

Report 13

Two-Stage Slurry Fischer-Tropsch ZSM-5 Process  
of Converting Syngas to High Octane Gasoline

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*Prepared by*

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TWO-STAGE SLURRY FISCHER-TROPSCH/ZSM-5 PROCESS  
OF CONVERTING SYNGAS TO HIGH OCTANE GASOLINE

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I. Introduction

The title of the contract is "Two-Stage Slurry Fischer-Tropsch/ZSM-5 Process of Converting Syngas to High Octane Gasoline". This contract began on October 1, 1980 and will end on April 1, 1983. The overall objective of the contract is to develop a two-stage slurry F-T/ZSM-5 process for direct conversion of syngas to high octane gasoline (Slide #1). To achieve this objective, specific tasks are the design, construction, and operation of a two-stage bench-scale pilot plant, and the acquisition of necessary process information for the evaluation of the technical and economic potential of the process.

II. Simplified Process Scheme and  
Present Status of the Project

Slide #2 illustrates a simplified scheme for this process concept. The syngas will be fed into a slurry F-T reactor, and the total product from that reactor will go to the second-stage ZSM-5 reactor. The products from the ZSM-5 reactor

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will contain unconverted H<sub>2</sub> and CO, CO<sub>2</sub>, some C<sub>3</sub> and C<sub>4</sub>, and high octane gasoline.

Slide #3 summarizes the status of the project to date. The design phase of the bench-scale unit is complete. The fabrication of BSU components in the machine shop has begun, and purchase orders for all major BSU components have been issued. Finally, a preliminary mathematical model of a slurry F-T bubble-column reactor is being developed. Both the design of the BSU and the mathematical model will be described in this paper.

### III. Advantages of This Two-Stage Process

Slide #4 explains the advantages of using a slurry F-T reactor for direct syngas conversion. Good reactor temperature control is the most important feature of a slurry reactor. Since the rate of the carbon formation due to the Boudouard reaction



increases drastically with catalyst temperature, good temperature control will minimize carbon formation on the catalyst and improve long-term catalyst stability. With lower carbon formation, one can afford to use low H<sub>2</sub>/CO ratio syngas, as opposed to those used in the conventional vapor-phase F-T processes; i.e., SASOL'S fixed-bed tubular and entrained fluid-bed processes. This is an important advantage since it avoids substantial costs associated with the shifting of a low

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H<sub>2</sub>/CO syngas to a high H<sub>2</sub>/CO one. Good reactor temperature control with a low H<sub>2</sub>/CO ratio syngas will reduce the methane and ethane yields. Since the methane and ethane are lower value products in comparison with gasoline, the reduced yields of methane and ethane are economically very important. The second major advantage of a slurry F-T operation is high single-pass syngas conversion. With this high single-pass conversion, substantial cost savings can result from not using a gas recycle operation and an efficient reaction heat recovery. The last major advantage of a slurry F-T reactor is its high toleration of carbon formation and catalyst disintegration.

The major disadvantages of a slurry F-T reactor are low gasoline yield and quality. The low gasoline yield results from the fact that large amounts of light olefins, hydrocarbons heavier than gasoline, and oxygenates are produced along with the gasoline. The second-stage ZSM-5 reactor can convert a major portion of these by-products into gasoline. Furthermore, the final gasoline has a high octane rating since it contains a large amount of aromatics and iso-paraffins. This concept was demonstrated in laboratory using a stirred-tank reactor as first-stage and a fixed-bed micro-reactor as second-stage. Slide #5 shows data indicating high single-pass syngas conversion, and a high yield of high quality C<sub>5</sub><sup>+</sup> gasoline.

#### IV. Bench-Scale Pilot Plant Design

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Slide #6 shows a simplified flow diagram of the planned bench-scale unit. The syngas is formed by mixing  $H_2$  and  $CO$ , and is then sent through a pre-heater and into the bubble-column reactor. As shown in Slide #7, the reactor has an inside diameter of 2" and a maximum slurry height of 25'. The normal gas feed rate is 70 SCFH with a design range from 35 to 140 SCFH. Slide #7 also gives the feed  $H_2/CO$  ratio and the  $H_2+CO$  conversion. The slurry reactor is jacketed with a circulating cooling-medium for proper reactor temperature control. It also has a drain-pipe to take out excess liquid and a hot container to add make-up catalyst or reactor liquid. Immediately downstream from the reactor, a partial condenser will be used in the case of a drop of the reactor liquid level. The condenser will condense out the heavier fraction of the F-T product to be sent back to the reactor through the hot container. There is an inter-reactor sampling line that can be used to sample the products from the F-T reactor. The whole product of the F-T reactor will be sent, after passage through a pre-heater, into one of the two ZSM-5 reactors. As shown in Slide #7, the dimensions of these ZSM-5 reactors are 2" ID and 18" maximum height. Since the ZSM-5 reactor will require occasional regeneration, two reactors will be used to maintain a continuous operation while the reactor with the aged catalyst is under regeneration. The total product from the ZSM-5 reactor will be sent to a hot condenser and separator in which a heavy hydrocarbon stream, if any, will be separated. The remaining vapor stream will be fed into a cold condenser and

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separator in which a hydrocarbon, an aqueous, and a vapor stream will be separated. The vapor is sent to a chilled condenser to minimize the amount of  $C_5^+$  hydrocarbon loss in the light gas. All the hydrocarbon liquid streams will be sent to a distillation column for proper product separation. The hot condenser and separator are expected to be useful only if the effluent from the F-T reactor by-passes the ZSM-5 reactor or the ZSM-5 reactor is not run properly.

Slide #8 summarizes the major design basis for the operation of both the slurry F-T and the ZSM-5 reactors. These data are required for the detailed mechanical design of the bench-scale unit.

## V. Slurry F-T Reactor Mathematical Model

The design and operation of the second-stage ZSM-5 reactor are rather straