dens.	Slurry Dens.	Kg Cat/m3	ko	koEpsilonL
42	200		702.5	794.6905077	99.36810108	0.00172988	0.001442112
43	210		696.95	788.6517548	98.61301542	0.003403846	0.002837446
44	220		691.4	782.6093307	97.85747071	0.006513473	0.005429631
45	230		685.85	776.5632319	97.10146652	0.01214194	0.010121521
46	240		680.3	770.5134552	96.34500244	0.022083047	0.018408428
47	250		674.75	764.4599972	95.58807805	0.03924075	0.032711089
48	260		669.2	758.4028544	94.83069292	0.06821642	0.056865207
49	266		665.87	754.7667988	94.37604052	0.094108054	0.078448474
50							
51	T - oC	Rate Constant in s <sup>-1</sup>				Hh = Ho/RT	koEpsilonL/Hh
52	200	0.01077932	0.00050586	0.006240593	0.004387184	5.825534097	0.00024755
53	210	0.0167724	0.00104346	0.009710234	0.006826367	5.561181682	0.000510224
54	220	0.02564438	0.0020902	0.014846589	0.010437264	5.316602872	0.001021259
55	230	0.03856848	0.00407302	0.02232888	0.015697371	5.08982521	0.001988579
56	240	0.05711249	0.00773319	0.033064775	0.023244785	4.879117343	0.003772901
57	250	0.08334348	0.01432702	0.04825097	0.033920785	4.682954546	0.006985139
58	260	0.11995236	0.02593597	0.069445358	0.048820609	4.499989849	0.012636741
59	266	0.16914547	0.04574411	0.097925279	0.068842207	4.396043873	0.017845244

## **APPENDIX D**

### **FISCHER-TROPSCH REACTOR SELECTION**

A comparison of slurry  
versus fixed-bed reactor  
design principles for  
methanol and Fischer-  
Tropsch distillate production.

J. M. Fox

Paper Presented at

The AIChE Spring National Meeting

Fischer-Tropsch Symposium  
Paper No. 91C

March 21, 1990

## Fischer-Tropsch Reactor Selection

### Introduction

Bechtel is currently carrying out for the DOE an economic comparison of fixed-bed versus slurry reactors for several applications, including Fischer-Tropsch synthesis. This paper is a report on the first phase of this study; a review of reactor design principles.

### Types of Fischer-Tropsch Reactors

The challenge in Fischer-Tropsch reactor design is to remove the large heat of reaction, some 55,000 to 60,000 kJ/kgmol (24,000 to 26000 Btu/lbmol) of synthesis gas reacted. For Fischer-Tropsch operations directed at gasoline production (i.e. values of the chain propagation probability factor of about 0.6) two types of reactor have been used:

1. The entrained fluidized-bed with riser coolers, called the Synthol reactor, used at Sasol.
2. The fixed fluidized-bed with internal cooling coils used at the Carthage-Hydrocol plant at Brownsville, Texas.

For waxy distillate production at values of the chain growth factor of about 0.9, the above reactor types are not satisfactory because the high molecular weight products cause fluidization problems. There is a great deal of interest in this type of operation today because yields of light gases and oxygenates are reduced and because an easily upgraded, high quality distillate is produced. Gasoline and other products produced in Synthol type operations require extensive upgrading before they are marketable. While numerous reactor types have been proposed for distillate production, the selection boils down to two main candidates:

3. The low conversion per pass, fixed-bed, tubular reactor used at Sasol (the ARGE reactors).
4. The higher conversion per pass, slurry bubble column reactor with internal cooling coils demonstrated by Rheinprussen in the 1950's.

It is of interest to note that for natural-gas-based Fischer-Tropsch distillate designs, Shell has selected the tubular fixed-bed for their new

plant in Malaysia, whereas Statoil has recently announced a slurry reactor design for the same type of application.

### Methanol Experience

The experience of Air Products with the liquid phase methanol process in the LaPorte demonstration unit is pertinent to any discussion of slurry reactors. This process was invented by Chem Systems to provide adequate heat removal in their once-through methanol process. Since there is no external gas recycle to remove part of the heat of reaction as sensible heat, heat evolution per unit volume of reactor is high and the best way of removing this heat seemed to be in a slurry reactor where a high heat flux [20 kW/m<sup>2</sup> or 6300 Btu/(h·ft<sup>2</sup>)] may be used because the rapid circulation of the liquid phase gives very uniform liquid temperatures.

In the course of their experimental work, Air Products investigated three types of slurry reactor:

1. An ebullating-bed system with liquid circulation through an external heat exchanger.
2. An entrained-bed system with slurry circulation through the external heat exchanger.
3. A slurry bubble column reactor with internal cooling coils.

The entrained-bed system was favored over the ebullating-bed because smaller particles could be used, giving higher effective catalyst activity. Both types required an external circulation pump and, ultimately the internally cooled, slurry bubble column reactor was chosen as the simplest and least costly design. Only about 4% of the reactor volume is occupied by the cooling coils, but heat removal has been limiting and a more practical design would increase this figure. The LaPorte reactor is operated with a superficial gas velocity of 0.15 m/s<sup>1</sup> and a catalyst concentration of 35 wt% or higher. Above 35 wt%, mass transfer limitations become significant [Studer, et.al. (1989)]. Typically, space velocity is in the range of 6 to 10 Nm<sup>3</sup>/(h·kgCat), the same as in fixed-bed methanol and the approach to equilibrium is similar at the same space velocity.

The primary application of the low conversion, once-through methanol process is in the coproduction of methanol and power in integrated gasification-combined cycle designs, an application selected in Clean Coal

---

<sup>1</sup> Multiply by m/s by 3.28 to obtain corresponding velocity in ft/s.

3 for further evaluation. The slurry reactor is not proposed as a replacement for conventional fixed-bed reactors in high yield, conventional, recycle methanol designs, although Air Products has suggested a novel two-step design with a slurry reactor operating once-through in the first step.

### Reactor Sizing Considerations

Conversion in a Fischer-Tropsch reactor is also correlated with space velocity per unit weight of catalyst. Satterfield, et. al. (1983) found that there was little difference between a slurry reactor and a fixed-bed reactor when expressed in these terms. Equivalent product distributions were observed. These tests were run under conditions where mass transfer resistances were virtually eliminated but, roughly speaking, the gas-liquid mass transfer resistance in the slurry reactor and the intraparticle resistance in the fixed-bed reactor are of similar magnitude. The same generalization is true of a methanol reactor.

While the rate of reaction is proportional to catalyst weight, the size and cost of the reactor is more closely related to the volume of the reactor<sup>2</sup>. How then does space velocity per unit *weight* of catalyst compare with space velocity per unit *volume* of catalyst and how much of the total volume is occupied by the heads, cooling coils and other internals? This question will be addressed for typical design values of catalyst concentration, particle density and gas holdup.

While essentially all of the experimental slurry F-T work appears to have been performed at slurry concentrations less than 25% and at superficial velocities less than 0.10 m/s, there does not appear to be any reason why a slurry Fischer-Tropsch reactor cannot be operated at the same conditions as a slurry methanol reactor. The systems are very similar. The primary differences are that the liquid phase in the F-T system is the product itself, molecular weight about 400, whereas the preferred liquid in the methanol reactor is Witco-40, a saturated mineral oil of about 340 molecular weight. Liquid densities are similar and so are the gas densities, the higher pressure in the methanol reactor being compensated for by a generally lower H<sub>2</sub>/CO ratio and thus a higher molecular weight gas in the F-T reactor. Use of the critical density concept of Roy, et. al.

---

<sup>2</sup> Cost is more directly related to vessel weight. Since wall thickness is related to diameter, reactor weight is determined by the same dimensional factors which determine volume and there is a rough proportionality.

(1964), indicates that up to 65 wt% solids could be suspended in either the F-T or methanol slurry systems.

In their review of Rheinprussen operations, Kolbel and Ralek (1980) state that "The optimum concentration of the catalyst in suspension proved to be about 10 wt% in terms of the iron present in the catalyst. Lower concentrations reduce the reactor efficiency, and higher concentrations up to 20% can be used, but they increase the viscosity of the suspension and thus decrease the interfacial area, which affects mass transfer and hence may cause a loss in conversion" (10 wt% iron corresponds to about 14.3 % slurry concentration). Part of this reluctance to increase slurry concentration may have had to do with physical limitations of the equipment on heat removal. It may also be tied in with a reluctance to go higher than about 0.10 m/s inlet gas velocity. Higher gas velocities will improve mass transfer, and should improve overall conversion, provided gas holdup remains reasonable.

Some Fischer-Tropsch modelling efforts have predicted a loss in conversion at superficial velocities above 0.09 m/s [Deckwer (1982)], but these results are confounded by the use of a simplified gas holdup expression which gives much too high a gas holdup (and therefore too low a catalyst holdup) at superficial velocities above 0.04 to 0.05 m/s. Operation at 0.15 m/s inlet superficial velocity and 35 wt% slurry concentration appears as feasible in a Fischer-Tropsch as in a methanol slurry reactor.

Assuming a 35 wt% catalyst concentration, a particle density of 1,500 kg/m<sup>3</sup> and a liquid density of 670 kg/m<sup>3</sup> at reaction temperature<sup>3</sup>, the slurry density is 830 kg/m<sup>3</sup> and the catalyst concentration in kg/m<sup>3</sup> of unaerated slurry becomes 290. The recent data of Bukur (1987) indicate that at 15 m/s superficial velocity the maximum gas holdup in these systems, without foaming, is roughly 27%. With contraction in the gas flow due to reaction, a somewhat lower gas holdup is predicted - say about 25%. The weight of catalyst per unit volume of aerated slurry is thus about 218 kg/m<sup>3</sup>. Adding an additional 15% for the heat transfer coils and 20% for disengaging space, the catalyst loading becomes about 150 kg/m<sup>3</sup> of reactor shell volume. It is, of course, possible that a non-supported catalyst of higher intrinsic density could be used, but even if the particle density is doubled, the catalyst loading increases only to

---

<sup>3</sup> 1,000 kg/m<sup>3</sup> is one g/cm<sup>3</sup> and corresponds to 62.4 lb/ft<sup>3</sup>

about 165 kg/m<sup>3</sup> of overall reactor volume. Table 1 summarizes the calculation for this case and for a fixed-bed reactor.

A fixed-bed reactor with the 1500 kg/m<sup>3</sup> particle density and a bed void fraction of 37% will have a catalyst loading of 945 kg/m<sup>3</sup> of reaction volume. In this case, the heat transfer tubes and headers take up about 40% of the reactor volume and the heads add an additional 25% bringing the catalyst loading to about 425 kg/m<sup>3</sup> of total reactor volume - more than 2 and 1/2 times that of the slurry reactor. The particle density of 1500 kg/m<sup>3</sup> is intended to represent a conservative value for supported precipitated iron catalyst. Supported cobalt catalysts appear to have lower particle densities but a higher activity per unit weight of catalyst so that the productivity per unit volume of reactor is the equivalent of or higher than iron based catalyst.

While this analysis shows that a slurry reactor must have twice the volume of a fixed-bed reactor for comparable operating conditions, it is not likely that operating conditions will be the same. The superficial velocity restriction on a slurry reactor makes it generally unsuitable for low conversion, high recycle operation. In methanol reactor design where there is an equilibrium limitation on conversion per pass, the slurry reactor, for high ultimate conversion levels, will be designed for higher pressure to increase conversion per pass, reduce recycle and increase gas density. Even so, reported space velocities per unit weight of catalyst appear to be comparable.

There are other differences. Temperature profiles will be different, for example. The slurry reactor will use continuous catalyst makeup from a prereduction system, whereas the fixed-bed reactor requires periodic shutdowns for catalyst replacement. Productivity per unit weight of catalyst consumption is believed to remain constant. The heat transfer tubes add significantly more to the weight of the fixed-bed reactor than the slurry reactor, but the shell of the slurry reactor must be designed for reaction pressure (60 to 100 atm in the methanol case, 15 to 30 atm for Fischer-Tropsch) whereas the shell of the fixed-bed reactor is designed for steam side pressure which ranges from 20 to 40 atmospheres.

These differences must be quantified in a more detailed study. Clearly, however, we can agree with Air Products' conclusion that the proper niche for slurry phase methanol is in the "once through methanol" application. There is little or no incentive to consider a slurry reactor for a recycle methanol operation except, perhaps, as a first stage reactor.



## Natural Gas Based Fischer-Tropsch Synthesis

The natural gas based Fischer-Tropsch plant is operated at close to 2.0 H<sub>2</sub>/CO ratio. The reactor design presents a somewhat different situation from methanol, in that recycle is not required by equilibrium limitations but is required in the fixed-bed reactor in order to achieve a mass velocity adequate for good heat transfer. A conversion per pass of 35 to 40% appears to be the practical limit in a fixed-bed F-T reactor, requiring a recycle to fresh feed ratio of about 2.3. (The ARGE reactors were limited to about 25% conversion per pass and 66% ultimate conversion because of the high level of inerts and methane in the reactor feed gas. With a natural gas feed and combined reforming or partial oxidation to produce synthesis gas, a lower inerts level is readily achievable and ultimate conversions of over 90% are possible.)

A slurry F-T reactor is not limited in this manner and can go to higher per-pass conversion levels. The limiting factor on conversion in the slurry bubble column is backmixing, particularly of the liquid phase, which makes it necessary to use lower space velocities to achieve a given conversion level than would be required in a plug flow reactor. Three simplified models have been used to investigate the effect of backmixing:

- Model 1 - plug flow, no axial mixing of either phase
- Model 2 - gas phase plug flow, liquid phase fully backmixed
- Model 3 - CSTR, both phases fully backmixed

These simplified models are based on the conversion rate being proportional to hydrogen concentration and on an overall gas contraction factor,  $\alpha$ , which is assumed constant with conversion. The model equations are summarized in an addendum to this paper.

Figure 1 shows space velocity requirements to achieve a given conversion level in a plug flow and a fully backmixed slurry reactor at two levels of the contraction factor, 0.0 and -0.5. Contraction factors of -0.5 to -0.6 are typical of F-T synthesis. Space velocity in Figure 1, is combined with the overall rate constant, K, in the dimensionless Stanton Number, K/SV. The overall rate constant combines the mass transfer rate constant, K<sub>M</sub>, and the reaction rate constant, K<sub>R</sub>, in the form of a summation of resistances:

$$1/K = 1/K_R + 1/K_M$$

Model 2, which approaches most closely what would be expected from a large, low L/D, F-T reactor, has the interesting characteristic that it reduces to Model 1 when mass transfer controls, ( $K_R \gg K_M$ ), and to Model 3, when reaction rate controls, ( $K_M \gg K_R$ ). Figure 2 shows the situation when  $K_M = K_R$ .

In Figure 3 the space time yield (STY), in Nm<sup>3</sup> syngas converted/(h·m<sup>3</sup>), is plotted versus conversion per pass for a Model 2 reactor, based on the curve shown in Figure 2. Two prediction lines are shown, the upper one being an ideal case with no inerts and the lower one being a more realistic case with 1.5% inerts in the feed gas and 95% ultimate conversion. Conditions for this plot are 533 °K and 1500 kPa. In the ideal case  $STY = GHSV$  times conversion per pass, and the ultimate conversion is 100%.

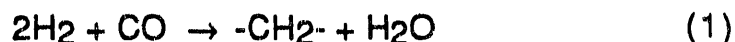
Figure 3 also shows the recycle to fresh feed ratio (R/FF) required at varying levels of conversion per pass for the same two cases. The gain in productivity at low conversion per pass is offset by a higher recycle ratio, [ $R/FF$  ratio =  $(1 + \text{conversion per pass} - 1)$ ], so there is an engineering evaluation to be made as to the best conversion level to design for. From heat transfer considerations, the fixed-bed reactor works best *low* conversion per pass, below 50%. The slurry reactor requires a *high* conversion per pass because of superficial velocity limitations. Nevertheless, it is apparent from Figure 3 that conversion levels over 90% should be avoided because of the sharp dropoff in STY and 80% conversion per pass may be a good compromise between recycle requirements and high productivity.

The fixed-bed reactor has the advantage that it behaves like a plug flow reactor, though the difference between models at 35 to 40% conversion is small. Since the fixed-bed reactor runs at a lower average temperature, it has a lower STY than would be read off from Figure 3. The trade-off between a slurry reactor and a fixed-bed reactor for the natural gas case is not obvious, a more detailed engineering and cost evaluation being required. This is not a part of Bechtel's assignment, which is concerned only with coal based plants.

### The Coal Based Fischer-Tropsch Design

A coal based Fischer-Tropsch plant for distillate production differs fundamentally from a natural gas based plant because of the composition of the raw synthesis gas. A natural gas plant using partial oxidation will

produce a synthesis gas with a H<sub>2</sub>/CO ratio of slightly under 2, the stoichiometric ratio for the reaction:

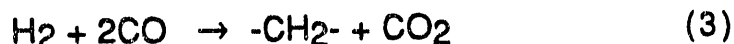


In this case, the water gas shift reaction is not desired since it produces unwanted CO<sub>2</sub>. Most of the recent developments in natural gas processing use cobalt type catalysts which do not have this activity.

A modern coal gasifier of the Texaco or Dow design produces a synthesis gas with a H<sub>2</sub>/CO ratio of about 0.75, a Shell gasifier produces something under 0.5 H<sub>2</sub>/CO ratio. A 0.667 ratio is stoichiometric for a F-T reactor, without steam addition, where the catalyst has high water gas shift activity. Precipitated iron catalysts have this activity. The reactions involved are reaction number (1) plus:



giving the overall reaction:



Because equilibrium in reaction 2 heavily favors CO<sub>2</sub> production at F-T conditions, reaction 3 predominates over reaction 1.

In this scenario, shift and CO<sub>2</sub> removal are not required prior to Fischer-Tropsch synthesis. This has the dual advantage of eliminating a separate reaction step with its steam requirement and simplifying the gas purification step. CO<sub>2</sub> removal after synthesis is more straightforward.

A slurry reactor may be ideal for low H<sub>2</sub>/CO ratio synthesis for the following reasons:

1. Low H<sub>2</sub>/CO ratio can lead to carbon formation via the Boudouard reaction:



A slurry reactor, however, raises the H<sub>2</sub>/CO ratio that the catalyst actually sees owing to combination of a higher mass transfer coefficient for hydrogen and a higher CO consumption by reaction 2..

2. Even if carbon formation does occur, the slurry reactor offers the possibility for its removal.
3. Catalyst deactivation can be handled by means of periodic catalyst withdrawal and addition, whereas replacement of fixed-bed catalyst requires a shutdown.
4. Distillate production requires low reaction temperatures for good yield. Because of uniform temperatures, a slurry reactor can be run continuously at end of run temperature for the fixed-bed reactor and give equivalent yield distribution. This gives both high reactor productivity and the potential for higher pressure steam generation.

Weighed against these advantages are the need to provide for product removal and separation from the catalyst as well as facilities for continuous addition of preactivated catalyst.

Since the fixed-bed reactor is not applicable to low H<sub>2</sub>/CO ratio operation, our DOE study will evaluate 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, steam will be added to conform with stoichiometry. The two processing schemes will be quite different between the gasifier and the downstream processing units. These, however, will be kept essentially unchanged. It is expected that the slurry reactor system will have an advantage under these assumptions and we hope to quantify this advantage in the remainder of our study.

#### Acknowledgement

The author wishes to recognize the assistance of Professor Emeritus J. M. Smith of the University of California at Davis and of Professor Aydin Akgerman of Texas A & M University who are acting as consultants to Bechtel on this study. The work is being done for the Department of Energy, Pittsburgh Energy Technology Center under Contract No. DE-AC22-89PC89867.

## Addendum

### Limiting Fischer-Tropsch Models

#### Model 1

Plug Flow Both Phases

$$(1 + \alpha^*) \cdot \ln(1 - X_H) + \alpha^* \cdot X_H = - K/SV$$

#### Model 2

Plug Flow Gas - Fully Mixed Liquid

$$((\alpha^* \cdot X_H + (1 + \alpha^* \cdot Y) \cdot \ln(1 - X_H/Y)) / (1 + \alpha^* \cdot n) = K_M/SV$$

where

$$Y = (1 - n) / (1 + \alpha^* \cdot n)$$

$$n = X_H / (K_R/SV)$$

#### Model 3

Both Phases Completely Mixed

$$X_H \cdot (1 + \alpha^* \cdot X_H) / (1 - X_H) = K/SV$$

In all cases:

$$K_R = k_H \cdot \epsilon_L / HH, \quad K_M = k_L a / HH$$

$$K = \frac{K_R \cdot K_M}{K_R + K_M}$$

$$SV = \frac{GHSV}{3600} \times \frac{T}{273} \times \frac{101.3}{P}$$

Models 1 and 2 follow the derivations of Deckwer ((1981) and Bukur (1983) and all models assume the reaction is first order in hydrogen concentration.

### Notation

a	gas-liquid interfacial area, $m^{-1}$
C <sup>Cat</sup>	catalyst concentration, $kg/m^3$
C <sup>G</sup>	hydrogen concentration in gas phase, $kg\ mole/m^3$
C <sup>*HL</sup>	hydrogen concentration, liquid, in equilibrium with gas, $kg\ mole/m^3$
C <sup>HL</sup>	hydrogen concentration in the liquid phase, $kg\ mole/m^3$
D	I.D. of reactor, m
GHSV	Gas hourly space velocity, $Nm^3 (H_2+CO)/[h \cdot m^3\ reactor\ volume]$ , (reactor volume is expanded slurry height times cross section area)
H	solubility coefficient of hydrogen = $C^G/C^{*HL}$
I	Inlet ratio of CO/H <sub>2</sub>
k <sub>L</sub>	liquid side mass transfer coefficient, m/s
k <sub>H</sub>	effective reaction rate constant for hydrogen consumption, $s^{-1}$ (note that to agree with space velocity in $Nm^3/[s \cdot kg\ Cat]$ , $k_H = k_H' \cdot C^{Cat}$ where $k_H'$ is in $m^3/[kg \cdot s]$ )
L	Length of expanded slurry bed, m
P	pressure, kPa
r	rate of hydrogen consumption, $r = k_H \cdot C^{HL}$ , $kg\ moles/[m^3 \cdot s]$
SV	Space velocity in actual $m^3$ inlet gas/ $[s \cdot m^3]$
T	temperature, °K
U	Usage ratio of CO/H <sub>2</sub>
X <sub>H</sub>	hydrogen fractional conversion per pass (If $U = I$ , $X_H = X_{CO}$ )
$\alpha$	contraction factor, $\alpha = [m^3/s(X_{H_2} + CO = 1) - m^3/s(\text{inlet})]/[m^3/s(\text{inlet})]$
$\alpha^*$	contraction factor modified for H <sub>2</sub> conversion, $\alpha^* = \alpha \cdot (1+U)/(1+I)$
$\epsilon_L$	fractional liquid hold-up

### References

- Bukur D. B., Chem. Engng. Sci., **38**, 441 (1983).  
Bukur D. B., Patel S. A., and Matheo R., Chem. Eng. Comm., **60**, 63 (1987).  
Deckwer W. D., Serpemen Y., Ralek M. and Schmidt B., Chem. Engng. Sci. **36**, 765 (1981).  
Deckwer W. D., Serpemen Y., Ralek M. and Schmidt B., IEC Proc. Des. Dev., **21**, 231 (1982).  
Kolbel H. and Ralek M., Catal. Rev. - Sci. Engng., **21**(2), 225 (1980).  
Roy N. K., Guha D. K. and Rao M. N., Chem. Eng. Sci., **19**, 215 (1964).  
Satterfield C. N., Huff G. A. Jr., Stenger H. G., Carter J. L., and Madon R. J., IEC Fundam., **24**, 450 (1985).  
Studer D. W., Henderson J. L., Hsiung T. H., and Brown D. M., EPRI 14th Annual Conference on Fuel Science and Conversion, Palo Alto, CA, 18-19 May (1989).

Table 1

Comparison of Catalyst Loadings  
kg/m<sup>3</sup>

	Slurry Reactor	Fixed-Bed Reactor
Particle density, kg/m <sup>3</sup>	3100	1500
Liquid density, kg/m <sup>3</sup>	670	
Slurry density, kg/m <sup>3</sup>	922	
Slurry concentration, kg/m <sup>3</sup>	323	
Gas holdup or voids, %	25	37
Loading (reaction volume), kg/m <sup>3</sup>	242	945
Heat transfer tubes, %	15	40
Heads & Disengagement, %	20	25
Loading (reactor volume), kg/m <sup>3</sup>	165	425

Figure 1  
COMPARISON OF MODELS  
HYDROGEN CONVERSION VS STANTON NUMBER

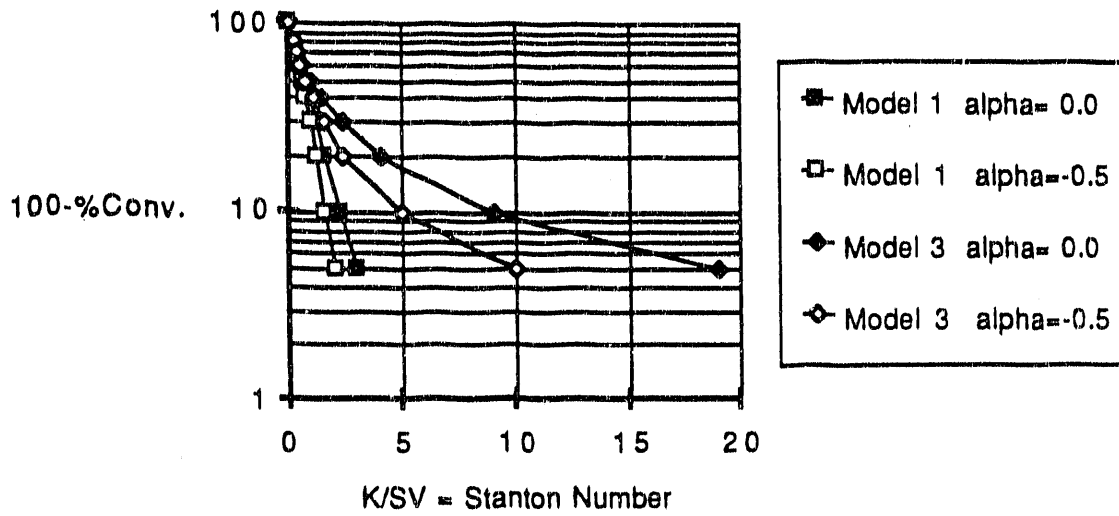


Figure 2  
COMPARISON OF MODELS  
KR = KL = 2K  
 $\alpha^* = -0.5$

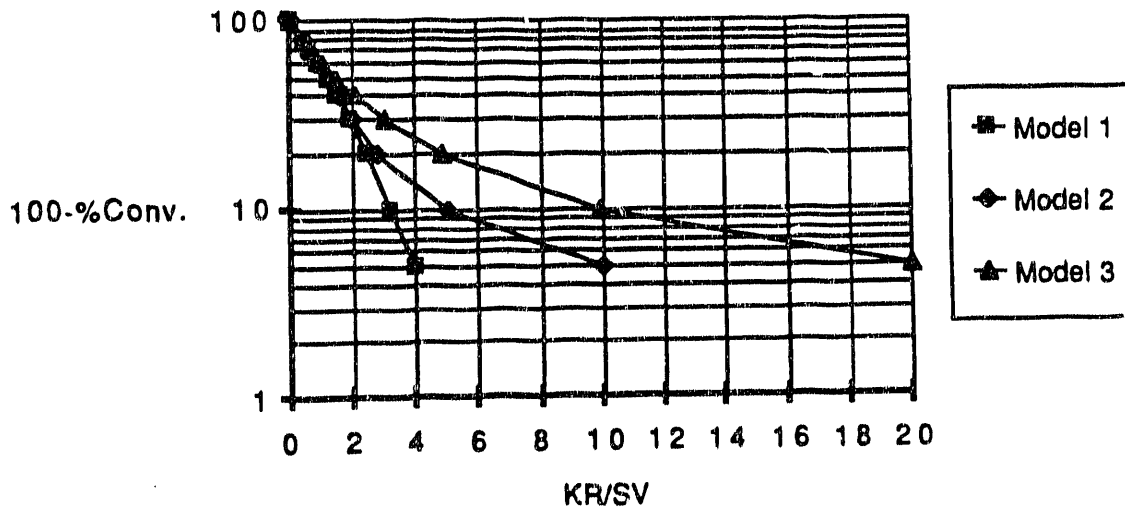
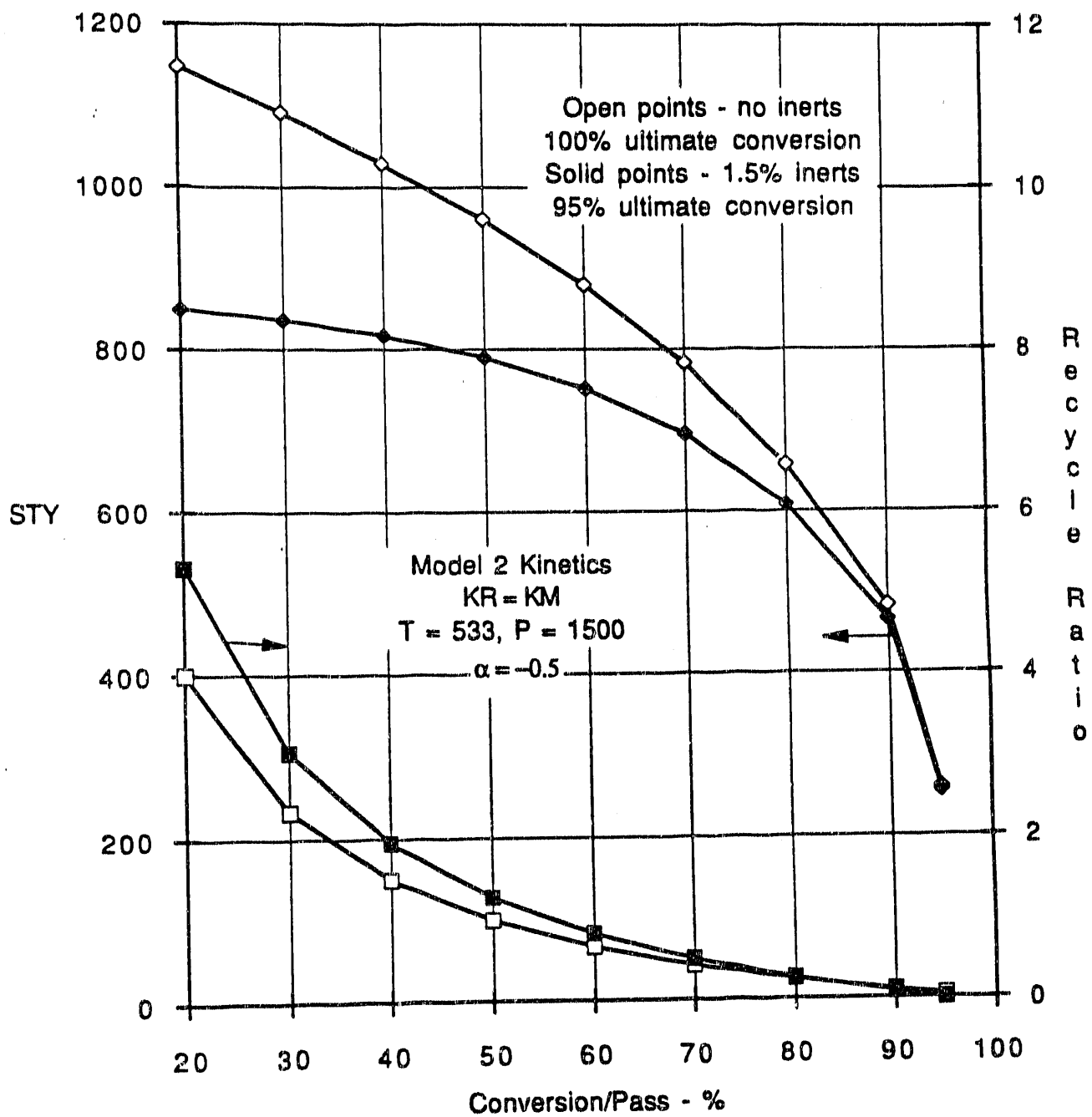




Figure 3  
 STY AND RECYCLE RATIO  
 VERSUS CONVERSION PER PASS



**APPENDIX E**  
**SLURRY REACTOR DESIGN STUDIES**  
**METHANOL AND MIXED ALCOHOLS**  
**DESIGN DATA SHEETS**

**Contents**

**Methanol Synthesis**

Table E-1	Equipment List - Slurry Reactor Case
Table E-2	Equipment List - Fixed-Bed Case
Figure E-1	PFD - Methanol Synthesis - Slurry Reactor Case
Figure E-2	PFD - Catalyst Pretreatment - Slurry Reactor Case
Figure E-3	PFD - Methanol Synthesis - Fixed-Bed Case

**Mixed Alcohols - Octamix™**

**Process Flow Diagram (Lurgi)**

Table E-1

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

METHANOL REACTION SECTION  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN COND.		MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
				PRESS	TEMP.	SHELL	INTERVALS	DIAM.	I-I	
				PSIG	F		INTERVALS	FT	FT	
C-1	STEAM DRUM	HORIZ	1	580	650	CS	CS	5.0	21.0	PROP. INTERNALS
C-2	SLURRY REACTOR	VERT	1	1600	650	2 1/4 Cr W/304 SS	CL	15.8	49.5	W/ 1250 TUBES
C-3	HP SEPARATOR	HORIZ	1	1600	250	CS	W/304 SS CL	8.5	14.0	W/ SS MESH PAD
C-4	LP SEPARATOR	HORIZ	1	150	250	CS	CS	5.5	14.0	W/ SS MESH PAD
C-5	PURGE LETDOWN SEP	VERT	1	450	250	CS	CS	4.5	8.0	W/ SS MESH PAD
C-6	CONDENSER OIL SURGE DRUM	VERT	1	1600	250	304 SS	CS	3.5	7.0	
C-7	SLURRY HOLD TANK	VERT	1	60	350	CS	CS	15.0	47.5	W/ INTERNAL COILS
C-8	REDUCTION REACTOR	VERT	1	175	600	CS	CS	7.5	9.5	JACKETED REACTOR W 18 HP AGITATOR
C-9	KO DRUM	HORIZ	1	150	250	304 SS	CS	7.0	14.0	W/ SS MESH PAD
C-10	FEED GAS COMPRESSOR KO DRUM	VERT	1	875	250	CS	CS	5.0	8.0	W/ SS MESH PAD
C-11	SPENT CATALYST SURGE DRUM	VERT	1	50	250	CS	CS	4.5	11.5	W/ SS MESH PAD
D-1	OIL TANK	VERT	1	ATM	250	CS	CS	20.0	24.0	1140 BBLs
D-2	CATALYST STORAGE BIN	VERT	1	ATM	250	CS	CS	11.0	14.0	W/ 60 BTM CONE
D-3	SPENT CATALYST HOPPER	VERT	1	ATM	250	CS	CS	4.0	4.0	W/ 60 BTM CONE

Table E-1

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

METHANOL REACTION SECTION  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO PER TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION			REMARKS
				PRESS. PSIG	SHELL TUBE	SHELL TUBES	TEMP. F	SHELL	TUBE	BASE TUBE AREA	
E-1	REACTOR FEED/EFFL EXCH	S&T	1	1650	1600	550	550	CS	304 SS	3950	
E-2	REACTOR EFFL/BFW HEATER	S&T	1	580	1600	500	550	CS	304 SS	2385	
E-3	EFFLUENT AIR COOLER	AIR	1	N/A	1600	N/A	400	N/A	304 SS	14900	220 HP FAN
E-4	EFFLUENT TRIM COOLER	S&T	1	1600	75	550	250	CS	CS	5660	
E-5	GAS COOLER	S&T	1	150	75	400	250	CS	304 SS	2550	
E-6	SPENT CATALYST COOLER	S&T	1	50	75	550	250	CS	CS	300	

Table E-1

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

METHANOL REACTION SECTION  
PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	FLOW (GPM/SCFM)	HEAD (FT)	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRIVER TYPE	POWER BHP	REMARKS
						HP	CS	CS	ROTATING UNIT			
G-1	BFW PUMP	CENTRIF	2	1660	69	24		CS	CI	MOTOR	29	
G-2	CONDENSATE OIL PUMPS	CENTRIF	2	120	200		304SS		CI	MOTOR	12	
G-3	OIL CHARGE PUMPS	CENTRIF	2	2.4	100	0.06	CS	CS	CI	MOTOR	0.3	
G-4	OIL RETURN PUMPS	RECP	2	1	3620		CS	CS	CI	MOTOR	1.5	
G-5	SLURRY HOLD TANK PUMP	CENTRIF	2	4800	60		CS	CS	CI	MOTOR	120	
G-6	CATALYST ADDITION PUMP	CENTRIF	2	84	3355		CS	CS	CI	MOTOR	150	
G-7	RECOVERED LIQUIDS PUMP	CENTRIF	2	2	150		CS	CS	CI	MOTOR	0.3	
G-8	SPENT CATALYST PUMP	CENTRIF	2	90	350	4	CS	CS	CI	MOTOR	8	
K-1	RECYCLE COMPRESSOR	CENTRIF	1	(196000)						STEAM TURBINE	6043	
K-2	SYNGAS COMPRESSOR	CENTRIF	1	(89400)						STEAM TURBINE	1050	
K-3	PURGE GAS EXPANDER	CENTRIF	1	(5100)						TURBINE MOTOR	475	
K-4	REDUCTION GAS COMPRESSOR	CENTRIF	1	(7000)						MOTOR	180	

Table E-1

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

METHANOL REACTION SECTION  
PACKAGE EQUIPMENT

EQUIP. NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	CAPACITY	OPERATING CONDITIONS	POWER KW	REMARKS
Y-1	AXIAL CYCLONE	SEPARATOR	6	4350 ACFM VAPOR	500 F, 1450 PSIA	50	
Y-2	OIL FILTER	CARTRIDGE FILTER	1	120 GPM	150 F, 1600 PSIG		
Y-3	SPENT CATALYST FILTER	TANK VERTICAL LEAF FILTER	1	45 GPM	150 F, 150 PSIG		

Table E-2

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

METHANOL REACTION SECTION  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN COND.		MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
				PRESS	TEMP. °F	SHELL	INTERIALS	DIAM., I-I	I-I	
C-1	STEAM DRUM	HORIZ	1	725	650	CS	CS	5.5	23	PROP INTERNALS
C-2	METHANOL REACTOR	VERT	1	870	650	CS	304 SS	15.8	25.5	W/INTERNAL TUBES
C-3	HP SEPARATOR	VERT	1	870	250	CS W/SS CL	CS	8.5	14	W/ SS MESH PAD
C-4	LP SEPARATOR	HORIZ	1	150	250	CS	CS	5.5	14	W/ SS MESH PAD
C-5	PURGE GAS LETDOWN DRUM	VERT	1	450	250	CS	CS	4.5	8	W/ SS MESH PAD

Table E-2

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

METHANOL REACTION SECTION  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO PER TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION			REMARKS
				PRESS, PSIG	SHELL TUBE	SHELL TUBES	SHELL TUBES	SHELL	TUBE	PIPE TUBE AREA	
E-1	REACTOR FEED EFFL EXCH	S&T	1	870	870	550	550	CS	CS	38615	
E-2	EFFLUENT AIR COOLER	AIR	1	N/A	870	N/A	500	N/A	CS	15200	225 HP FANS
E-3	EFFLUENT TRM COOLER	S&T	1	870	75	250	250	CS	CS	7065	



Table E-2

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

METHANOL REACTION SECTION  
PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM (SCFM)	HEAD FT	HYDRAULIC HP	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRIVER TYPE	POWER BLE	REMARKS
							HEAD EI	HP	CASE	ROTATING UNIT			
G-1	EFW PUMP	CENTRIF	2	2030	70	30	CS	CS	CI	MOTOR	36		
K-1	RECYCLE GAS COMPRESSOR	CENTRIF	1	(268000)			SS	SS	SS	STEAM TURBINE	2500		

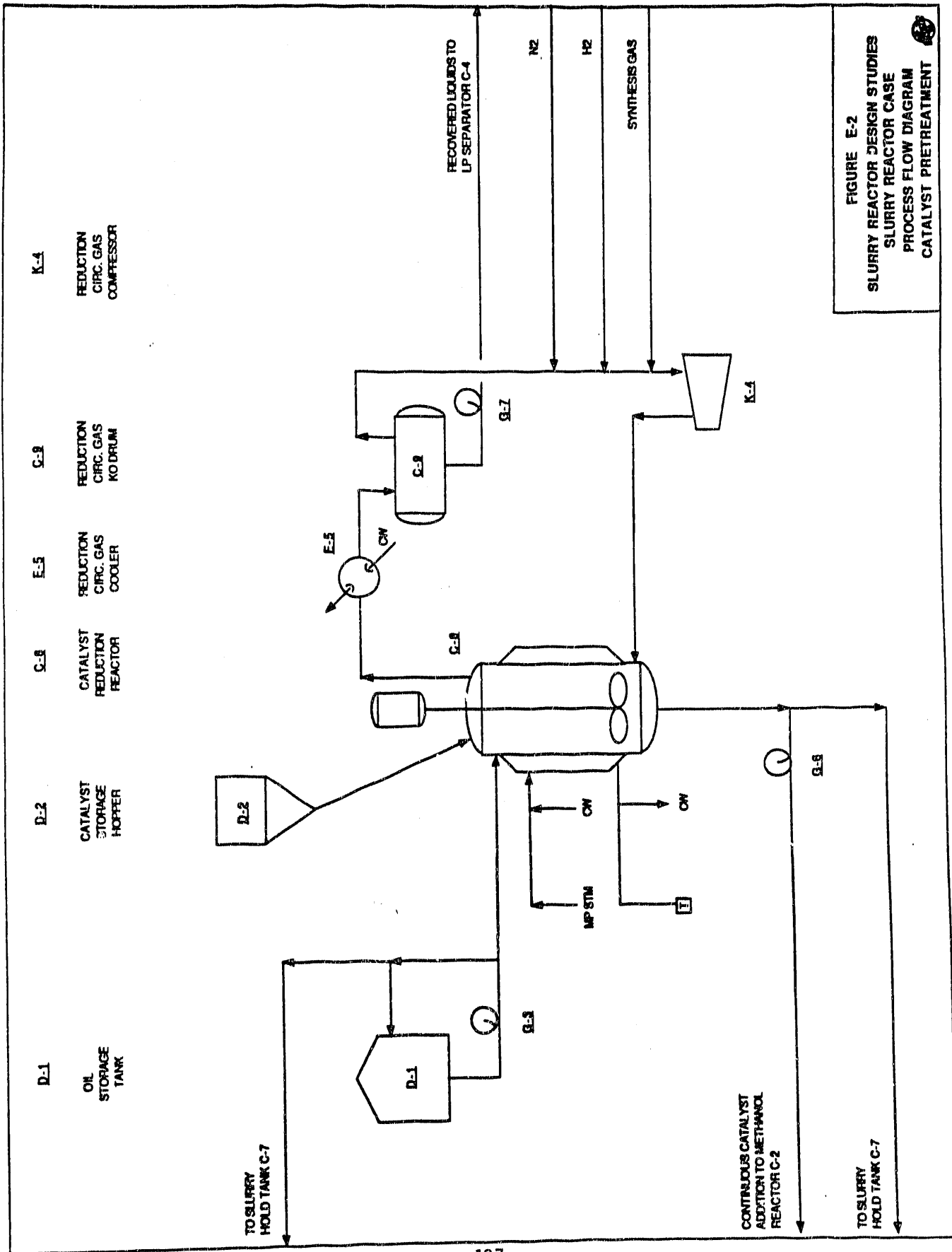


FIGURE E-2  
 SLURRY REACTOR DESIGN STUDIES  
 SLURRY REACTOR CASE  
 PROCESS FLOW DIAGRAM  
 CATALYST PRETREATMENT

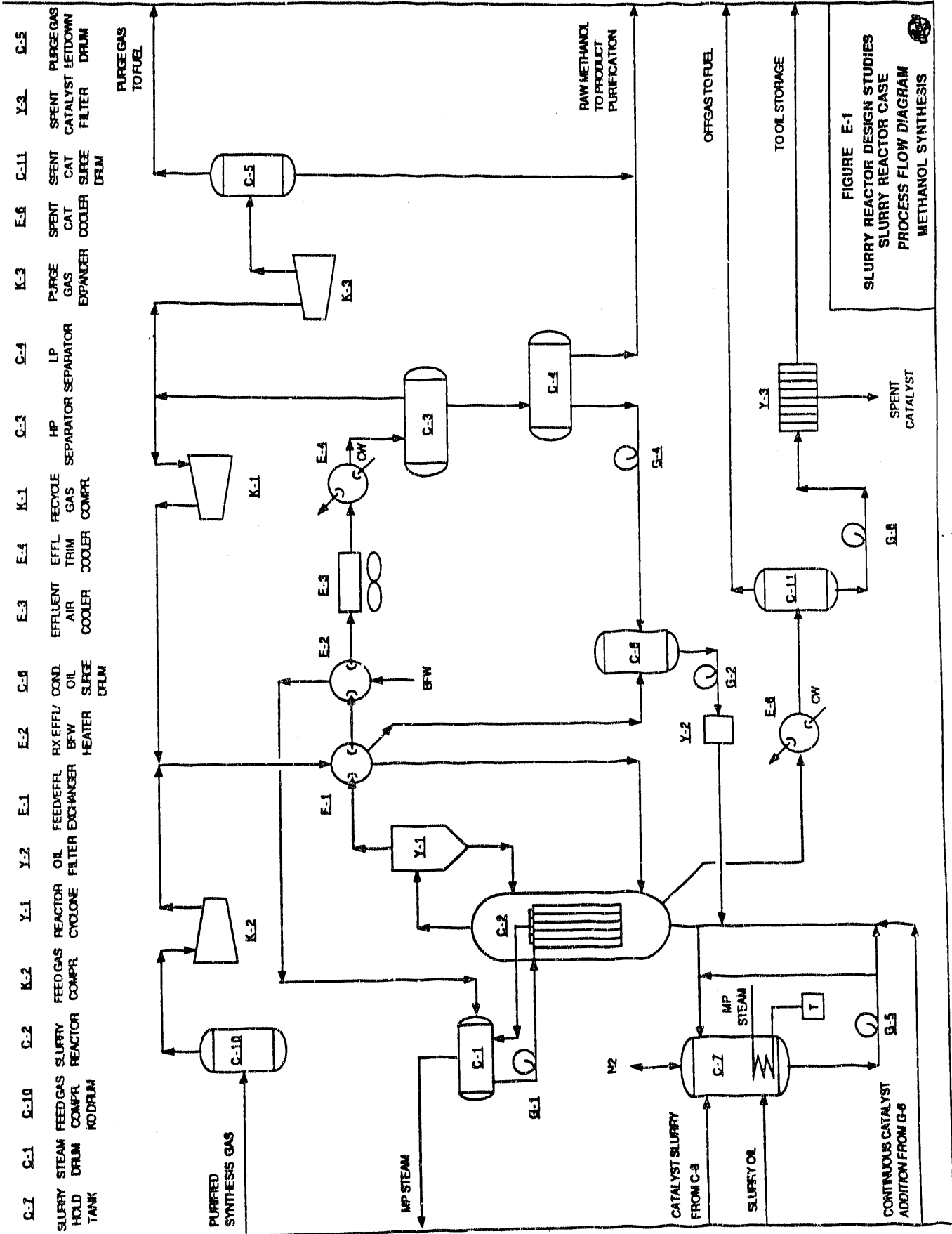


FIGURE E-1  
 SLURRY REACTOR DESIGN STUDIES  
 PROCESS FLOW DIAGRAM  
 METHANOL SYNTHESIS

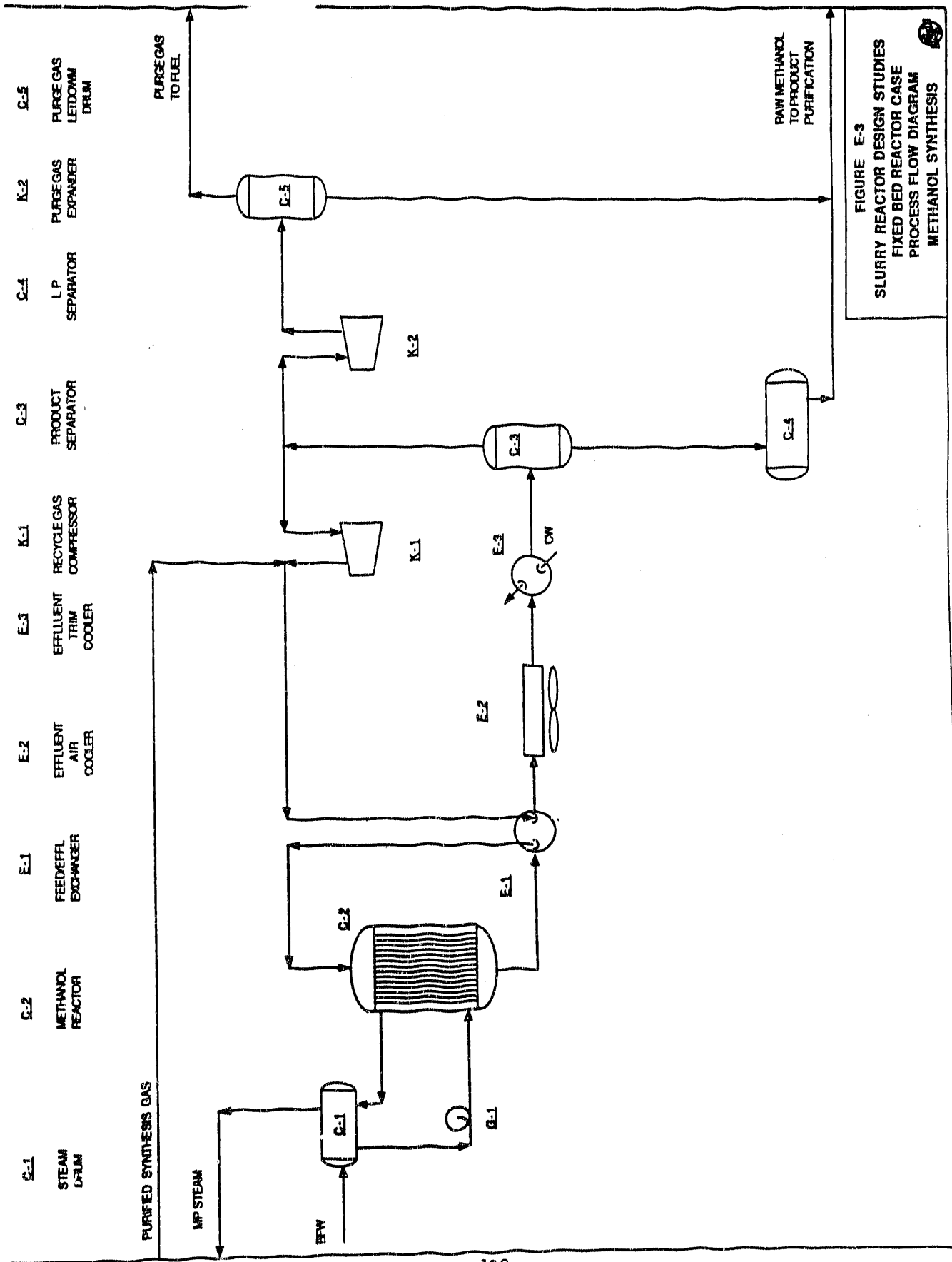
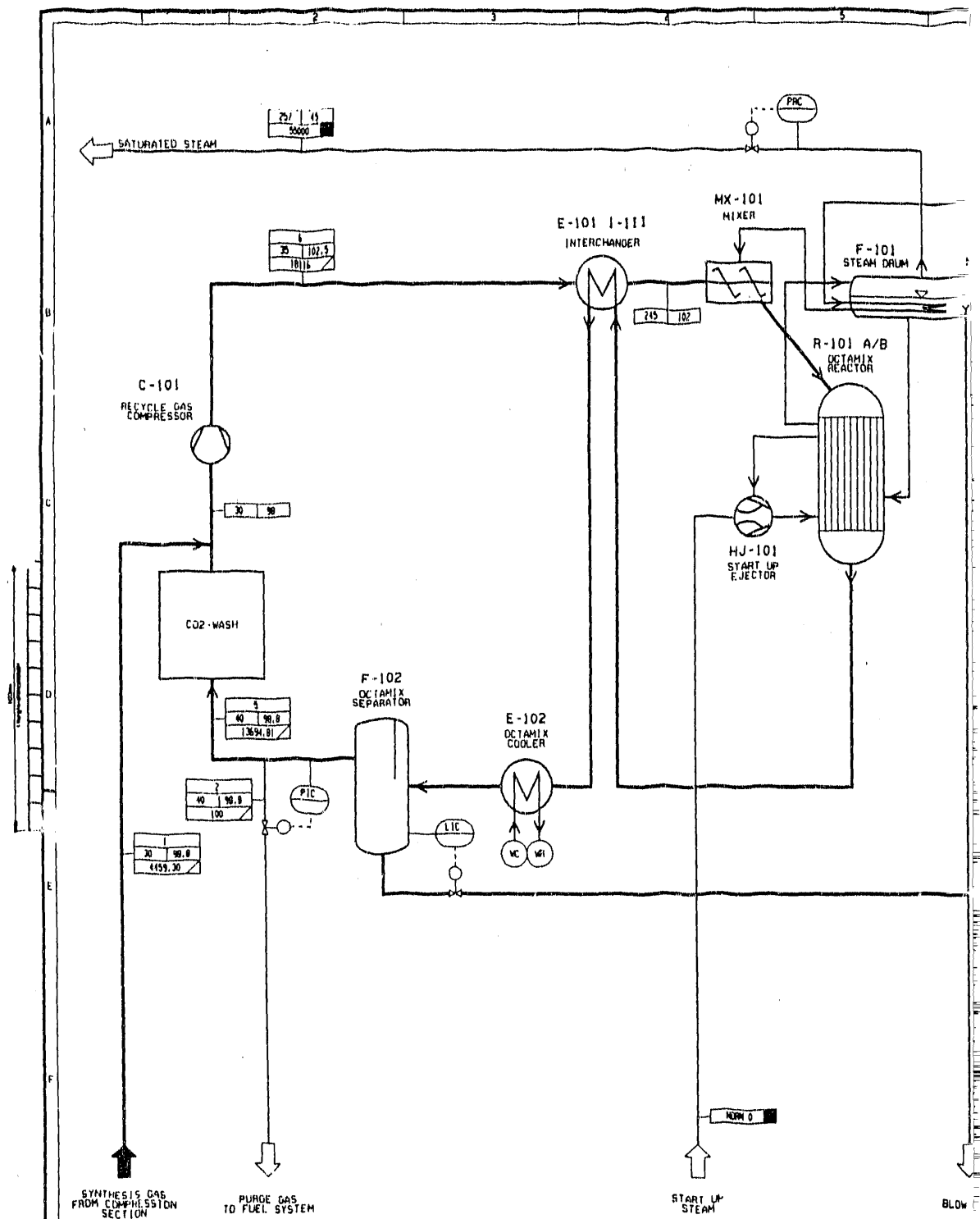
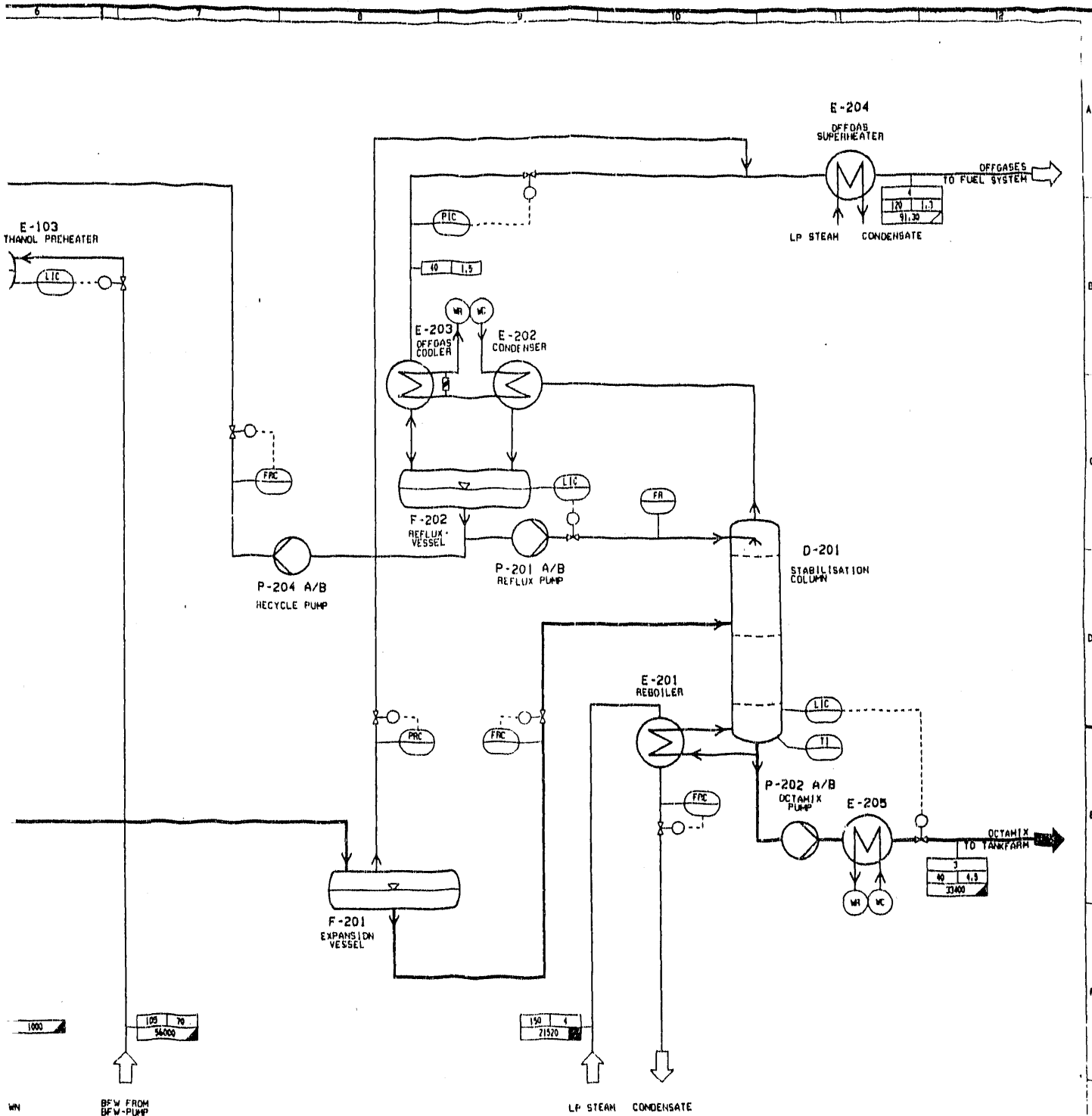


FIGURE E-3  
 SLURRY REACTOR DESIGN STUDIES  
 FIXED BED REACTOR CASE  
 PROCESS FLOW DIAGRAM  
 METHANOL SYNTHESIS



STREAM NO.	1	2	3	4	5	6
PROCESS STREAM	SYNTHESIS GAS	PURGE GAS	OCTAMIX	OFFGASES	RECYCLE GAS	REACTOR INLET GAS
PHASE	STEAM/GAS + LIQUID	GAS	LIQUID	GAS	GAS	GAS
CO2	1.00	4.50		40.78	1.50	1.00
CO	46.64	68.28		41.95	68.28	64.95
H2	51.30	8.14		2.44	8.14	19.01
CH4	0.23	7.34		10.41	7.34	5.78
N2	0.83	11.56		4.82	11.56	9.25
METHANOL		SAT.	69.70	SAT.	SAT.	
OXYGENAES		SAT.	30.00	SAT.	SAT.	
H2O		SAT.	0.30	SAT.	SAT.	
GASPROD.		0.10		SAT.	0.10	
FLOW RATE	4459	284	33400	91.30	14157	18116
TEMPERATURE	30	40	40	120	40	30
PRESSURE	99	98.8	4.5	1.3	98.8	102.5

1) DRY ANALYSIS



**BASES**

STREAM NO	°C	BAR	kg/h	°C	BAR	kg/h
°C	BAR	kg/h	°C	BAR	kg/h	

**LIQUID**

STREAM NO	°C	BAR	kg/h
°C	BAR	kg/h	

**STEAM**

°C	BAR	kg/h
°C	BAR	kg/h

Date		11.02.90		Rev		001		Lurgi GmbH	
Project		OCTAMIX SYNTHESIS /		OCTAMIX STABILISATION		UNIT 100&200		PROCESS FLOW DIAGRAM	
Client		DEM		Contract		BECHTEL		Scale	
Drawing No.		11		Revision		1		Date	
Author		JL		Checked				Date	

# APPENDIX F

## SLURRY REACTOR DESIGN STUDIES

### FISCHER-TROPSCH DESIGN DATA SHEETS

#### Tables

F-1	Material Balance - Slurry Reactor Case
F-2	Equipment List - COS Hydrolysis and Cooling
F-3	Equipment List - Selexol Acid Gas Removal Plant
F-4	Equipment List - Syngas Compression Plant
F-5	Equipment List - F-T Reaction Section
F-6	Equipment List - F-T Gas Plant
F-7	Equipment List - CO <sub>2</sub> Removal Plant
F-8	Utility Summary - Slurry Reactor Case
F-9	No Table - Cancelled
F-10	Material Balance - Fixed-Bed Case
F-11	Equipment List - Shift Conversion and Cooling
F-12	Equipment List - Acid Gas Removal - Rectisol
F-13	Equipment List - Syngas Compression
F-14	Equipment List - F-T Reaction Section
F-15	Equipment List - F-T Gas Plant
F-16	Equipment List - CO <sub>2</sub> Removal Plant
F-17	Utility Summary - Fixed-Bed Case

#### Figures

F-1	BFD Product Refining - Slurry Reactor Case
F-2	PFD - COS Hydrolysis
F-3	PFD - Acid Gas Removal - Selexol
F-4	PFD - Fischer-Tropsch Synthesis
F-5	PFD - Catalyst Pretreatment
F-6	PFD - F-T Gas Plant
F-7	PFD - CO <sub>2</sub> Removal
F-8	Steam Diagram - Slurry Reactor Case
F-9	BFD Product Refining - Fixed-Bed Case
F-10	PFD - Shift Conversion Plant
F-11	PFD - Acid Gas Removal - Rectisol
F-12	PFD - Fischer Tropsch Synthesis
F-13	PFD - F-T Gas Plant
F-14	PFD - CO <sub>2</sub> Removal Plant
F-15	Steam Diagram - Fixed-Bed Case

Table F-1

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

STREAM NO DESCRIPTION	NET FT YIELD	NET FISHER TROPSCH YIELD	LT ENDS TO FUEL GAS	21 ALCOHOLS LBS/HR	22 RAW F-T LIQUIDS LBS/HR	23 WAX TO HYDRO- CRACKER LBS/HR	24 H2 TO WAX H/C LBS/HR	25 WAX H/C PROD LBS/HR	26 CAT POLY FEED LBS/HR	27 CAT POLY OFF GAS PROD LBS/HR	28 CAT POLY LT GASOL LBS/HR	29 CAT POLY HEAVY GASOL LBS/HR	30 FT PROD HTU FEED LBS/HR
H2	0.00	0	0				1397						
C1	446.36	7161	7161				136						
C2 <sup>a</sup>	142.73	4004	4004				136						
C2	45.93	1381	1382		2885		0		2885	263			
C3 <sup>a</sup>	153.44	6457	3572		728		817		728	728			
C3	25.86	1140	413		85		0		85	85			
C4	1.51	88	3		935		0		935	402	533		
NCA	19.96	1160	225		5707		0		5707	286			
C4 <sup>a</sup>	107.77	6047	340		2259		5444						2259
C5	31.60	2280	21		8997		0						8997
C5 <sup>a</sup>	130.07	9122	125		1927		5444						1927
C6	22.40	1930	4		7695		0						7695
C6 <sup>a</sup>	91.65	7714	19		27457		0						27457
C7-C11	226.26	16603			16603		19597						16603
C12-C18	83.54	3569			0	3569		43548					3569
C19-C24	12.44	103904			0	103904		29395					103904
C25+	131.31	10678		10678							4106		10678
ALCOHOLS	157.60												
C7H14													
C10H20													
C8 REFORM													
C7 ALKY													
C8 ALKY													
HVY POLY GAS													
TOTAL	1830.4	210696	17267	10678	75278	107474	1397	108871	10340	1763	4639	3938	64938
BFO(MMASCFD)		20004	2486	896	7507	8508 (6.31)	10099	10099	1249	223	464	356	6257
SG@60F		0.7227	0.4766	0.8182	0.6881	0.8668		0.7397	0.5680	0.5424	0.6857	0.7590	0.7121

NOTE 1

(1) ALCOHOL CONTAINS AN ADDITIONAL 3529.3 LBS/HR OF WATER



Table F-1 Continued

MATERIAL BALANCE - BASIS 3 SHELL GASIFIERS 2500 T/D M/F COAL EACH-SLURRY REACTOR CASE												
STREAM NO.	31	32	33	34	35	36	37	38	39	40	27+39	42
DESCRIPTION	H2 TO HTU LBS/HR	FT PROD HTU LBS/HR	HTU PROD FRACT FEED LBS/HR	HTU PROD FRACT OFF GAS LBS/HR	HTU PROD FRACT C5/C6 LBS/HR	HTU PROD FRACT TO CAT REFORM LBS/HR	HTU PROD FRACT TO DIESEL LBS/HR	CAT REFORM H2 LBS/HR	CAT REFORM LT ENDS LBS/HR	CAT REFORM PROD LBS/HR	HF ALKY FEED LBS/HR	HF ALKY OFF GAS LBS/HR
COMPONENT												
H2	1077	0	0	0	0	0	0	751	0	0	0	0
C1		158	294	294				615	0	0	0	0
C2=		0	0	0				0	0	0	0	0
C2		580	716	716				1539	0	0	0	0
C3=		0	0	0				0	0	0	263	26
C3		0	817	817				0	4018	0	4746	4746
IC4		0	0	0				0	2921	0	3006	2413
NCA		747	5102	5102				0	2444	0	2847	2847
CA=		0	0	0				0	0	5739	286	29
C4=		11515	16959	16959	16959			0	0	0	0	0
C5		0	0	0	0			0	0	0	0	0
C5=		9806	15249	15249	15249			0	0	0	0	0
C8		0	0	0	0			0	0	0	0	0
C8=		26927	46524	46524	46524	46524		0	0	0	0	0
C7-C11		16282	59831	59831	59831	59831	59831	0	0	0	0	0
C12-C18			29395	29395	29395	29395	29395	0	0	0	0	0
C19-C24												
C25+												
ALCOHOLS												
C7H14												
C10H20												
C8 REFORM										28495		
C7 ALKY												
C8 ALKY												
HVY POLYGAS												
TOTAL	1077	66015	174886	6928	32308	46524	89226	2906	9384	34234	11147	10060
BPD(MMSCFD)	(4.87)	6503	16601	914	3421	4415	7851	(4.21)	1186	3170	1409	1276
SG@60F	0.6986	0.7226	0.5199	0.6460	0.7230	0.7798	0.5429	0.5428	0.5428	0.5428	0.5408	0.5408

6/6/90 REV.3

Table F-1 Continued

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

STREAM NO	43	44	45	46	47
DESCRIPTION	ALKY GASO- LINE	HVY POLYGAS HTU FD	HVY POLY GASOL	LT ENDS MAKE	GASOL
COMPONENT	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR
H2		57		0	
C1				909	
C2=				0	
C2				2255	
C3=					
C3					
IC4					533
NC4					
C4=					22697
C5					
C5=					15249
C8					
C8=					
C7-C11					
C12-C18					
C19-C24					
C25+					
ALCOHOLS					4106
C7H14					
C10H20		3938			
C8 REFORM					28495
C7 ALKY	563				563
C8 ALKY	523				523
HVY POLYGAS	0		3995		3995
TOTAL	1088	3995	3995	3164	76162
BPD(MMSCFD)	108.464	356.019	373		7535
SG@60	0.7001	0.7699	0.7342		0.6935

Table F-1 Continued

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

COMPONENT	FEED			PRODUCT									
	FT FEED LB/HR	H2 LB/HR	TOTAL FEED LB/HR	H2 LB/HR	LT ENDS LB/HR	C3/C4 LB/HR	GASOL LB/HR	DIESEL LB/HR	ALCOHOLS LB/HR	FT BLEED GAS LB/HR	TOTAL PRODUCTS LB/HR		
H2	0	2531	2531	751	0	0	0	0	0	0	751		
C1	7161	0	7161	0	509	0	0	0	0	7161	8070		
C2=	4004	0	4004	0	0	0	0	0	0	4004	4004		
C2	1361	0	1361	0	2255	0	0	0	0	1382	3637		
C3=	6457	0	6457	0	0	26	0	0	0	3572	3598		
C3	1140	0	1140	0	0	5563	0	0	0	413	5975		
ICA	88	0	88	0	0	2413	0	0	0	3	2416		
NCA	1160	0	1160	0	0	7949	533	0	0	225	8707		
C4=	6047	0	6047	0	0	29	0	0	0	340	368		
C5	2280	0	2280	0	0	0	22697	0	0	21	22718		
C5=	9122	0	9122	0	0	0	0	0	0	125	125		
C6	1930	0	1930	0	0	0	15249	0	0	4	15253		
C6=	7714	0	7714	0	0	0	0	0	0	19	19		
C7-C11	27457	0	27457	0	0	0	0	0	0	0	0		
C12-C18	16603	0	16603	0	0	0	0	59831	0	0	59831		
C19-C24	3569	0	3569	0	0	0	0	29395	0	0	29395		
C25+	103904	0	103904	0	0	0	0	0	0	0	0		
ALCOHOLS	10678	0	10678	0	0	0	0	0	10678	0	10678		
C7H14	0	0	0	0	0	0	4106	0	0	0	4106		
C10H20	0	0	0	0	0	0	0	0	0	0	0		
C8 REFORM	0	0	0	0	0	0	28495	0	0	0	28495		
C7 ALKY	0	0	0	0	0	0	563	0	0	0	563		
C8 ALKY	0	0	0	0	0	0	523	0	0	0	523		
HVY POLYGAS	0	0	0	0	0	0	3995	0	0	0	3995		
TOTAL	210696	2531	213227	751	3164	15979	76162	89226	10678	17267	213227		
FUEL MMBTU/HR				65.6							626.4		
H2 CONSUMED	1397	693.03	H2 MAKE	751	372.37								
WAX H/C	1077	534.21	CAT REFORMER	1780	882.95								
F-T HTU	57	28.08	FT PURGE	2531	1255.32								
HCP GAS HTU	2531	1255.32	TOTAL										

6/6/90 REV.3

Table F-2

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

COS HYDROLYSIS AND COOLING  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN COND. PRESS PSIG	TEMP. °F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS	
						EXTERNAL	INTERNAL	DIAM., FT	T-T FT		
C-1	COS HYDROLYSIS REACTOR	VERT	1	380	500	CS	W/304SS	304L	18	19	W/HEMI HEADS 6100FT3 CAT
C-2	COLD SEPARATOR	VERT	1	380	250	CS	W/304SS	304SS	11	8	W/MESH PAD CLAD

Table F-2

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

COS HYDROLYSIS AND COOLING  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION			TUBEREMARKS
				PRESS. PSIG	TEMP. F	SHELL	TUBE	SHELL	TUBE	AREA	
E-1	FEED HEATER	S&T	1	380	650	500	650	CS	304L	3000	
E-2	EFFLUENT AIR COOLER	AIR	1	N/A	380	N/A	500	N/A	304L	18550	FAN BHP-275
E-3	EFFLUENT TRIM COOLER	S&T	1	380	75	250	250	CS	304L	5030	

Table F-3

SLURRY REACTOR DESIGN STUDIES  
 SLURRY REACTOR CASE  
 EQUIPMENT LIST  
 SELEXOL ACID GAS REMOVAL PLANT

VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN COND. PRESS PSIG	TEMP. °F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
						SHELL	INTERIALS	DIAM. IN	H. IN	
C-1	FEED GAS SEPARATOR	VERT	1	550	250	CS	316 SS	8.5	7.5	WSS MESH PAD
C-2	ABSORBER	VERT	1	550	250	CS	410 SS	12	127	
C-3	RICH SOLUTION FLASH DRUM	HORIZ	1	50	250	SS	316 SS	7.5	24	WSS MESH PAD
C-4	REGENERATOR	VERT	1	50	350	CS W/SS CLAD TOP	410 SS	8	143	
C-5	REGENERATOR OVHD RECEIVER	HORIZ	1	50	250	CS W/SS CLAD	316 SS	2.5	7	WSS MESH PAD
C-6	1ST STG COMPRESSOR KO DRUM	VERT	1	200	300	CS	316 SS	2.5	7	WSS MESH PAD
C-7	PROPYLENE ACCUMULATOR	HORIZ	1	260	250	CS	316 SS	4.5	15	
C-8	LOW LEVEL PROPYLENE KO DRUM	HORIZ	1	100	250	CS	316 SS	4.5	11.5	WSS MESH PAD
D-1	SELEXOL STORAGE	VERT	1	ATM	250	CS	316 SS	4.5	11.5	55000 BBLs

Table F-3

SLURRY REACTOR DESIGN STUDIES  
 SLURRY REACTOR CASE  
 EQUIPMENT LIST  
 SELEXOL ACID GAS REMOVAL PLANT

HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION				REMARKS
				SHELL PRESS.	SHELL TUBE	SHELL TEMP.	SHELL TUBES	SHELL	TUBE	AREA	AREA	
E-1	FEED GAS/TREATED GAS	S&T	1	550	550	250	250	CS	CS	13620		
E-2	LEAN SOLUTION CHILLER	KETTLE	1	550	550	250	250	CS	CS	13175		
E-3	LEA/RICH EXCHANGER	S&T	1	550	550	250	250	CS	CS	116400		
E-4	REGEN OVHD CONDENSER	S&T	1	50	550	250	250	304SS	304SS	1235		
E-5	REGENERATOR REBOILER	KETTLE	1	50	550	250	250	304SS	304SS	7500		
E-6	1ST STG COMPR AFTER COOLER	DBL PIPE	1	200	75	260	250	CS	CS	40		
E-7	2ND STG COMPR AFTER COOLER	DBL PIPE	1	550	75	260	360	CS	CS	40		
E-8	PROPYLENE DESUPERHEATER	S&T	1	260	75	340	400	CS	CS	800		
E-9	PROPYLENE CONDENSER	S&T	1	260	75	260	400	CS	CS	4920		

Table F-3

SLURRY REACTOR DESIGN STUDIES  
 SLURRY REACTOR CASE  
 EQUIPMENT LIST  
 SELEXOL ACID GAS REMOVAL PLANT

ITEM NO.	EQUIPMENT NAME	TYPE	NO. FEED TRAIN	FLOW GPM (SCFM)	DESIGN CONDITIONS			MATERIALS OF CONSTRUCTION		DRIVER	B-P
					HEAD FT	HP	HYDRAULIC HP	CASE	ROTATING UNIT		
G-1	LEAN SOLUTION PUMP	CENTRIF	2	1600	1600			CS	CI	MOTOR	750
G-2	REGENERATOR REFUX	CENTRIF	2	8	210			CS	SS	MOTOR	2
G-3	REGENERATOR FEED	CENTRIF	2	1375	250			CS	SS	MOTOR	110
K-1	RECYCLE COMPRESSOR	RECP	2							MOTOR	225
K-2	REFRIGERATION COMPRESSOR	CENTRIF	2							STEAM TURBINE	1000



Table F-4

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

SYNGAS COMPRESSION PLANT  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. TRAINS	DESIGN COND. PRESS PSIG	TEMP. °F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
						SHELL	INTERIALS	DIAM., FT	T-T FT	
C-1	FEED GAS KO DRUM	VERT	1	345	250	CS	316 SS	13.5	9.5	W/SS MESH PAD
C-2	COMPR. DISCHARGE KO DRUM	VERT	1	580	250	CS	316 SS	12	9	W/SS MESH PAD

Table F-4

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

SYNGAS COMPRESSION PLANT  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION			REMARKS	
				SHELL PRESS.	TUBE PRESS.	SHELL TEMP.	TUBE TEMP.	SHELL	TUBE	AREA		
E-1	COMPRESSOR AFTER COOLER	AIR	1	N/A	560	N/A	250	N/A	CS	CS	6600	FAN BHP-96
E-2	COMPRESSOR TRIM COOLER	S&T	1	560	75	250	250	CS	CS	CS	5640	
E-3	COMPRESSOR SURFACE COND	S&T	1	50	75	250	250	CS	CS	CS	10000	

Table F-4

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

SYNGAS COMPRESSION PLANT  
PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM (SCHEM)	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		ROTATING UNIT	DRIVER TYPE	POWER BHP	REMARKS
					HEAD EI	HYDRAULIC HP	CASE	UNIT				
K-1	SYNGAS COMPRESSOR	CENTRIF	1	(326900)						STEAM TURBINE	16500	

Table F-5

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

F-T REACTION SECTION  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. FEED TRAIN	DESIGN COND. PRESS PSIG	TEMP. °F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
						SHELL	INTERNAL	DIAM., FT	T-T FT	
C-1	STEAM DRUM	HORIZ	6	700	650	CS	CS	6.5	30	
C-2	SLURRY REACTOR	VERT	6	460	550	CS	CHROMIZED TUBES	15.75	46.3	W/2500 TUBES
C-3	WAX SURGE DRUM	VERT	1	50	510	CS	CS	15	50	W/MIXER
C-4	PRODUCT SEPARATOR	HORIZ	1	450	250	304 SS	316 SS	13	42	
C-5	FILTER PRECOAT DRUM	VERT	1	50	250	CS	CS	4	12	
C-6	SPENT WAX OFFGAS DRUM	HORIZ	1	50	250	304 SS	316 SS	4	12	
C-7	SLURRY PREPARATION DRUM	VERT	1	50	350	CS	CS	17	22	W/MIXER
C-8	CATALYST PRETREATER	VERT	1	250	600	CS	CHROMIZED TUBES	15	40	W/INTERNAL COILS
C-9	CAT PRETREATER CIRC. KO DRUM	HORIZ	1	250	250	304 SS	316 SS	7	14	
C-10	PRETREATED CATALYST FEED DRUM	VERT	1	50	600	CS	CS	15	40	W/INTERNAL COILS & MIXER
T-1	SPENT WAX STORAGE		1	ATM	250	CS	CS	23	26	1600 BBLS
T-2	CLEAN WAX STORAGE		1	ATM	250	CS	CS	23	26	1600 BBLS
T-3	CATALYST STORAGE BIN		1	ATM	250	CS	CS	16	27	60 CONE BTM

Table F-5

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

F-1 REACTION SECTION  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO PER TRAIN	DESIGN CONDITIONS			MATERIALS OF CONSTRUCTION ARE TUBE REMARKS		
				PRESS.PSIG	SHELL TUBE	TEMP. F	SHELL	TUBE	AREA
E-1	REACTOR FEED/EFFL EXCH	S&T	1	500	460	550	CS	CS	11220
E-2	EFFLUENT AIR COOLER	AIR	1	460	460	350	CS	304 SS	7800
E-3	EFFLUENT TRIM COOLER	S&T	1	460	75	250	304 SS	304 SS	6150
E-4	SPENT CAT COOLER	S&T	1	100	75	350	CS	CS	750
E-5	SPENT WAX OFF GAS CONDENSER	S&T	1	50	75	350	304 SS	304 SS	200
E-6	SPENT WAX HEATER	S&T	1	75	600	400	CS	CS	350
E-7	CLEAN WAX HEATER	S&T	1	600	50	400	CS	CS	350
E-8	CATALYST PRETREATER HEATER	S&T	1	600	200	400	CS	CS	210
E-9	PRETREATER CIRC. GAS COOLER	S&T	1	250	75	350	304 SS	CS	3000
F-1	PRETREATER CIRC. GAS HEATER	FFED	1	NA	250	NA	CS	CS	23MMBTU/HR

Table F-5

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

F-I REACTION SECTION  
PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM/(SCFM)	DESIGN CONDITIONS			MATERIALS OF CONSTRUCTION		DRIVER TYPE	POWER H.P.	REMARKS
					LEAD EI	HYDRAULIC HP	ROTATING UNIT	ROTOR CASE	DRIVER TYPE			
G-1	BFW PUMP	CENTRIF	6	2750	69	39	CS	CI	MOTOR	49		
G-2	WAX WITHDRAWAL PUMP	CENTRIF	2	66	110	1.7	CS	CI	MOTOR	4		
G-3	SPENT WAX RECIRC. PUMP	CENTRIF	2	600	670	36	CS	CI	MOTOR	66		
G-4	FILTER AID PUMP	CENTRIF	2	10	100	0.3	CS	CI	MOTOR	1		
G-5	RECOVERED LIQUIDS PUMP	CENTRIF	2	10	1500	2.6	CS	CI	MOTOR	10		
G-6	SPENT WAX PUMP	CENTRIF	2	150	90	2.6	CS	CI	MOTOR	5		
G-7	CLEAN WAX FEED	CENTRIF	2	300	115	6.8	CS	CI	MOTOR	10		
G-8	CAT PRETREATER FEED	CENTRIF	2	340	590	54	CS	CI	MOTOR	95		
G-9	CAT PRETREATER PRODUCT	CENTRIF	2	393	75	6.9	CS	CI	MOTOR	10		
G-10	CATALYST MAKEUP	CENTRIF	2	9	1275	2.7	CS	CI	MOTOR	14		
K-1	RECYCLE COMPRESSOR	CENTRIF	1	(45000)							1200	

Table F-5

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

F.T. REACTION SECTION  
PACKAGE EQUIPMENT

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	CAPACITY	OPERATING CONDITIONS	POWER KW	REMARKS
Y-1	SPENT CAT CENTRIFUGE	CENTRIFUGE	1	360 GPM 29 TONS/HR SOLIDS	300-500 F, 5 PSIG	250	
Y-2	HYDROCLONES	CYCLONES	12	85 GPM 5 TONS/HR SOLIDS	500 F, 410 PSIG		
Y-3	WAX FILTERS	TANK VERTICAL LEAF FILTER	3		300 F, 5 PSIG		
Y-4	AXIAL CYCLONE	SEPARATOR	6	2350 ACFM VAPOR	500 F, 410 PSIG		
Y-5	CAT PRETREATMENT HEATER	HOT OIL SYSTEM	1	20 MMBTU/HR DUTY	700 F HOT OIL	50	

Table F-6

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

F-T GAS PLANT  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN COND.		MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
				PRESS PSIG	TEMP. °F	SHELL	INTERNAL	DIAM. EI	H I-I	
C-1	DEETHANIZER	VERT	1	450	450	CS	410 SS	5.5	101	
C-2	DEETHANIZER REFLUX DRUM	HORZ	1	450	250	CS	304 SS	3	12	W/SS MESH PAD
C-3	STABILIZER	VERT	1	90	400	CS	410 SS	4	84	
C-4	STABILIZER REFLUX DRUM	HORZ	1	90	250	CS	304 SS	4	15	W/SS MESH PAD
C-5	RECYCLE GAS KO DRUM	VERT	1	550	250	LT CS	CS	7	9	W/SS MESH PAD
C-6	PROPYLENE ACCUMULATOR	HORZ	1	250	250	LT CS	304 SS	4.5	16.5	
C-7	LOW LEVEL PROPYL KO DRUM	VERT	1	100	250/-50	LT CS	304 SS	4	15	W/SS MESH PAD
C-8	HI LEVEL PROPYL KO DRUM	VERT	1	100	250/-50	LT CS	304 SS	4.5	16	W/SS MESH PAD



Table F-6

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

F-I GAS PLANT  
HEAT EXCHANGERS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN CONDITIONS			MATERIALS OF CONSTRUCTION			REMARKS
				PRESS	SHELL	TEMP. F	SHELL	TUBE	AREA	
E-1	RECYCLE COMP AFTERCOOLER	AIR	1	N/A	575	N/A	304 SS	304 SS	1440	FAN BHP=40
E-2	RECYCLE COMP TRIM COOLER	S&T	1	575	75	250	304 SS	304 SS	2310	
E-3	DEETHANIZER CONDENSER	S&T	1	440	150	250	CS	CS	840	
E-4	DEETHANIZER REBOILER	KET	1	440	650	550	CS	CS	680	
E-5	DEETHANIZER SIDE REBOILER	S&T	1	440	440	500	CS	CS	970	
E-6	STABILIZER REBOILER	KET	1	100	650	550	CS	CS	490	
E-7	STABILIZER CONDENSER	S&T	1	100	75	250	304 SS	304 SS	5425	
E-8	STABILIZER BOTTOM COOLER	AIR	1	N/A	120	N/A	N/A	CS	1515	FAN BHP=22
E-9	FEEDOFFGAS EXCH	S&T	1	525	500	250	CS	LTCS	8520	
E-10	FEED LIQUID EXCH	S&T	1	525	500	250	CS	LTCS	11230	
E-11	RECYCLE GAS CHILLER	S&T	1	150	525	250/-50	LTCS	LTCS	5080	
E-12	PROPYLENE DESUPERHEATER	S&T	1	250	75	250	CS	CS	1240	
E-13	PROPYLENE CONDENSER	S&T	1	250	75	250	CS	CS	6230	
E-14	RECYCLE COMP. SURF. COND.	S&T	1	5	75	250	CS	CS	2900	

Table F-6

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE

F-I GAS PLANT  
PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM (SCHEM)	HEAD EI	HYDRAULIC HP	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRIVER TYPE	POWER BHP	REMARKS
							ROTATING UNIT	CASE	ROTATING UNIT	CASE			
G-1	DEETHANIZER REFLUX	CENTRIF	2	36	205	1	CS	CI		MOTOR	3		
G-2	STABILIZER REFLUX	CENTRIF	2	159	185	4.1	CS	CI		MOTOR	7		
G-3	STABILIZER BOTTOMS	CENTRIF	2	348	90	4	CS	CI		MOTOR	5		
K-1	RECYCLE COMPRESSOR	CENTRIF	1	(105000)						STM TURB	4000		
K-2	REFRIGERATION COMPRESSOR	CENTRIF	1							STM TURB	1740		

Table F-7

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE  
EQUIPMENT LIST  
CO2 REMOVAL PLANT

VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. TRAIN	DESIGN COND. PRESS	TEMP. F	SHELL	MATERIALS OF CONSTRUCTION	DIMENSIONS		REMARKS
								DIAM. EI	H I-I	
C-1	FEED GAS KO DRUM	VERT	1	400	250	CS	316 SS MESH	8	7	SS MESH PAD
C-2	ABSORBER	VERT	1	400	250	CS	410 SS TRAYS	14.5	94	SS MESH PAD
C-3	TREATED GAS KO DRUM	VERT	1	400	250	CS	316 SS MESH	10	30	SS MESH PAD
C-4	RICH SOLUTION FLASH DRUM	HORIZ	1	50	250	SS	316 SS MESH	7.5	24	SS MESH PAD
C-5	REGENERATOR	VERT	1	50	350	CS W/SS CLAD TOP	304 SS PACK.	19.5	83	
C-6	REGENERATOR OVERHEAD RECEIVER	VERT	1	50	250	CS W/SS CLAD	316 SS MESH	12	9	SS MESH PAD
D-1	SOLUTION STORAGE TANK	VERT	1	ATM	250	CS				7000 BBLs

Table F-7

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE  
EQUIPMENT LIST  
CO2 REMOVAL PLANT

HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION			REMARKS
				PRESS. PSIG	TEMP. °F	SHELL TUBES	TEMP. °F	SHELL	TUBES	TUBE	
E-1	LEAN SOLUTION COOLER	S&T	1	400	75	250	250	CS	CS	30400	
E-2	LEAN SOLUTION AIR COOLER	AIR	1	N/A	400	250	250	N/A	CS	27600	FAN BHP=785
E-3	LEANRICH EXCHANGER	S&T	1	50	400	250	250	CS	CS	59600	
E-4	REGENERATOR CONDENSER	AIR	1	N/A	50	250	250	N/A	304SS	16500	FAN BHP=460
E-5	REGENERATOR REBOILER	KETTLE	1	50	75	350	400	304SS	304SS	48200	
E-6	RECLAIMER	KETTLE	1	50	250	650	650	304SS	304SS		

Table F-7

SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE  
EQUIPMENT LIST  
CO2 REMOVAL PLANT

PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. FEED TRAIN	FLOW GPM (SCFM)	HEAD FT	HYDRAULIC HP	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRAINER	BHP
							CS	CS	CS	ROTATING UNIT		
G-1	LEAN SOLUTION PUMP	CENTRIF	2	6700	110	176	CS	CS	CI	MOTOR	215	
G-2	LEAN SOLUTION BOOSTER PUMP	CENTRIF	2	6360	850	1390	CS	CS	SS	MOTOR	1700	
G-3	REGENERATOR REFLUX	CENTRIF	2	280	140	10	CS	CS	SS	MOTOR	15	

Table F-9

SLURRY REACTOR DESIGN STUDIES  
FISCHER-TROPSCH SLURRY REACTOR CASE  
UTILITY SUMMARY

PLANT DESCRIPTION	HIGH PR		MED PR		MED PR		200 PSI		LOW PR		COND		WATER, GPM		FUEL, MBTU/HR		
	ELEC. KW	PSG	PSG	PSG	PSG	PSG	PSG	PSG	PSG	PSG	PSG	BRW	WASTE WATER	C.W. CIRC.	HEAT ABS	TOTAL FRED DUTY	
<b>GAS PREP. AND SYNTHESIS</b>																	
101 SH-FT GASIFIER												1617	133				
102 SH-FT CONVERSION	446					232						461		90			
103 CO2 HYDROLYSIS	81	184.9							39.1 (39.1)			1410		910			
104 GAS COMPRESSION	57								27.1 (27.1)		3929			1410			
105 SOUR WATER STRIPPING	1908	15.8							65.6 (65.6)		101			101		40.5	
106 ACID GAS REMOVAL					2.4												
107 SLURRY RECOVERY & TGT	1150										2504			2095	19.1	24.0	
108 SLURRY POLISHING	1373				57.5 (1,227.3)				1250.1 (1,250.1)					58400			
109 F-T SYNTHESIS	7450													160	7.5	10.0	
110 CO2 REMOVAL	62													3540			(626.4)
111 DEHYDRATION																	
112 F-T GAS PLANT	388	74.8			25.7												
113 H2 RECOVERY																	
<b>F-I PRODUCT REFINING</b>																	
200 ALCOHOL RECOVERY	168				0.2			21.5						7	280		8.4
201 F-T PRODUCT HTU	128				0.0									215			52.5
202 HTU PROD FRACT.	798				74.2			1.6 (1.6)					3	1581			18.8
203 CAT REFORMER	218				13.3									560			1.7
204 CS28 ISOMERIZATION	392				0.9			79.8 (81.0)						170			
205 CAT POLYMERIZATION	102				13.3									115			
206 HF ALKYLATION	83				3.7			1.8 (1.8)						229			0.3
207 HMY GASOLINE HTU	56				1.8									34			(65.3)
208 LT ENDS RECOVERY	812				0.0			6.3 (6.3)						510			
209 H2 PURIFICATION	345				0.0									50			
210 WAX HYDROCRACKING	856				8.7			3.0 (3.0)						242			48.4
<b>GEBSITE UNITS</b>																	
300 OXYGEN PLANT	1703	895.5			80									135505			
301 INSTRUMENT/PLANT AIR																	
302 COAL HANDLING	1881				67.1												
303 POWER DISTRIBUTION	1530																
304 BW PREPARATION																	
305 COOLING WATER TREATMENT	8633																
306 CW TOWER	(81410)	516.6															1118.3
307 POWERGEN	1148																
308 WW TREATMENT																	
309 BLDWDOWN																	
310 STORAGE																	
311 INTERCOGN PIPING																	
312 REFRIGERATION	80																
313 GASOLINE BLENDING	250																
MISCELLANEOUS	(16070)	874.5			80	265.8 (995.3)		72.9 (1501.1)	1386.3 (1501.1)	5619	604	210105	26.8	631.2			
<b>TOTAL</b>																	

Table F-10 MATERIAL BALANCE -BASIS 3 SHELL GASIFIERS 2500 T/D M/F COAL EACH-FIXED BED CASE

STREAM NO	NET FT YIELD	NET FISHER TROPSCH YIELD	LT ENDS TO FUEL GAS	ALCOHOLS	RAW F-T LIQUIDS	WAX TO HYDRO-CRACKER	H2 TO WAX H/C	WAX H/C PROD	CAT POLY FEED	CAT POLY OFF GAS PROD	CAT POLY LT GASOL	CAT POLY HEAVY GASOL	FT PROD HTU FEED
COMPONENT	MFH	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR
H2	0.00	0	0	0	0	0	1174	0	0	0	0	0	0
C1	503.56	8079	8078	0	0	0	0	136	0	0	0	0	0
C2=	30.97	869	869	0	0	0	0	0	0	0	0	0	0
C2	151.64	4560	4559	0	0	0	0	136	0	0	0	0	0
C3=	74.53	3139	669	0	2470	0	0	0	2470	225	0	0	0
C3	102.40	4516	647	0	3869	0	0	815	3869	3869	0	0	0
IC4	4.42	257	7	0	250	0	0	0	250	250	0	0	0
NCA	58.78	3417	92	0	3324	0	0	4345	3324	2951	373	0	0
C4=	65.49	3674	118	0	3556	0	0	0	3556	178	0	0	0
C5	78.45	5516	29	0	5487	0	0	5432	0	0	0	0	5487
C5=	85.23	5977	48	0	5930	0	0	0	0	0	0	0	5930
C6	53.00	4567	5	0	4563	0	0	5432	0	0	0	0	4563
C6=	61.13	5149	7	0	5142	0	0	0	0	0	0	0	5142
C7-C11	226.67	27670	0	0	27670	0	0	19554	0	0	0	0	27670
C12-C18	83.48	16727	0	0	16727	0	0	43453	0	0	0	0	16727
C19-C24	12.49	3597	0	0	0	0	0	29331	0	0	0	0	0
C25+	130.97	103861	0	0	0	103861	0	0	0	0	0	0	0
ALCOHOLS	158.84	10762	0	10762	0	0	0	0	0	0	2670	0	0
C7H14	0.00	0	0	0	0	0	0	0	0	0	0	2753	0
C10H20	0.00	0	0	0	0	0	0	0	0	0	0	0	0
C6 REFORM	0.00	0	0	0	0	0	0	0	0	0	0	0	0
C7 ALKY	0.00	0	0	0	0	0	0	0	0	0	0	0	0
C8 ALKY	0.00	0	0	0	0	0	0	0	0	0	0	0	0
HVY POLY GAS	0.00	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	1880.15	212336	15129	10762	78986	107458	1174	108632	13469	7473	3243	2753	65518
BPD(MMSCFD)		20474	3062	903	7011	8507	(5.3)	10077	1674	950	324	249	6328.57
SG@60F		0.7444	0.3390	0.3182	0.7730	0.8668		0.7397	0.5520	0.5399	0.6857	0.7590	0.7104

NOTE 1

NOTES  
(1) ALCOHOL CONTAINS AN ADDITIONAL 243857 LB/HR OF WATER

Table F-10 Continued

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

STREAM NO	31	32	33	34	35	36	37	38	39	40	27+39	42
DESCRIPTION	H2 TO PROD HTU	FT PROD HTU PROD	HTU PROD FRACT FEED	HTU PROD FRACT OFF GAS	HTU PROD FRACT C5/C6	HTU PROD FRACT TO CAT REFORM	HTU PROD FRACT TO DIESEL	CAT REFORM H2 PROD	CAT REFORM LT ENDS PROD	CAT REFORM PROD REFORMATE	HF ALKY FEED	HF ALKY OFF GAS
COMPONENT	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR
H2	678	0	0	0	0	0	0	751	0	0	0	0
C1	0	159	295	295	0	0	0	616	0	0	0	0
C2=	0	0	0	0	0	0	0	0	0	0	0	0
C2	0	584	720	720	0	0	0	1540	0	0	0	0
C3=	0	0	0	0	0	0	0	0	0	0	225	22
C3	0	0	815	815	0	0	0	0	4019	0	7888	7888
IC4	0	0	0	0	0	0	0	0	2921	0	3171	2726
NC4	0	753	5098	5098	0	0	0	0	2445	0	5396	5396
CA=	0	0	0	0	0	0	0	0	0	0	178	18
C4	0	11587	17019	0	17019	0	0	0	0	5740	0	0
C5	0	0	0	0	0	0	0	0	0	0	0	0
C5=	0	0	0	0	15259	0	0	0	0	0	0	0
C6	0	9828	15259	0	0	0	0	0	0	0	0	0
C6=	0	0	0	0	0	0	0	0	0	0	0	0
C7-C11	0	26977	46531	0	0	46531	0	0	0	0	0	0
C12-C18	0	16308	59761	0	0	0	59761	0	0	0	0	0
C19-C24	0	0	29331	0	0	0	29331	0	0	0	0	0
C25+	0	0	0	0	0	0	0	0	0	0	0	0
ALCOHOLS	0	0	0	0	0	0	0	0	0	0	0	0
C7H14	0	0	0	0	0	0	0	0	0	0	0	0
C10H20	0	0	0	0	0	0	0	0	0	0	0	0
C8 REFORM	0	0	0	0	0	0	0	0	0	28500	0	0
C7 ALKY	0	0	0	0	0	0	0	0	0	0	0	0
C8 ALKY	0	0	0	0	0	0	0	0	0	0	0	0
HVY POLYGAS	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	678	66195	174828	6927	32278	46531	89092	2906	9385	34239	16858	16050
BPD(MMSCFD)	(3.06)	6522	16598	915	3428	4416	7839	(4.21)	1186	3171	2136	2037
SG@60F		0.6965	0.7227	0.5197	0.6460	0.7230	0.7798		0.5429	0.7409	0.5416	0.5407

6/6/90 REV 4



Table F-10 Continued  
 MATERIAL BALANCE - BASIS 3 SHELL GASIFIERS 2500 T/D M/F COAL EACH-FIXED BED CASE

STREAM NO DESCRIPTION	43 ALKY GASO- LINE	44 HVY POLYGAS HTUFD	45 HVY POLY GASOL	46 LT ENDS MAKE	47 GASOL
COMPONENT	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR
H2	0	40	0	0	0
C1	0	0	0	910	0
C2-	0	0	0	0	0
C2	0	0	0	2259	0
C3-	0	0	0	0	0
C3	0	0	0	0	0
iC4	0	0	0	0	0
nC4	0	0	0	0	373
C4-	0	0	0	0	0
C5	0	0	0	0	22758
C5-	0	0	0	0	0
C6	0	0	0	0	15259
C6-	0	0	0	0	0
C7-C11	0	0	0	0	0
C12-C18	0	0	0	0	0
C19-C24	0	0	0	0	0
C25+	0	0	0	0	0
ALCOHOLS	0	0	0	0	0
C7H14	0	0	0	0	2870
C10H20	0	2753	0	0	0
C8 REFORM	0	0	0	0	28500
C7 ALKY	482	0	0	0	482
C8 ALKY	326	0	0	0	326
HVY POLYGAS	0	0	2793	0	2793
TOTAL	808	2793	2793	3170	73361
BFD	79	249	261		7264
SG@60F	0.6983	0.7699	0.7342		0.6930

Table F-10 Continued  
 MATERIAL BALANCE -BASIS 3 SHELL GASIFIERS 2500 T/D M/F COAL EACH-FIXED BED CASE

DESCRIPTION	FEED			PRODUCTS									
	FT FEED LB/HR	H2 LB/HR	TOTAL FEED LB/HR	H2 LB/HR	LT ENDS LB/HR	C3/C4 LB/HR	GASOL LB/HR	DIESEL LB/HR	ALCOHOLS LB/HR	FT BLEED GAS LB/HR	TOTAL PRODUCTS LB/HR		
H2	0	1891	1891	751	0	0	0	0	0	0	751		
C1	8079	0	8079	0	910	0	0	0	0	8078	8989		
C2=	869	0	869	0	0	0	0	0	0	869	869		
C2	4560	0	4560	0	2259	0	0	0	0	4559	6815		
C3=	3139	0	3139	0	0	22	0	0	0	669	692		
C3	4516	0	4516	0	0	8702	0	0	0	647	9349		
IC4	257	0	257	0	0	2726	0	0	0	7	2732		
NCA	3417	0	3417	0	0	10494	373	0	0	92	10959		
CA=	3674	0	3674	0	0	18	0	0	0	118	136		
C5	5516	0	5516	0	0	0	22758	0	0	29	22787		
C5=	5977	0	5977	0	0	0	0	0	0	48	48		
C6	4567	0	4567	0	0	0	15259	0	0	5	15264		
C6=	5149	0	5149	0	0	0	0	0	0	7	7		
C7-C11	27670	0	27670	0	0	0	0	0	0	0	0		
C12-C18	16727	0	16727	0	0	0	0	59761	0	0	59761		
C19-C24	3597	0	3597	0	0	0	0	29331	0	0	29331		
C25+	103861	0	103861	0	0	0	0	0	0	0	0		
ALCOHOLS	10762	0	10762	0	0	0	0	0	10762	0	10762		
C7H14	0	0	0	0	0	0	2870	0	0	0	2870		
C10H20	0	0	0	0	0	0	0	0	0	0	0		
C8 REFORM	0	0	0	0	0	0	28500	0	0	0	28500		
C7 ALKY	0	0	0	0	0	0	482	0	0	0	482		
C8 ALKY	0	0	0	0	0	0	326	0	0	0	326		
HVY POLYGAS	0	0	0	0	0	0	2793	0	0	0	2793		
TOTAL	212336	1891	214227	751	3170	21953	73361	89092	10762	15129	214227		
FUEL/MBTU/HR					65.7					514.7			
H2 CONSUMED	1174	582.2	H2 MAKE	751	MPH								
WAX H/C	678	336.4	CAT REFORMER	1141	LB/HR								
F-T HTJ	40	19.6	FT PURGE	1891	MPH								
HCP GAS HTU	1891	938.2	TOTAL										
TOTAL													

Table F-11

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

SHIFT CONVERSION AND COOLING  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. TRAIN	DESIGN CONDITIONS			MATERIALS OF CONSTRUCTION			TUBE AREA	REMARKS
				PRESS	SHELL TUBE	TEMP. F	SHELL	TUBE	AREA		
E-1	EFFLUMP STEAM GENERATOR	S&T	1	650	380	650	CS	321 SS	8440		
E-2	FEED/EFFLUENT EXCHANGER	S&T	1	400	380	500	CS W/321 CL	321 SS	6650		
E-3	EFFLUMP STEAM GENERATOR	S&T	1	75	380	500	CS	304L	4325		
E-4	EFFLUMP BW PREHEATER	S&T	1	380	650	500	CS	304L	3365		
E-5	EFFLUMP BW PREHEATER	S&T	1	380	75	500	CS	304L	600		
E-6	EFFLUENT AIR COOLER	AIR	1	N/A	380	N/A	N/A	304L	39750	FAN BHP=585	
E-7	EFFLUENT TRIM COOLER	S&T	1	380	75	250	CS	304L	8400		
F-1	STARTUP HEATER		1		650			321 SS		19MM BTU/HR FIRED DUTY	

Table F-11

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

SHIFT CONVERSION AND COOLING  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN COND. PRESS PSIG	TEMP. °F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS	
						SHELL	INTERIALS	DIAM., FT	T-T FT		
C-1	SHIFT CONVERTER	VERT	1	380	930	1.25Cr	.5Mo	321 SS	15.0	12.5	
C-2	COOLD SEPARATOR	VERT	1	380	250	W/321 SS	CLAD	304 L	11.5	9.5	

Table F-12

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE  
EQUIPMENT LIST  
ACID GAS REMOVAL PLANT  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. TRAIN	DESIGN COND. PRESS PSIG	TEMP. °F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
						SHELL	INTERVALS	DIAM., FT.	T-T FT.	
C-1	FEED GAS SEPARATOR	VERT	1	550	100/-50	LOW TEMP CS	316 SS	8.5	10	W/SS MESH PAD
C-2	ABSORBER	VERT	1	550	100/-100	3% NI	410 SS	13	217	
C-3	CO2 RICH FLASH DRUM	HORIZ	1	200	100/-50	LOW TEMP CS	316 SS	12	36	W/SS MESH PAD
C-4	H2S RICH FLASH DRUM	HORIZ	1	200	100/-50	LOW TEMP CS	316 SS	8	24	W/SS MESH PAD
C-5	H2S CONCENTRATION COL	VERT	1	60	100/-100	3% NI	410 SS	17	144	
C-6	HOT REGENERATOR	VERT	1	60	250	CS	410 SS	17	102	
C-7	HOT REGEN REFLUX DRUM	HORIZ	1	60	150	CS		5	12	
C-8	CONDENSATE DRUM	HORIZ	1	60	100/-50	LOW TEMP CS		6.5	13	
C-9	METHANOL SURGE DRUM	HORIZ	1	60	150	CS		16	42	TOP
C-10	METHANOL/H2O COLUMN	VERT	1	75	320	CS	410 SS	6	79	BTM
C-11	PROPYLENE ACCUMULATOR	HORIZ	1	320	150	CS		7	20	
C-12	LOW LEVEL PROPYLENE KO	VERT	1	150	100/-50	LOW TEMP CS	316 SS	9.5	8	W/SS MESH PAD
C-13	MED LEVEL PROPYLENE KO	VERT	1	150	100/-50	LOW TEMP CS	316 SS	8	14	W/SS MESH PAD
C-14	HIGH LEVEL PROPYLENE KO	VERT	1	150	100/-50	LOW TEMP CS	316 SS	9	14	W/SS MESH PAD
D-1	METHANOL STORAGE	VERT	1	ATM		CS				11000 BBLs

Table F-12

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE  
EQUIPMENT LIST  
ACID GAS REMOVAL PLANT

HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN CONDITIONS			MATERIALS OF CONSTRUCTION			REMARKS
				PRESS. PSIG	SHELL TEMP. F	TUBES TEMP. F	SHELL	TUBE	AREA	
E-1	FEED GAS/CO2 VENT	S&T	1	60	550	150/-50	150/-50	LOW TEMP C.S	LOW TEMP C.S	6140
E-2	FEED GAS/TREATED GAS	S&T	1	550	550	150/-50	150/-50	LOW TEMP C.S	LOW TEMP C.S	17130
E-3	FEED GAS CHILLER	S&T	1	150	550	150/-50	150/-50	LOW TEMP C.S	LOW TEMP C.S	5965
E-4	ABSORBER INTERCOOLER	S&T	1	150	550	150/-50	150/-50	LOW TEMP C.S	LOW TEMP C.S	11600
E-5	LEAN METHANOL CHILLER	S&T	1	150	550	150/-50	150/-50	LOW TEMP C.S	LOW TEMP C.S	9000
E-6	HOT REGEN FEED/BOTTOMS	S&T	1	185	550	200/-100	200/-100	3%NI	3%NI	144000
E-7	HOT REGEN FEED/BOTTOMS	S&T	1	185	75	260	250	CS	CS	130300
E-8	HOT REGEN REBOILER	S&T	1	60	75	260	360	CS	CS	7400
E-9	METHANOL/H2O REBOILER	S&T	1	75	150	340	400	CS	CS	1170
E-10	METHANOL H2O FD/REFLUX	S&T	1	75	180	260	400	CS	CS	100
E-11	METHANOL/H2O BTM COOL	S&T	1	75	150	260	200	CS	CS	70
E-12	HOT REGEN CONDENSER	S&T	1	60	150	260	200	CS	CS	11300
E-13	H2S REHEAT EXCHANGER	S&T	1	60	60	150/-50	150/-50	LOW TEMP C.S	LOW TEMP C.S	400
E-14	HOT REGEN OVHD CHILLER	S&T	1	150	60	150/-50	150/-50	LOW TEMP C.S	LOW TEMP C.S	1500
E-15	PROPYLENE DESUPERHEATER	S&T	1	320	150	320	200	CS	CS	3170
E-16	PROPYLENE CONDENSER	S&T	1	320	150	260	200	CS	CS	19300
E-17	ABSORBER INTERCOOLER	S&T	1	100	550	150/-50	150/-50	LOW TEMP C.S	LOW TEMP C.S	23180
E-18	REFRIG COMP SURF. COND.	S&T	1	50	75	250	250	CS	CS	8500

Table F-12

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE  
EQUIPMENT LIST  
ACID GAS REMOVAL PLANT  
PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM (SCHEM)	HEAD FT	HYDRAULIC HP	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRIVER TYPE	POWER BHP	REMARKS
							286	339	3% NI	3% NI			
G-1	HOT REGENERATOR FEED	CENTRIF	2		286	339	3% NI			MOTOR	410		
G-2	LEAN METHANOL	CENTRIF	2	6300	1670	2350	CS	CI		MOTOR	2940		
G-3	HOT REGENERATOR COND	CENTRIF	2	5	225	0.25	LOW TEMP	CS	LOW TEMP	MOTOR	1.2		
G-4	HOT REGENERATOR REFLUX	CENTRIF	2	301	194	11	CS	CI		MOTOR	25		
G-5	METHANOL/H <sub>2</sub> O REFLUX	CENTRIF	2	50	250	3	CS	CI		MOTOR	10		
G-6	METHANOL MAKEUP	CENTRIF	2	300		4	CS	CI		MOTOR	6		
K-1	RECYCLE COMPRESSOR	RECIP	1			275	LOW TEMP	CS		STM TURB	370	SINGLE STAGE	
K-2	REFRIGERATION COMPRESS	CENTRIF	1			6160	LOW TEMP	CS		STM TURB	8000	MULTIPLE SIDE LOAD	

Table F-13

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

SYNGAS COMPRESSION PLANT  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. TRAYS	DESIGN COND. PRESS PSIG	TEMP. °F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
						SHELL	INTERNAL	DIAM., FT	T-T FT	
C-1	FEED GAS KO DRUM	VERT	1	320	250	CS	316 SS	15	10.5	W/ SS MESH PAD
C-2	COMPRI DISCHARGE KO DRUM	VERT	1	570	250	CS	316 SS	13.5	10	W/ SS MESH PAD



Table F-13

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

SYNGAS COMPRESSION PLANT  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN CONDITIONS			MATERIALS OF CONSTRUCTION			REMARKS		
				PRESS. PSIG	TEMP. F	AREA	SHELL	TUBE	AREA			
E-1	COMPRESSOR AFTER COOLER	AIR	1	N/A	570	N/A	N/A	N/A	CS	CS	10330	FAN BHP=155
E-2	COMPRESSOR TRIM COOLER	S&T	1	570	75	250	CS	CS	CS	CS	7820	
E-3	COMPRESSOR SURFACE COND	S&T	1	50	75	250	CS	CS	CS	CS	14780	

Table F-13

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

SYNGAS COMPRESSION PLANT  
PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM (SCCM) (423000)	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRIVER TYPE	POWER BHP	REMARKS
					HEAD EI	HYDRAULIC HE	ROTATING UNIT	CASE CI			
K-1	SYNGAS COMPRESSOR	CENTRIF	1						STEAM TURBINE	25000	

Table F-14

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

ITEM NO.	EQUIPMENT NAME	TYPE	NO. TRAIN	DESIGN COND. PRESS PSIG	TEMP. F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
						SHELL	INTERNALS	DIAM. I-I	I-I	
C-1	STEAM DRUM	HORIZ	8	700	650	CS	CS	5.5	27	
C-2	FISCHER-TROPSCH REACTOR	VERT	8	460	550	CS	CS	15.75	48	W/9606 TUBES
C-3	WAX FLASH DRUM	HORIZ	1	50	510	CS	CS	5.5	15	
C-4	PRODUCT SEPARATOR	HORIZ	1	450	250	CS	CS	20	63	
C-5	SPENT WAX OFFGAS DRUM	VERT	1	50	250	CS	CS	3	8	
D-1	CATALYST STORAGE BIN	VERT	2	ATM.	250	CS	CS	25	28	W/60 CONE

Table F-14

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

F-T REACTION SECTION  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION ARE TUBEREMARKS			
				PRESS. PSIG	SHELL TUBE	SHELL TUBES	TEMP. F	SHELL	TUBE	AREA	FI2
E-1	REACTOR FEED/FL EXCH	S&T	1	500	460	550	550	CS	CS	111250	
E-2	EFFLUENT AIR COOLER	AIR	1	N/A	460	N/A	350	N/A	CS	48000	710 HP FANS
E-3	EFFLUENT TRM COOLER	S&T	1	460	75	250	250	CS	CS	24200	
E-4	WAX OFF GAS CONDENSER	AIR	1	N/A	50	N/A	500	N/A	CS	60	2 HP FNS
E-5	WAX PRODUCT COOLER	AIR	1	N/A	50	N/A	500	N/A	CS	1300	25 HP FANS

Table F-14

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

F-I REACTION SECTION  
PUMPS AND COMPRESSORS

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM/(SCFM)	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRIVER TYPE	POWER BHP	REMARKS
					HEAD EI	HYDRAULIC HP	HEAD EI	ROTATING UNIT			
G-1	BFW PUMP	CENTRIF	16	1650	70	48	CS	CI	MOTOR	60	
G-2	WAX PRODUCT PUMP	CENTRIF	2	442	110	17	CS	CI	MOTOR	22	
G-3	WAX CONDENSATE PUMP	CENTRIF	2	5	2000	1	CS	CI	MOTOR	7	
K-1	OFFGAS COMPRESSOR	RECP	1						MOTOR	10	

Table F-15

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

F-I GAS PLANT  
VESSELS, DRUMS & TANKS

ITEM NO.	EQUIPMENT NAME	TYPE	NO. FEED TRAYS	DESIGN COND. PRESS PSIG	TEMP. °F	MATERIALS OF CONSTRUCTION		DIMENSIONS		REMARKS
						SHELL	INTERIALS	DIAM. EI	H I-I	
C-1	DEETHANIZER-TOP	VERT	1	450	450	CS	410 SS	5.5	101	40 VALVE TRAYS
C-2	DEETHANIZER REFLUX DRUM	HORIZ	1	450	250	CS	304 SS	3	12	W/ SS MESH PAD
C-3	STABILIZER	VERT	1	100	400	CS	410 SS	4	84	34 VALVE TRAYS
C-4	STABILIZER REFLUX DRUM	HORIZ	1	100	250	CS	304 SS	3.5	13.5	W/ SS MESH PAD
C-5	RECYCLE GAS KO DRUM	VERT	1	550	250	LTCS	CS	7.5	15	W/ SS MESH PAD
C-6	PROPYLENE ACCUMULATOR	HORIZ	1	250	250	LTCS	304 SS	5.5	19.5	
C-7	LOW LEVEL PROPYL KO DRUM	HORIZ	1	150	250/-50	LTCS	304 SS	6	21	W/ SS MESH PAD
C-8	HI LEVEL PROPYL KO DRUM	HORIZ	1	150	250/-50	LTCS	304 SS	5	18	W/ SS MESH PAD

Table F-15

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

F-I GAS PLANT  
HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION ARE TUBE REMARKS			
				PRESS. PSIG	SHELL TUBE	SHELL TUBES	TEMP. F	SHELL	TUBE	AREA	ET2
E-1	RECYCLE COMP AFTER COOLER	AIR	1	N/A	575	N/A	250	N/A	304 SS	10800	FAN BHP=307
E-2	RECYCLE COMP TRIM COOLER	S&T	1	575	75	250	250	304 SS	304 SS	15540	
E-3	DEETHANIZER CONDENSER	S&T	1	440	150	250	250	CS	CS	1190	
E-4	DEETHANIZER REBOILER	S&T	1	440	650	440	525	CS	CS	1340	
E-5	DEETHANIZER SIDE REBOILER	S&T	1	440	440	440	300	CS	CS	1050	
F-6	STABILIZER REBOILER	S&T	1	100	650	400	525	CS	CS	410	
E-7	STABILIZER CONDENSER	S&T	1	100	75	250	250	304 SS	304 SS	4570	FAN BHP=22
E-8	STABILIZER BOTTOM COOLER	AIR	1	N/A	120	N/A	400	N/A	CS	1515	
E-9	FEED-OFF GAS EXCH	S&T	1	525	500	250	250/-50	CS	CS/LTCS	100950	
E-10	FEED LIQUID EXCH	S&T	1	525	500	250	250/-50	CS	CS/LTCS	1360	
E-11	RECYCLE GAS CHILLER	S&T	1	150	525	250/-50	250/-50	LTCS	LTCS	15220	
E-12	PROPYLENE DESUPERHEATER	S&T	1	300	75	250	250	CS	CS	2560	
E-13	PROPYLENE CONDENSER	S&T	1	300	75	250	250	CS	CS	13500	
E-14	RECYCLE COMP SURF. COND.	S&T	1	50	75	250	250	CS	CS	17400	
E-15	REFRIG. COMP SURF. COND.	S&T	1	50	75	250	250	CS	CS	2315	

Table F-15

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE

ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM(SCFM)	HEAD FT	HYDRAULIC HP	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRIVER TYPE	POWER HP	REMARKS
							EL	HP	CASE	ROTATING UNIT			
G-1	DEETHANIZER REFLUX	CENTRIF	2	58	216	1.5	CS	CI	MOTOR	4			
G-2	STABILIZER REFLUX	CENTRIF	2	116	186	2.9	CS	CI	MOTOR	5			
G-3	STABILIZER BOTTOMS	CENTRIF	2	348	90	4.1	CS	CI	MOTOR	6			
K-1	RECYCLE COMPRESSOR	CENTRIF	2	(33000)			CS	CI	STM TURB	29400			
K-2	REFRIGERATION COMPRESSOR	CENTRIF	2				LTCS	CI	STM TURB	3600			
K-3	WAX OFF GAS COMPRESSOR	RECIP	1				CS	CI	MOTOR	100			



Table F-16

**SLURRY REACTOR DESIGN STUDIES**  
**FIXED BED REACTOR CASE**  
EQUIPMENT LIST  
CO2 REMOVAL PLANT

**VESSELS, DRUMS & TANKS**

ITEM NO.	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN COND. PRESS	COND. TEMP. °F	MATERIAL OF CONSTRUCTION	DIMENSIONS		REMARKS
							DIAM. I-I	H I-I	
C-1	FEED GAS KO DRUM	VERT	1	400	250	CS	15	9	
C-2	ABSORBER	VERT	1	400	250	CS	15	74	
C-3	TREATED GAS KO DRUM	VERT	1	400	250	CS	13	8.5	MIST ELIM
C-4	RICH SOLUTION FLASH DRUM	HORIZ	1	50	250	SS	5.5	17	
C-5	REGENERATOR	VERT	1	50	350	CS W/SS CLAD 304SS PACKING TOP	14.5	75	2" PALL RINGS
C-6	REGENERATOR OVERHEAD RECEIVER	VERT	1	50	250	CS W/SS CLAD 316 SS MESH	5	8	MIST ELIM
D-1	SOLUTION STORAGE TANK	VERT	1	ATM	250	CS			1500 BBLs

Table F-16

SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE  
EQUIPMENT LIST  
CO2 REMOVAL PLANT

HEAT EXCHANGERS

ITEM NO	EQUIPMENT NAME	TYPE	NO. PER TRAIN	DESIGN CONDITIONS				MATERIALS OF CONSTRUCTION			REMARKS
				SHELL PRESS, PSIG	SHELL TEMP, F	TUBE PRESS, PSIG	TUBE TEMP, F	SHELL	TUBE	AREA, FT <sup>2</sup>	
E-1	LEAN SOLUTION COOLER	S&T	1	400	75	250	250	CS	CS	5900	
E-2	LEAN SOLUTION AIR COOLER	AIR	1	N/A	400	250	250	N/A	CS	4830	FAN BHP=133
E-3	LEANRICH EXCHANGER	S&T	1	50	400	250	250	CS	CS	22900	
E-4	REGEN OVHD CONDENSER	AIR	1	N/A	50	250	250	N/A	304SS	16500	FAN BHP=95
E-5	REGENERATOR REBOLER	KETTLE	1	50	75	350	400	304SS	304SS	9930	
E-6	RECLAIMER	KETTLE	1	50	250	650	650	304SS	304SS	7000	

Table F-16

**SLURRY REACTOR DESIGN STUDIES  
FIXED BED REACTOR CASE  
EQUIPMENT LIST  
CO<sub>2</sub> REMOVAL PLANT**

**PUMPS AND COMPRESSORS**

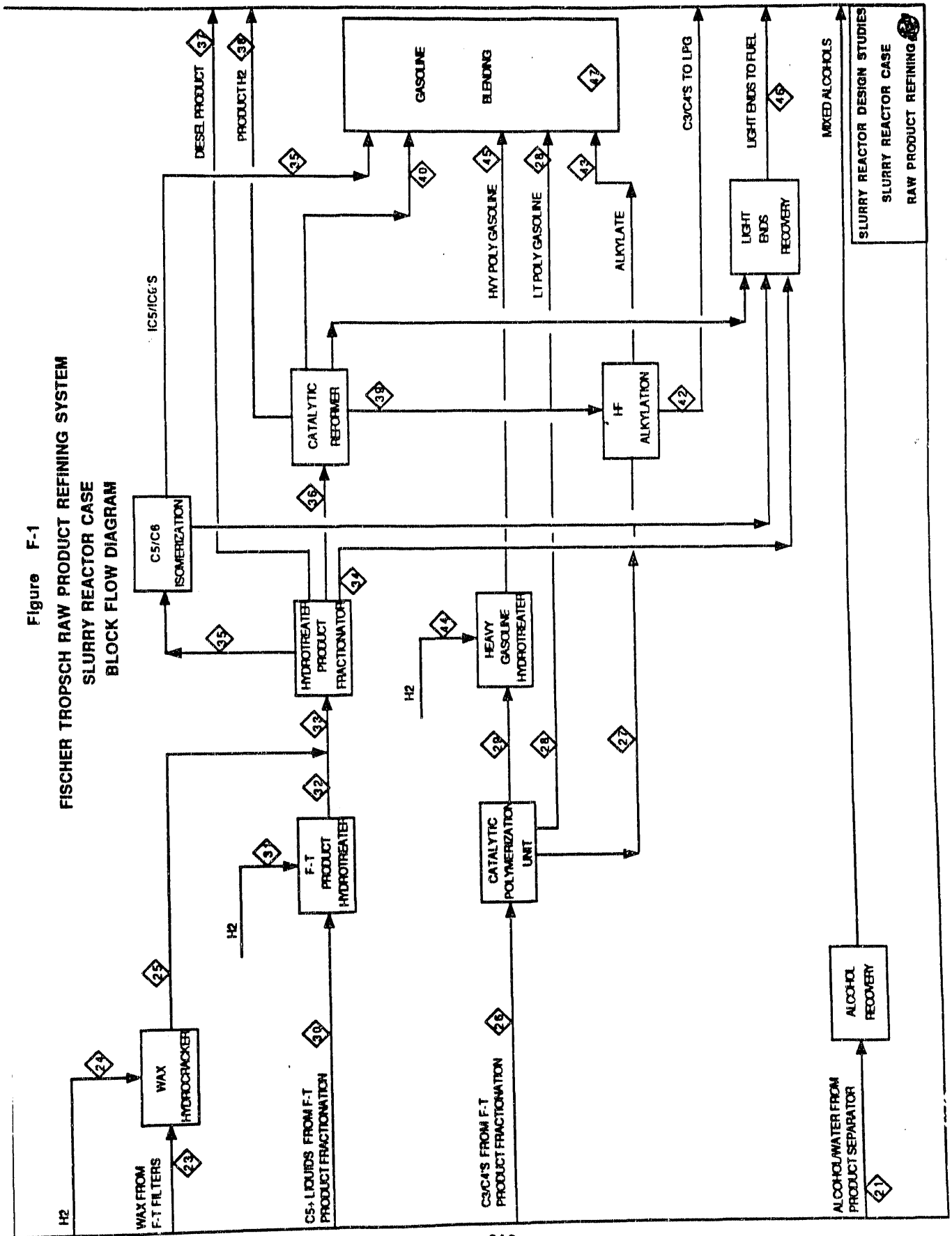
ITEM NO.	EQUIPMENT NAME	TYPE	NO PER TRAIN	FLOW GPM/SCHEM	HEAD FT	HYDRAULIC HP	DESIGN CONDITIONS		MATERIALS OF CONSTRUCTION		DRIVER	BHP
							EL	40	CASE	ROTATING UNIT		
G-1	LEAN SOLUTION PUMP	CENTRIF	2	1440	110	40	CS	CS	CI	MOTOR	50	
G-2	LEAN SOLUTION BOOSTER PUMP	CENTRIF	2	1520	875	650	CS	CS	SS	MOTOR	400	
G-3	REGENERATOR REFUX	CENTRIF	2	60	134	2	CS	CS	SS	MOTOR	3	

Table F-17

**SURRY REACTOR DESIGN STUDIES  
FISCHER-TROPSCH FIXED BED REACTOR CASE  
UTILITY SUMMARY**

PLANT DESCRIPTION NO	B.L.C. PWR KW	HIGH PR				STEAM, M LB/HR				WATER, GPM			FUEL, MBTU/HR
		700 F PSG	424(SAT) PSG	307 PSG	200 PSG	476(SAT) PSG	424(SAT) PSG	302(SAT) PSG	297(SAT) PSG	200 PSI COND	50 COND	50 COND	
<b>GAS PREP. AND SYNTHESIS</b>													
101 SHELL GASIFIER	670	(782.8)	21.8	535.1	(75.8)	133	3010						
102 SHIFT CONVERSION													
103 COG HYDROLYSIS	127	145.4			87.8 (87.8)	1034	3170						
104 GAS COMPRESSION	123				141.3 (157.4)	7	20280						
105 SOUR WATER STRIPPING	2836	82.9			16.1 (37.6)								40.4
106 ACID GAS REMOVAL	1148		2.4		65.4 (65.4)	122							
107 SULFUR RECOVERY & TOT													
108 SULFUR POLISHING	686			(1014.0)	171.6 (171.6)	2069	3910						(514.1)
109 F.T SYNTHESIS	1050						8360						
110 CO2 REMOVAL	156						1340						69.6
111 DEHYDRATION	388	193.1	25.1		(25.1)		15873						
112 F.T GAS PLANT													
113 H2 RECOVERY													
<b>F.I. PRODUCT REFINING</b>													
200 ALCOHOL RECOVERY	0		0.0		0.0		0						8.5
201 F.T PRODUCT HTU	127		0.0		0.0		217						52.4
202 HTU PROD FRACT.	737		74.1		1.6 (75.7)		88						18.8
203 CAT REFORMER	218		13.3		(13.3)								1.7
204 C5/C6 ISOMERIZATION	392		0.0		79.8		170						
205 CAT POLYMERIZATION	103		13.3		(13.3)		116						
206 HF ALKYLATION	122		5.5		2.6 (6.1)		339						0.2
207 HVT GASOLINE HTU	30		1.0		(1.0)		18						(65.7)
208 LT ENDG RECOVERY	753		0.0		7.7		628						
209 H2 PURIFICATION	345		0.0		(0.0)		50						
210 WAX HYDROCRACKING	856		6.7		3.0 (9.7)		242						48.4
<b>CEPESITE UNITS</b>							135505						
300 OXYGEN PLANT	1703	695.5	80.0										
301 INSTRUMENT/PLANT AIR													
302 COAL HANDLING	15981		67.1										
303 POWER DISTRIBUTION	1800												
304 BFW PREPARATION													
305 COOLING WATER TREATMENT													
306 CW TOWER	8232		485.7 (80.0)		(197.4)								1231.7
307 FOWMGEN	(42232)												
308 WW TREATMENT	3326												
309 BLOWDOWN													
310 STORAGE													
311 INTERCOOL PIPING													
312 REFRIGERATION													
313 GASOLINE BLENDING	50												
MISCELLANEOUS	280												
TOTAL	0	809.9	0.0	32.9 (478.9)	66.0 (717.1)	2902	1750 204265						55.7 891.9

Figure F-1  
 FISCHER TROPSCH RAW PRODUCT REFINING SYSTEM  
 SLURRY REACTOR CASE  
 BLOCK FLOW DIAGRAM



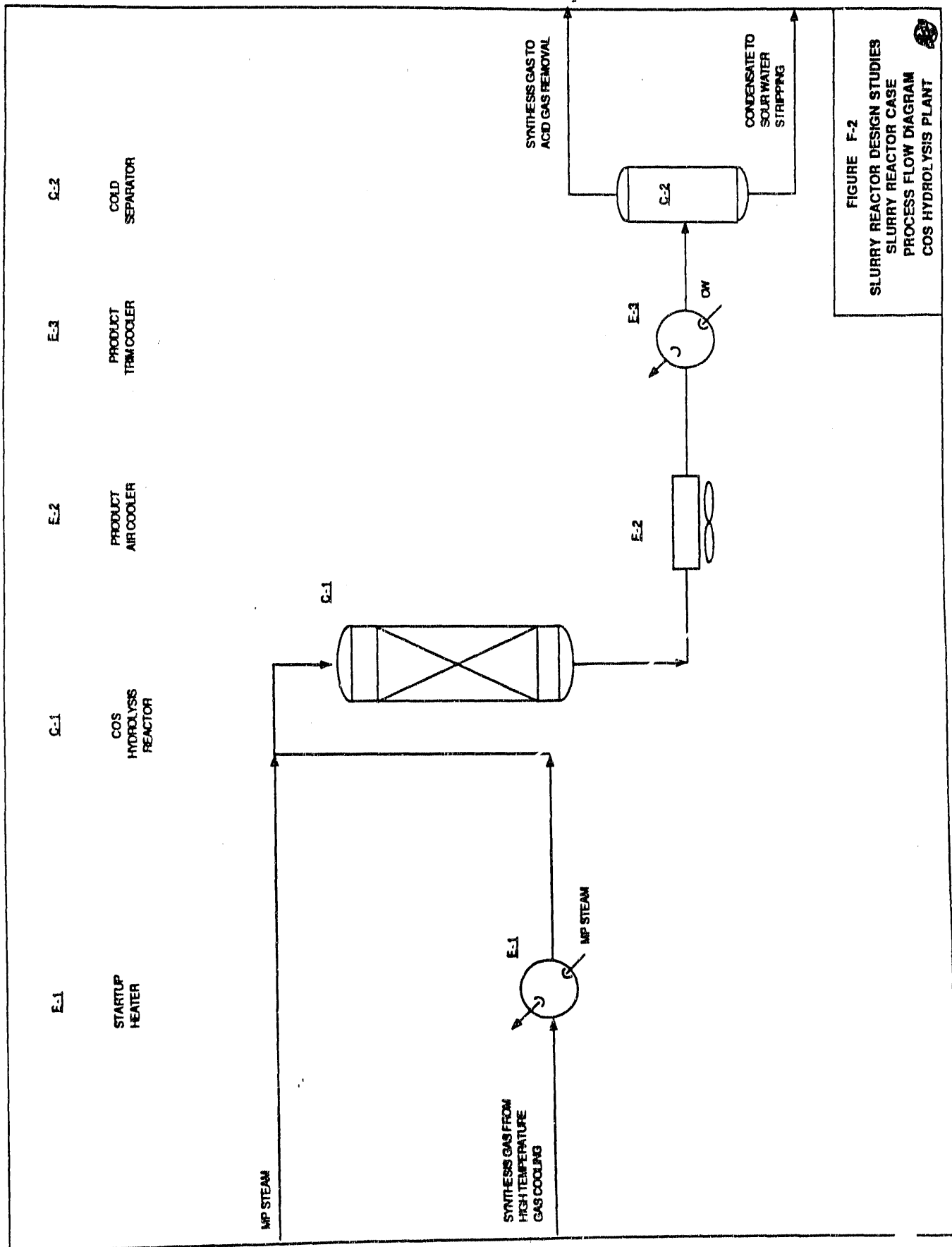


FIGURE F-2  
 SLURRY REACTOR DESIGN STUDIES  
 SLURRY REACTOR CASE  
 PROCESS FLOW DIAGRAM  
 COS HYDROLYSIS PLANT

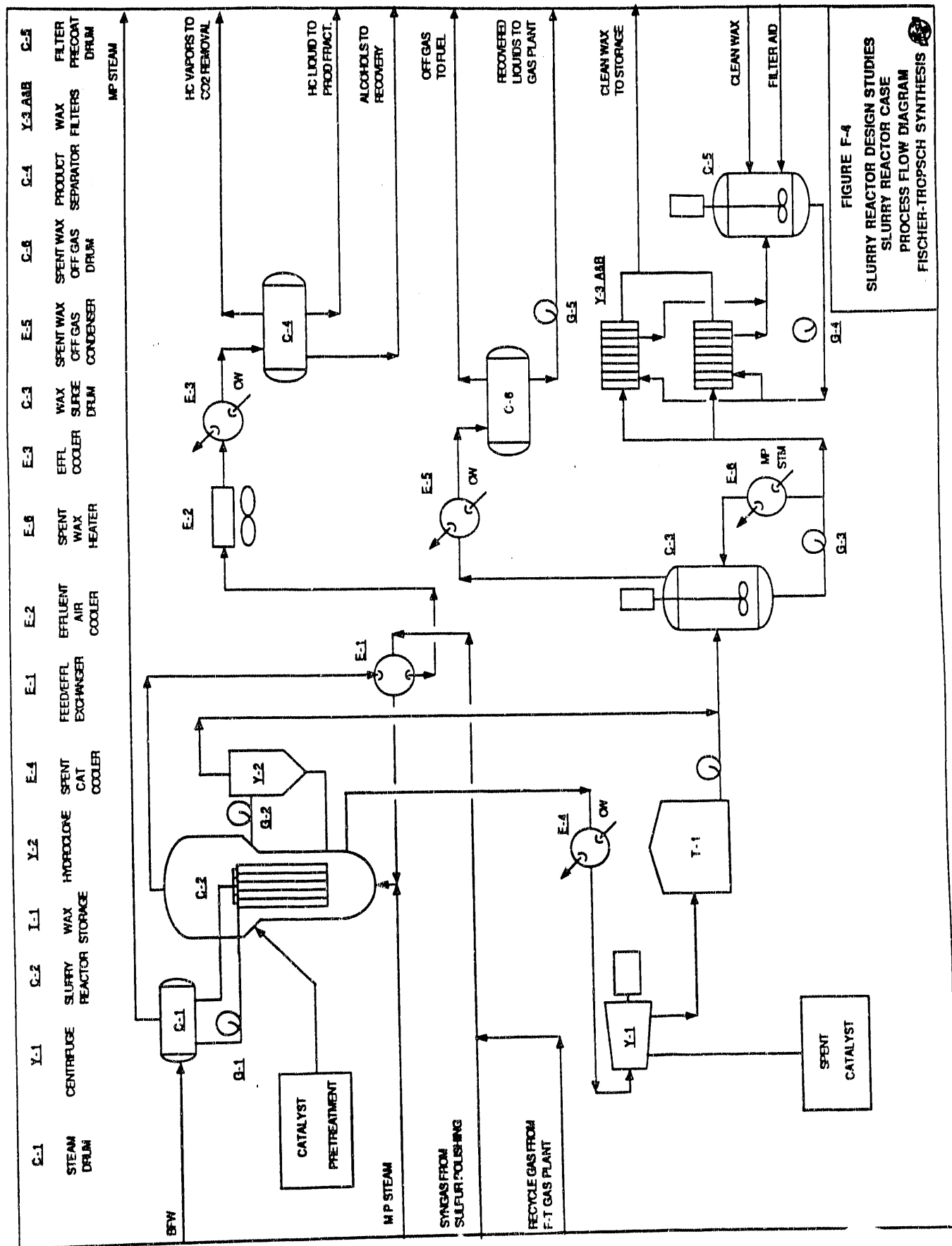
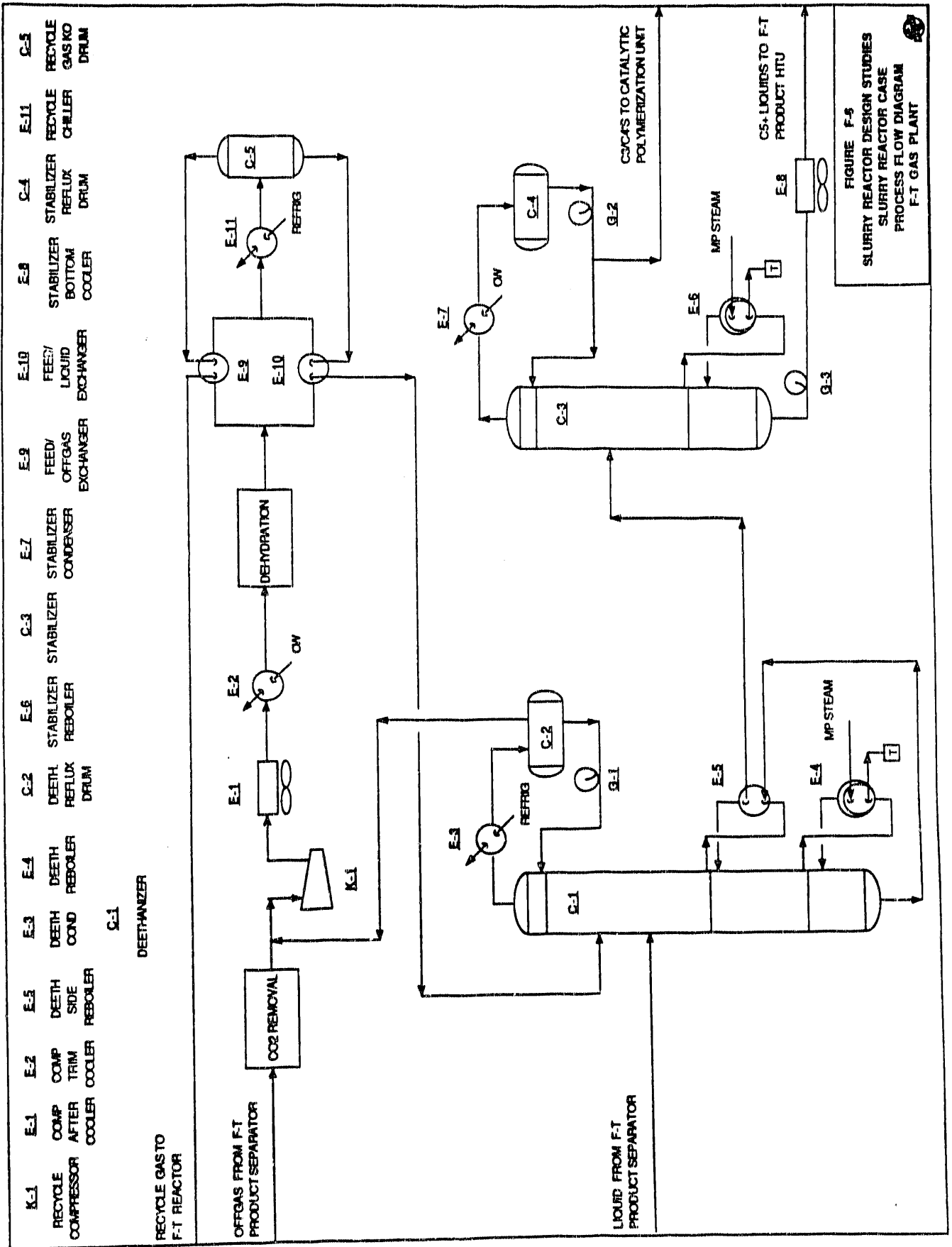


FIGURE F-4  
 SLURRY REACTOR DESIGN STUDIES  
 SLURRY REACTOR CASE  
 PROCESS FLOW DIAGRAM  
 FISCHER-TROPSCH SYNTHESIS







K-1	E-1	E-2	E-3	E-4	C-2	E-6	E-7	E-9	E-10	E-8	C-4	E-11	C-5
RECYCLE COMPRESSOR AFTER COOLER	COMP AFTER TRIM COOLER	COMP TRIM COOLER	DEETH COND	DEETH REBOILER	DEETH REFLUX DRUM	STABILIZER REBOILER	STABILIZER CONDENSER	FEED OFFGAS EXCHANGER	FEED LIQUID EXCHANGER	STABILIZER BOTTOM COOLER	STABILIZER REFLUX DRUM	REFRIG CHILLER	RECYCLE GAS/KO DRUM

C-1  
DEETHANIZER

RECYCLE GAS TO F-T REACTOR

OFFGAS FROM F-T PRODUCT SEPARATOR

LIQUID FROM F-T PRODUCT SEPARATOR

C3/C4/S TO CATALYTIC POLYMERIZATION UNIT

C5+ LIQUIDS TO F-T PRODUCT HTU

FIGURE F-5  
SLURRY REACTOR DESIGN STUDIES  
SLURRY REACTOR CASE  
PROCESS FLOW DIAGRAM  
F-T GAS PLANT

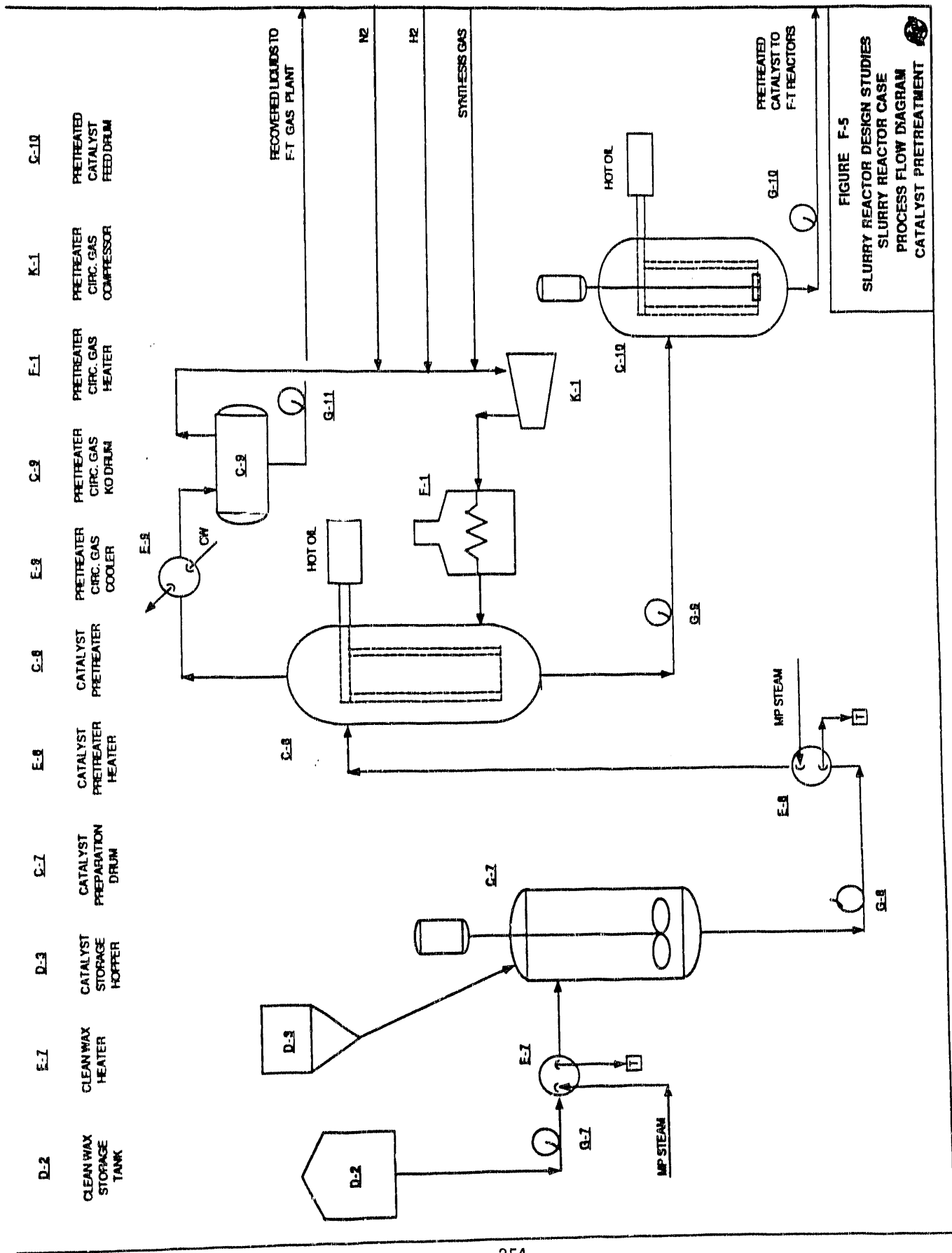
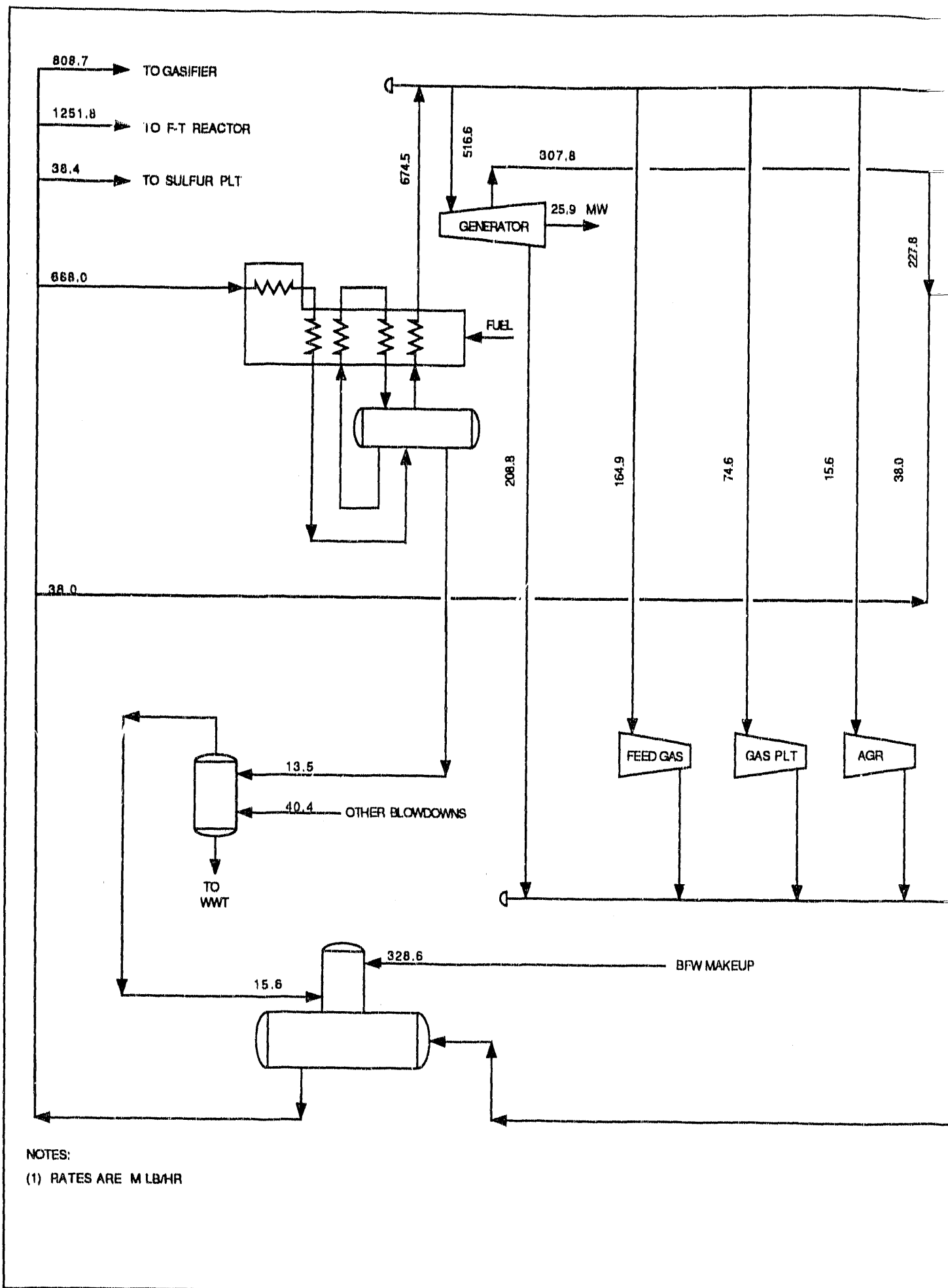
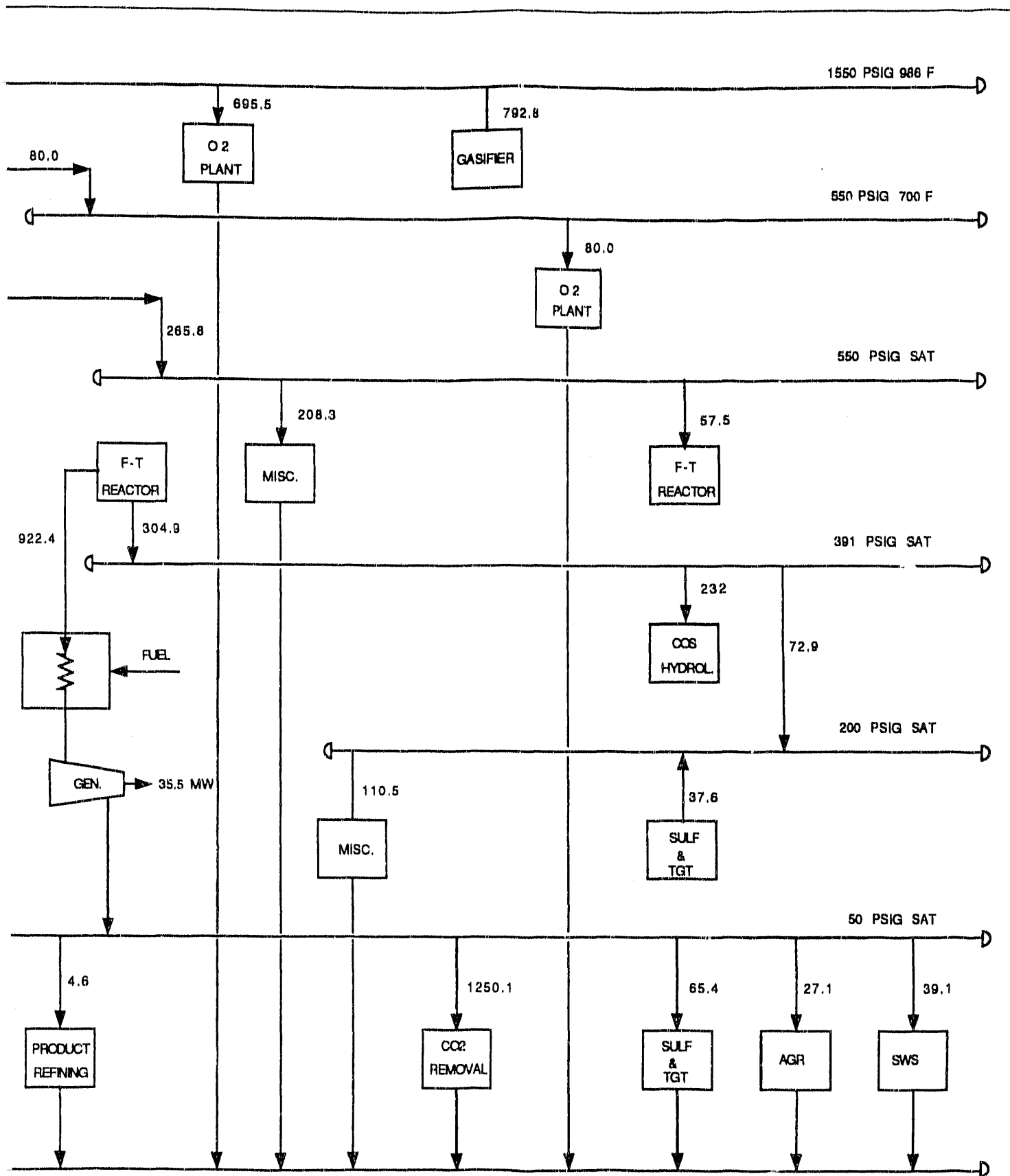


FIGURE F-5  
 SLURRY REACTOR DESIGN STUDIES  
 SLURRY REACTOR CASE  
 PROCESS FLOW DIAGRAM  
 CATALYST PRETREATMENT





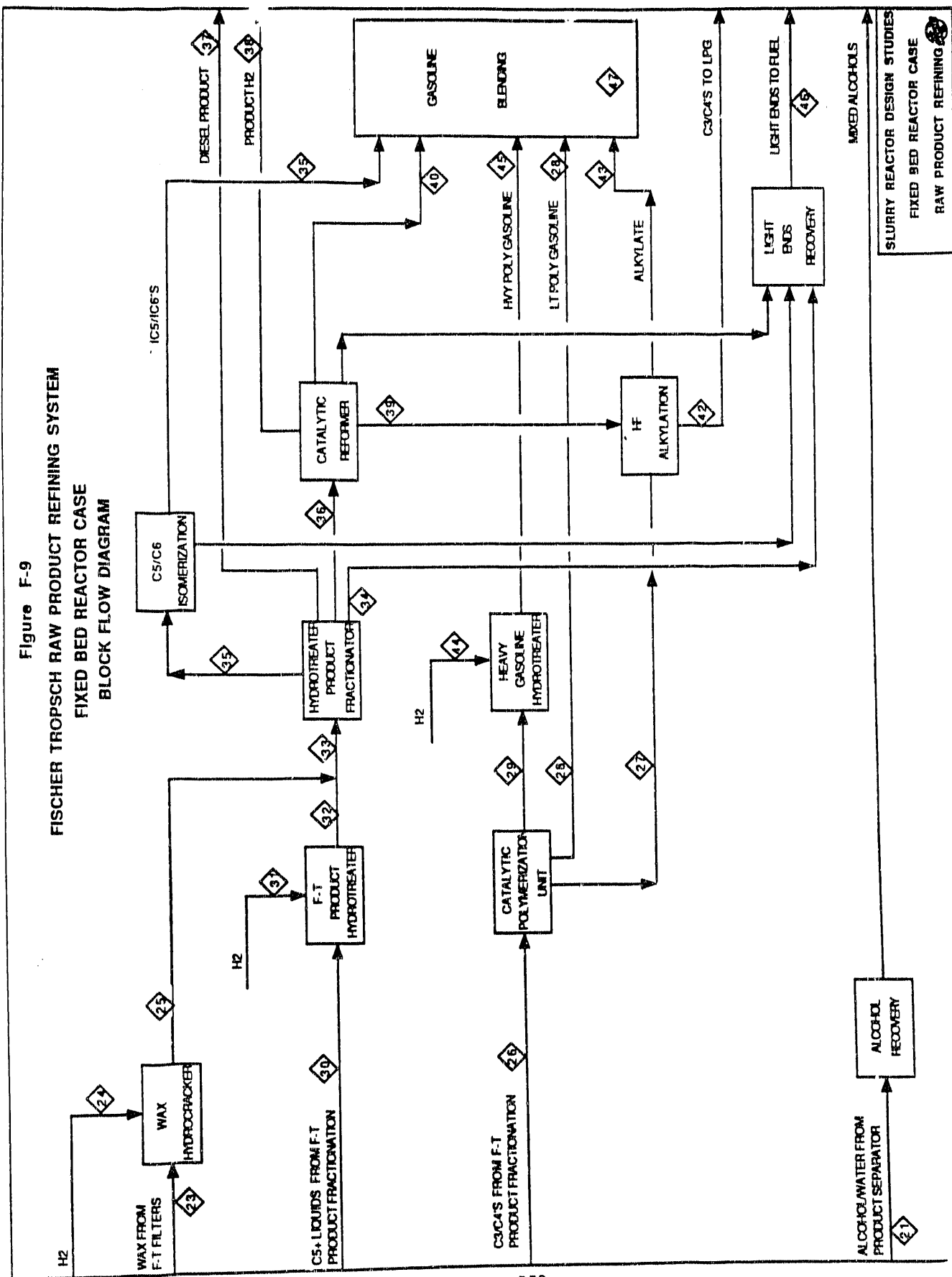
NOTES:  
 (1) RATES ARE M LB/HR



**FIGURE F-8**  
**SLURRY REACTOR DESIGN STUDIES**  
**SLURRY REACTOR CASE**  
**STEAM DIAGRAM**



Figure F-9  
 FISCHER TROPSCH RAW PRODUCT REFINING SYSTEM  
 FIXED BED REACTOR CASE  
 BLOCK FLOW DIAGRAM



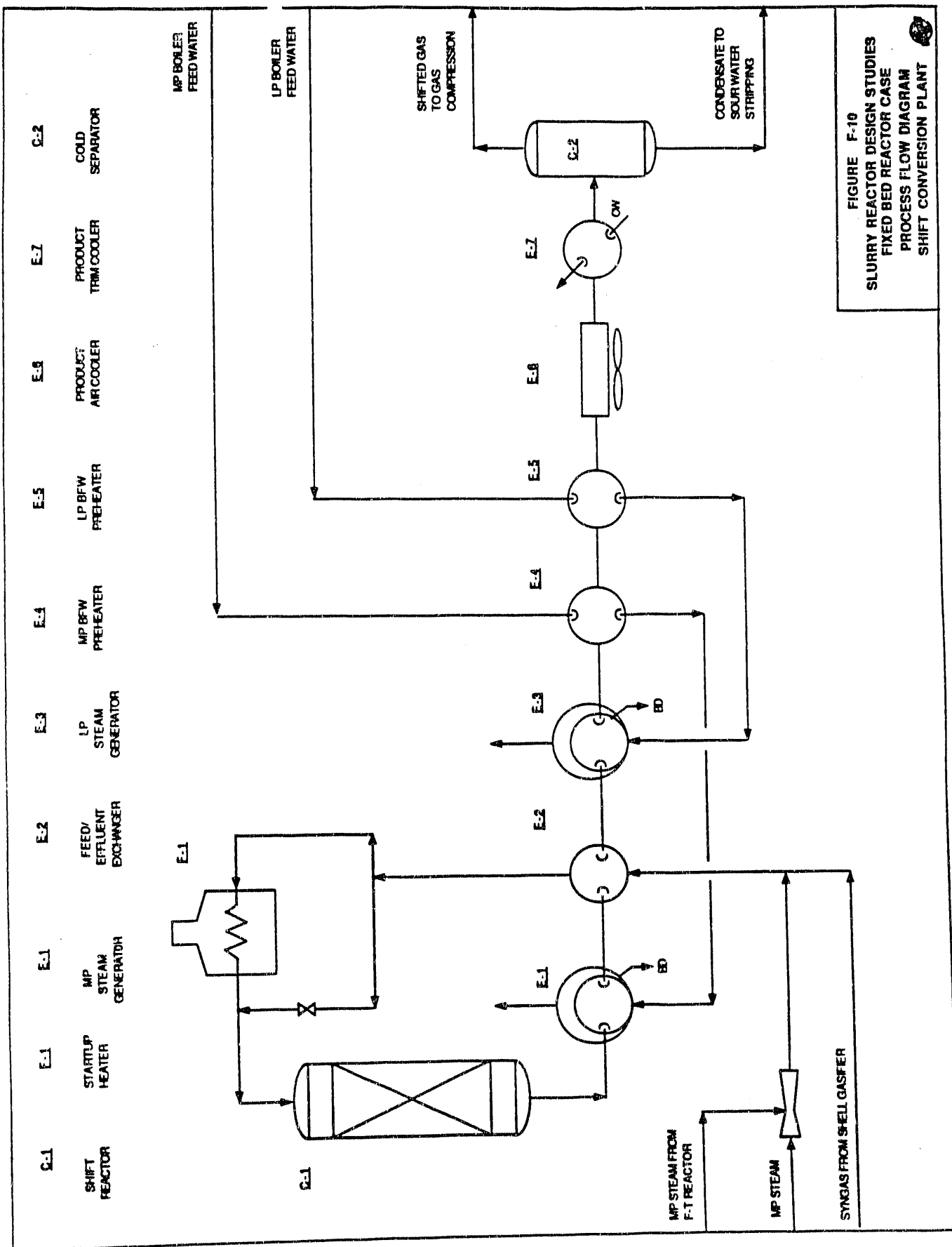
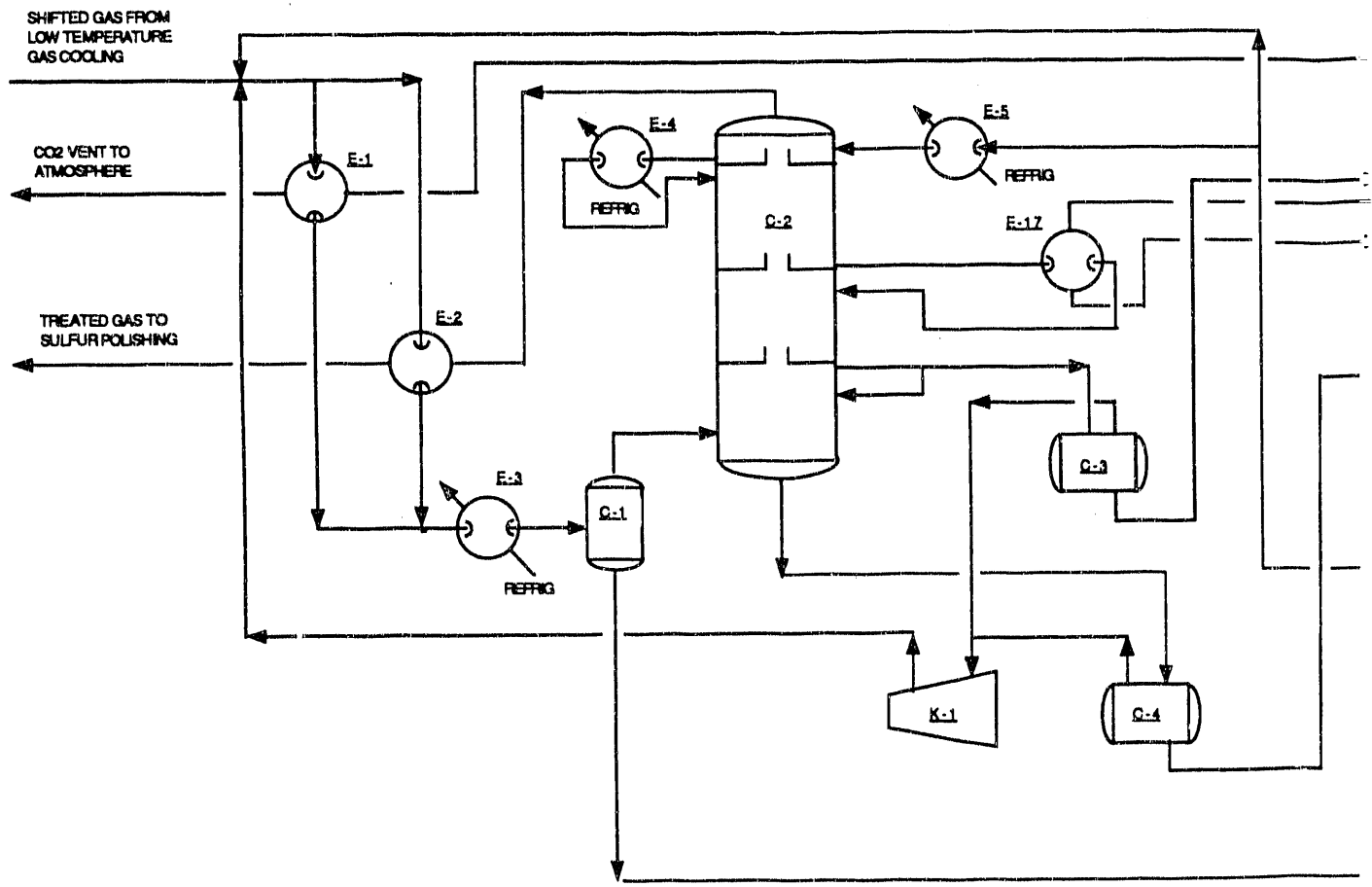


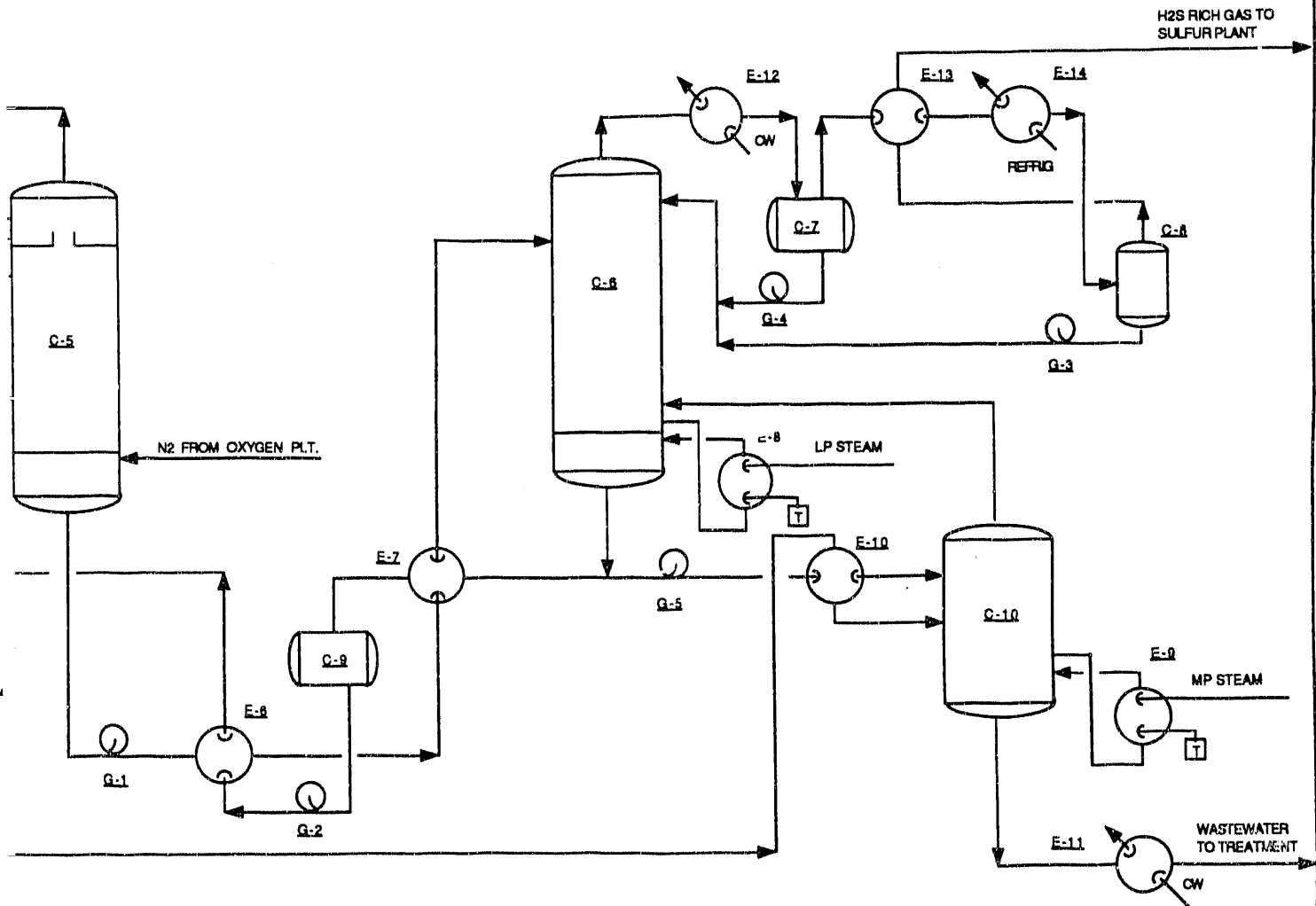
FIGURE F-10  
 SLURRY REACTOR DESIGN STUDIES  
 FIXED BED REACTOR CASE  
 PROCESS FLOW DIAGRAM  
 SHIFT CONVERSION PLANT

E-1	E-2	E-3	E-4	C-2	E-5	Q-4
FEED GAS/ CO2 VENT	FEED GAS/ TREATED GAS	FEED GAS CHILLER	ABSORBER INTERCOOLER	ABSORBER	LEAN METHANOL CHILLER	H2S RICH FLASH DRUM
		Q-1		K-1	Q-3	E-17
		FEED GAS SEPARATOR		RECYCLE COMPRESSOR	CO2 RICH FLASH DRUM	ABSORBER INTERCOOLER





Q-5	E-6	E-7	E-12	Q-7	E-13	E-14	E-9
CONCENTRATION COLUMN	HOT REGEN FEED/BOTTOMS	HOT REGEN FEED/BOTTOMS	HOT REGEN CONDENSER	HOT REGEN REFLUX DRUM	H2S REHEAT EXCHANGER	HOT REGEN OVER-HEAD CHILLER	METHANOL/H2O REBOILER
	Q-8	Q-8	E-8	E-10	Q-10	Q-8	E-11
	METHANOL SURGE DRUM	HOT REGENERATOR	HOT REGEN REBOILER	METHANOL/H2O FEED/REFLUX	METHANOL/H2O COLUMN	CONDENSATE DRUM	METHANOL/H2O BOTTOM COOLER



**FIGURE F-11**  
**SLURRY REACTOR DESIGN STUDIES**  
**FIXED BED REACTOR CASE**  
**PROCESS FLOW DIAGRAM**  
**ACID GAS REMOVAL PLANT**



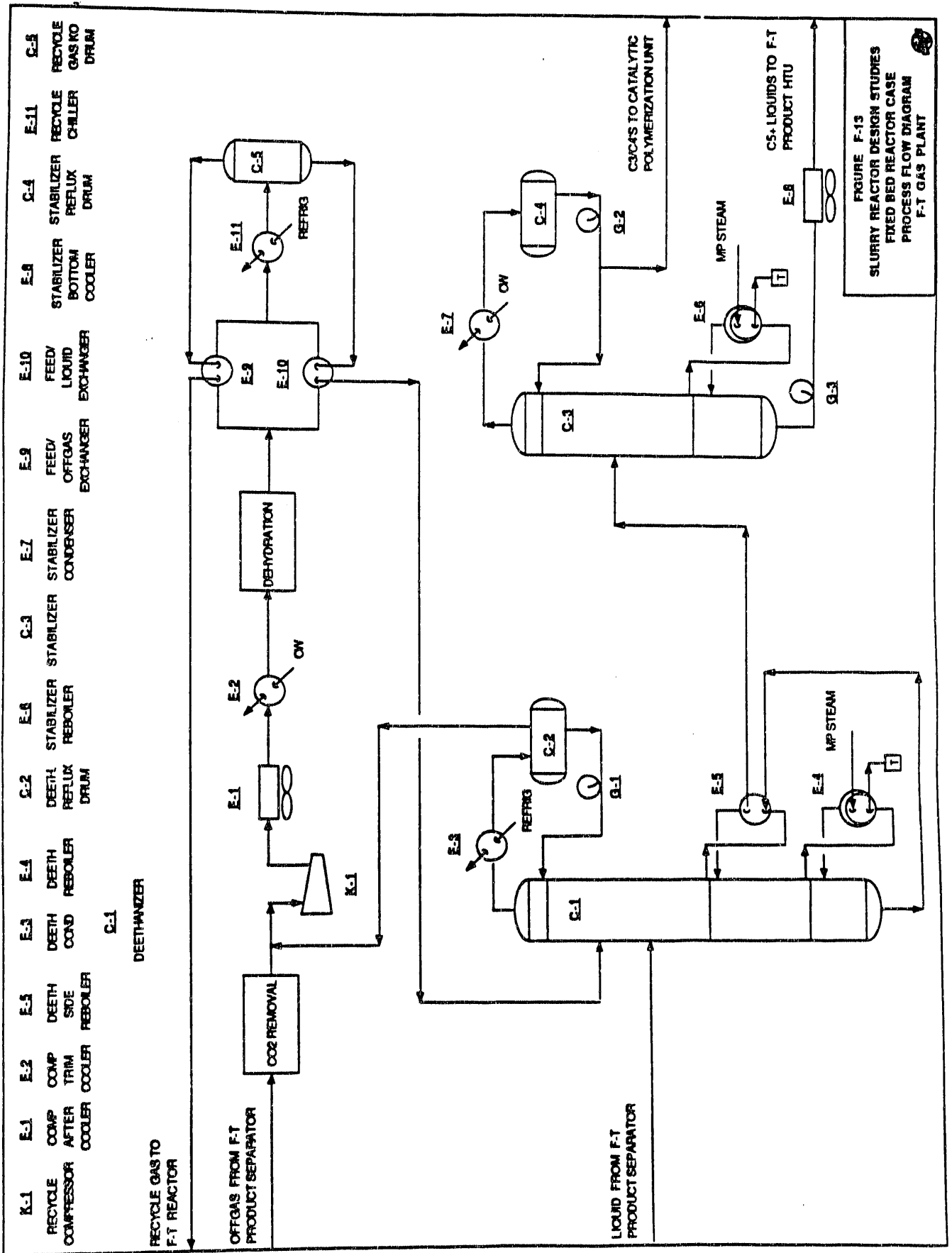


FIGURE F-13  
 SLURRY REACTOR DESIGN STUDIES  
 FIXED BED REACTOR CASE  
 PROCESS FLOW DIAGRAM  
 F-T GAS PLANT

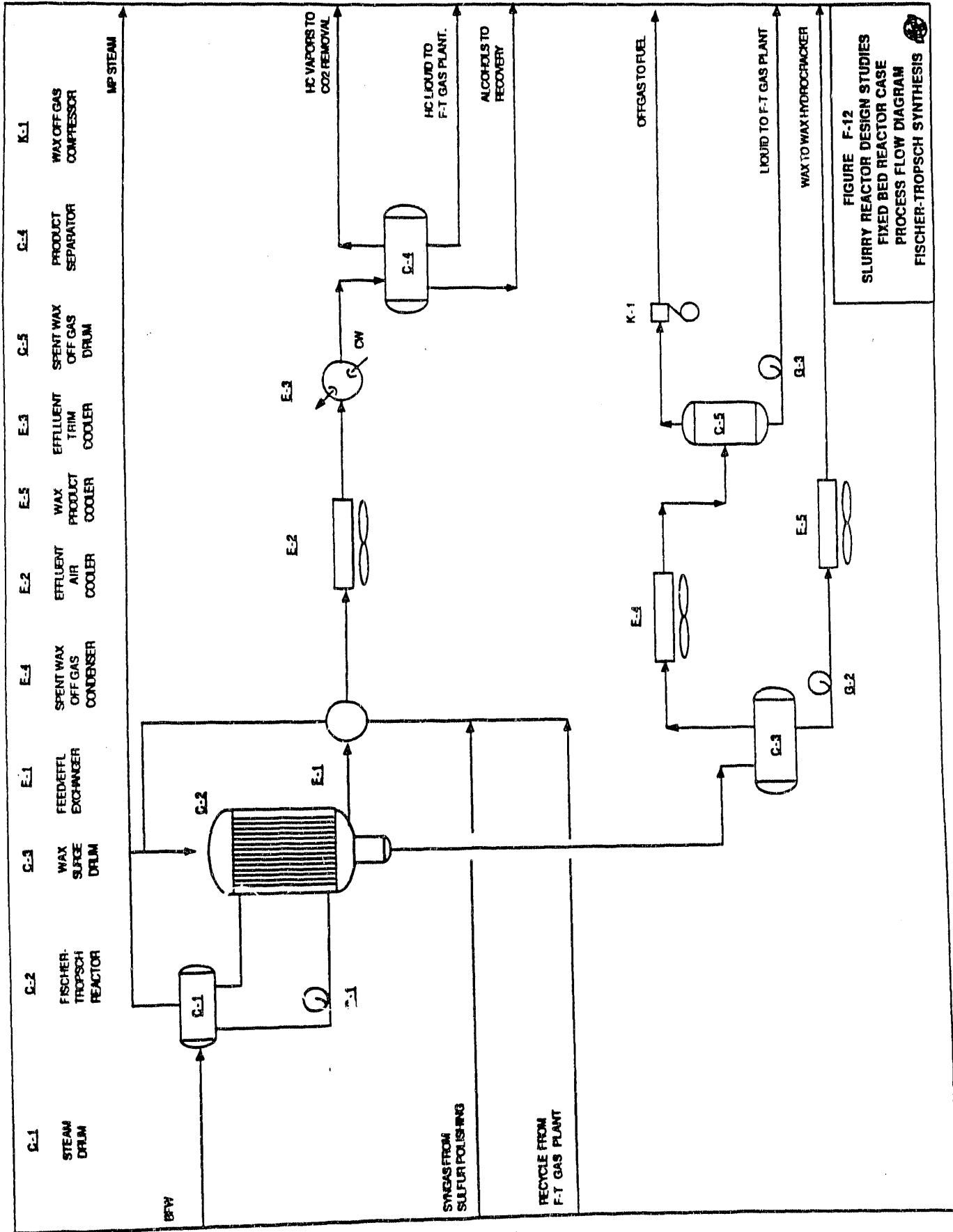
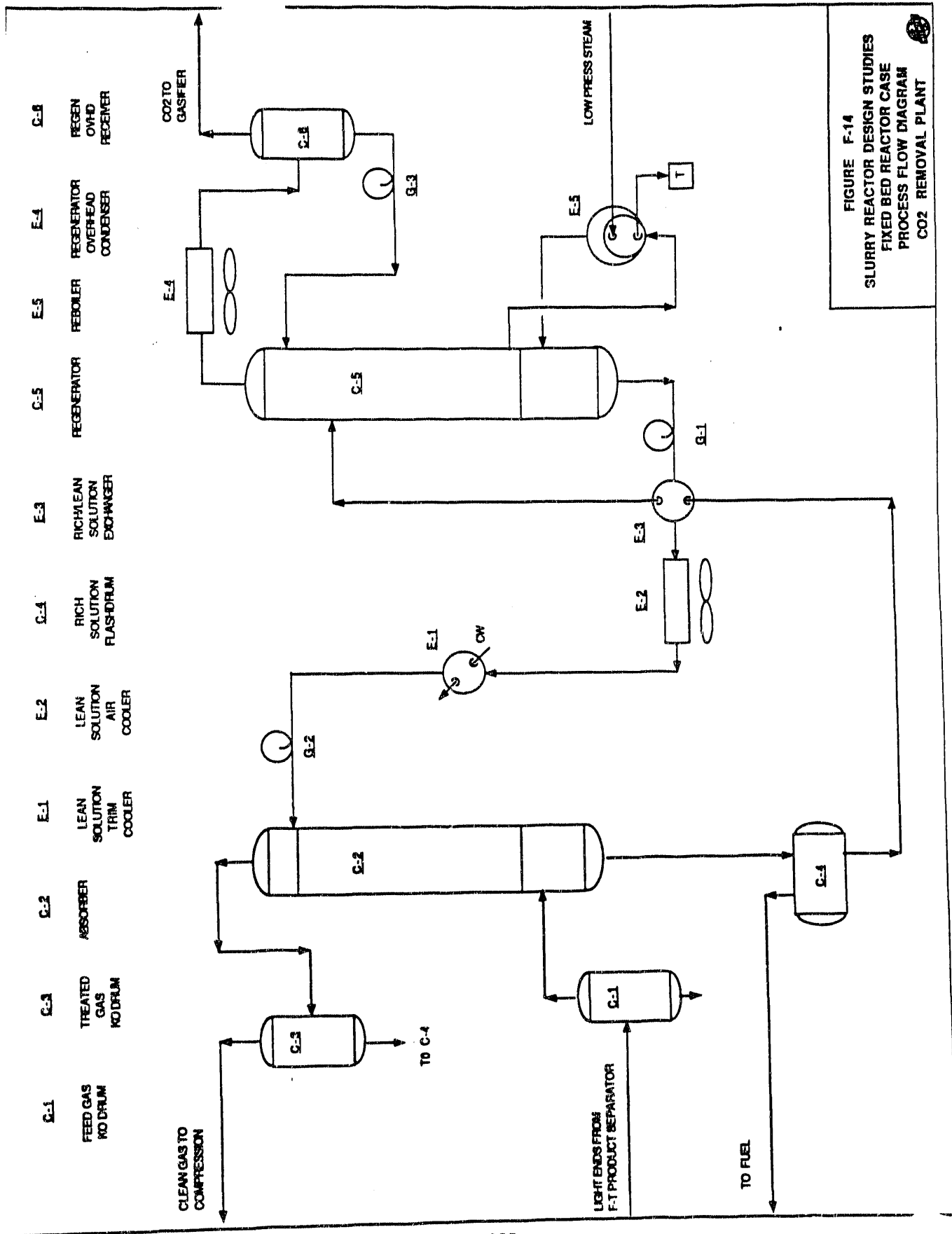
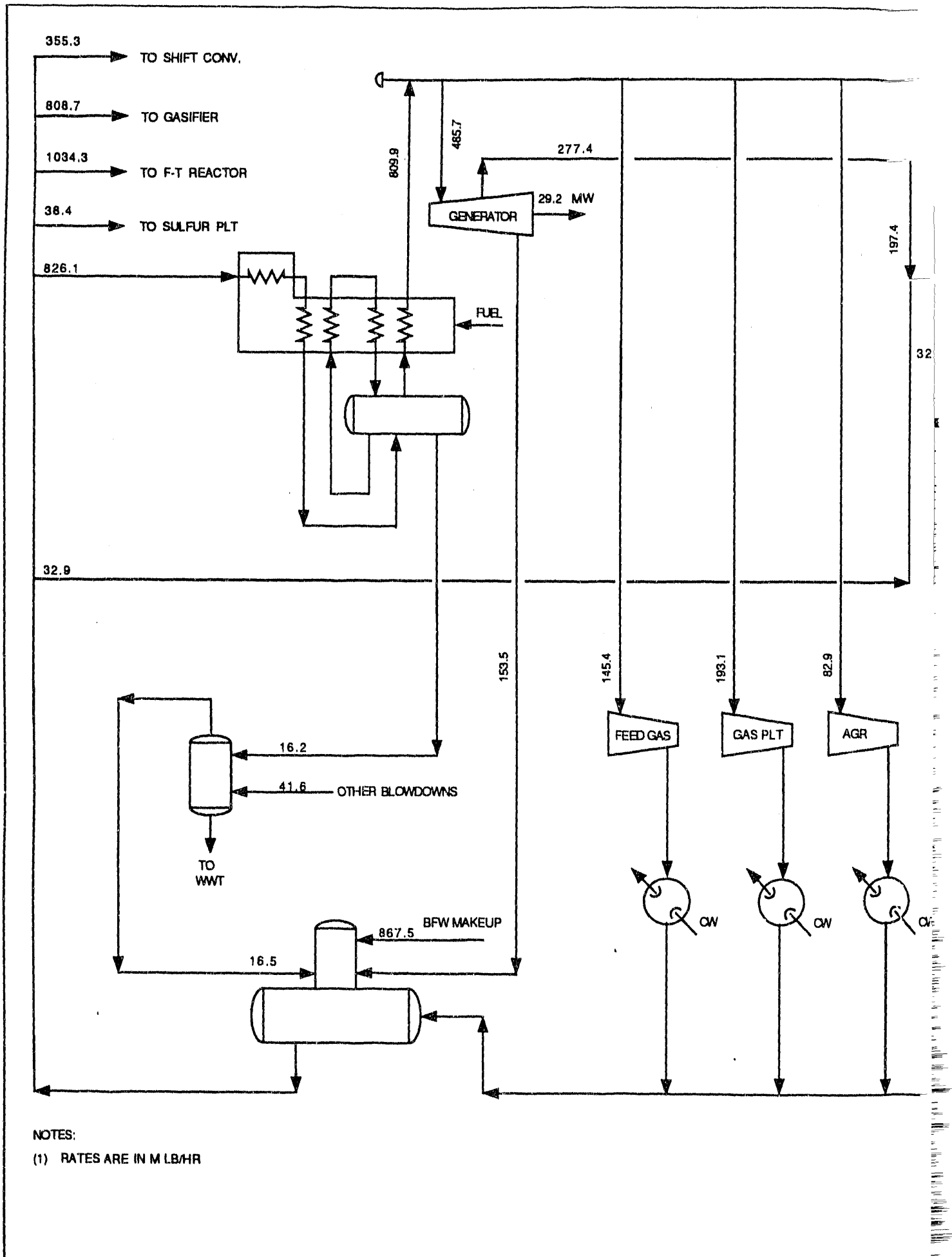


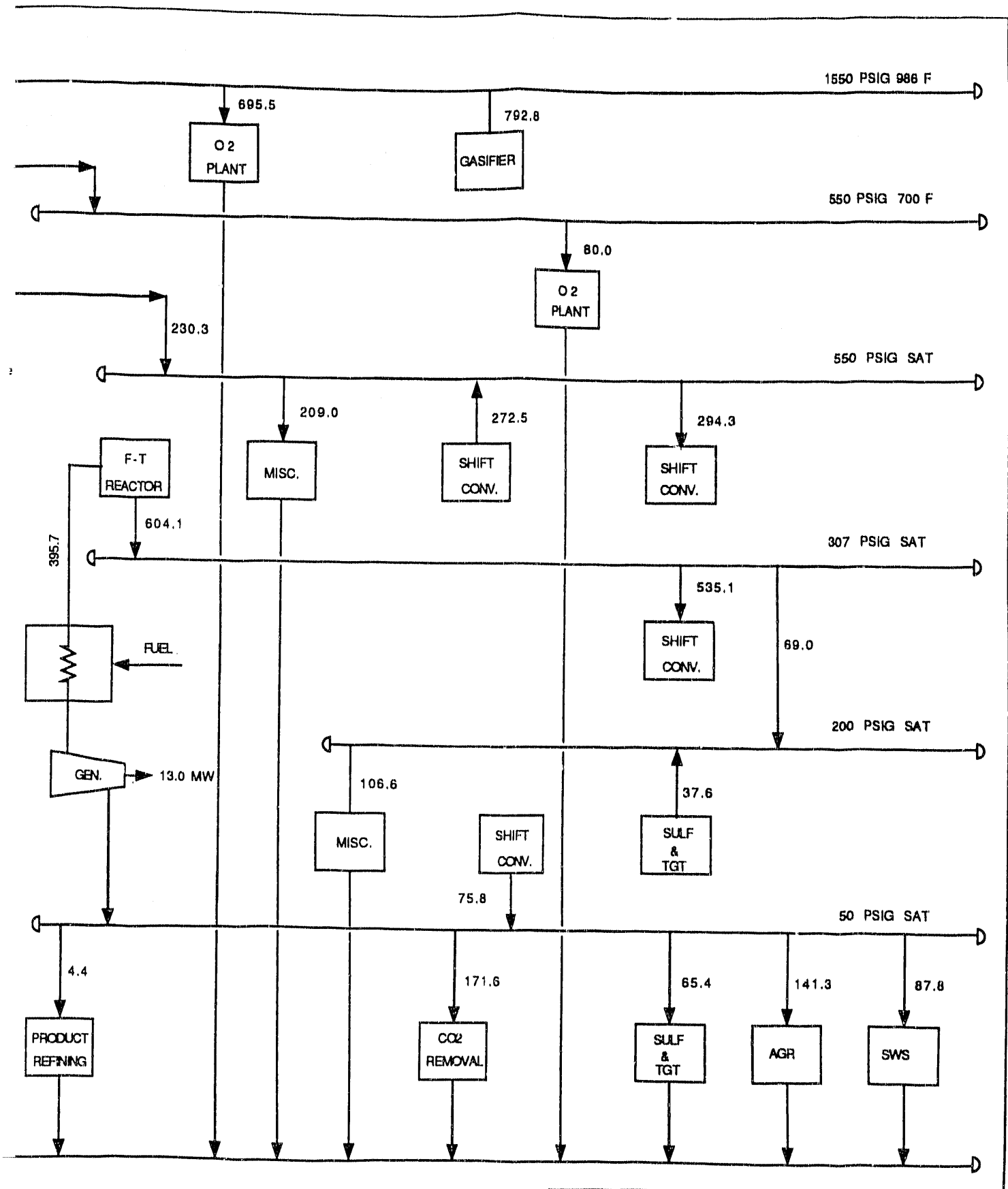
FIGURE F-12  
 SLURRY REACTOR DESIGN STUDIES  
 FIXED BED REACTOR CASE  
 PROCESS FLOW DIAGRAM  
 FISCHER-TROPSCH SYNTHESIS





NOTES:

(1) RATES ARE IN M LB/HR



**FIGURE F-15**  
**SLURRY REACTOR DESIGN STUDIES**  
**FIXED BED REACTOR CASE**  
**STEAM DIAGRAM**



## INSERT

### SLURRY REACTOR DESIGN STUDIES CONTRACT NO. DE-AC22-89PC89867

#### ADDITIONAL CLARIFICATION AND ERRATA

#### ANSWERS TO QUESTIONS FROM DOE PERSONNEL

1. What is the basis used for choosing the plant size at 20,000 BPSD? The gasifiers have three trains, but some of the downstream sections only have one train.

Answer: The basis was three Shell gasifiers of the largest size currently being considered (2500 TPD of coal). The resulting production of roughly 20000 BPD of products was deemed to be a reasonable commercial scale operation. The number of trains in each case are as follows:

	Number of Trains	
Plant Section/Case	Slurry	Fixed-Bed
Coal Gasification	3	3
Shift Conversion or COS Hydrolysis	2	2
Acid Gas Removal	2	2
Syngas Compression	1	1
Fischer-Tropsch Synthesis	1	1
F-T Gas Plant	1	1
CO <sub>2</sub> Removal	3	2
Upgrading Units	1	1

2. If an iron catalyst pellet is used in the fixed bed reactor, it should have some silica (inert) as a binder. Were Satterfield's data on the fixed bed reactor based on catalyst weight including silica, if pellets were used? What were the catalysts used by Satterfield; fused or precipitated iron?

Answer: Satterfield and coworkers at Exxon used fused-magnetite catalyst with 64.4 wt% Fe. At MIT (slurry) it was crushed to 270-325 mesh, at Exxon (fixed-bed) it was 170-230 mesh. In the fixed-bed reactor the catalyst was diluted 10:1 by volume with silica sand of the same particle size. Results were correlated in each case per unit weight of catalyst (not inert). The pressure drop in the fixed bed reactor was 0.05 to 0.22 MPa, but the authors calculated that this did not affect their results (see Satterfield, et al, I.E.C.Fund., 24, pp 450-454, 1985).

3. What does 30°F mean in the discussion on Page 25 (last paragraph) under 4.1.2 Reactor Design?

Answer: In the context cited, 30°F refers to the approach to equilibrium used to calculate the conversion in a fixed-bed methanol reactor operating at a given outlet temperature.

4. What is the ultimate conversion in the slurry F-T reactor case, when compared to the 97% ultimate conversion in the fixed bed case?

Answer: Single pass and ultimate conversions may be back-calculated from Tables 4.3 and 4.4. The following values are obtained for H<sub>2</sub>, CO and syngas conversion:

	Fixed-Bed		Slurry	
	Per Pass	Ultimate	Per Pass	Ultimate
CO Conversion	37.17	96.32	82.93	95.67
H <sub>2</sub> Conversion	36.74	94.52	72.28	87.58
H <sub>2</sub> + CO Conversion	36.89	95.15	79.63	93.25

Differences between actual ultimate conversion and 100% conversion have to do with losses to the bleed stream and the amount of hydrogen product removed for treating the products.

#### ERRATA

Section	Paragraph	Line	Page	Correction
Title Page				Add the name "Elaine Chang, Process Engineer".
2.4.1	5	3	12	Change "31000 cm/s" to "31000 cm <sup>2</sup> /s".
2.4.2	1	4&5	12	Should read "(2) is required in most expressions for predicting mass transfer coefficient."
2.4.2	4	last	13	Change " $\epsilon_G^{1.1}$ " to " $\epsilon_G^{1.1}$ ".
4.3.3	5	7	40	Change "increased" to "increase".
4.7	1	last	57	Change "0,7 m/s" to "0.07 m/s".
Appendix C - CSTR Model -	page 3			Change equation under Assumption 8 to read: " $k'_H = 3.3 \cdot 10^9 \cdot e^{(-130,000/RT)} \cdot (1100/P)^{0.5}$ ".
Appendix D - last paragraph -	page 4			Change "15 m/s" to "0.15 m/s".

Insert Dated 9/28/90



**END**

**DATE FILMED**

04 / 26 / 91

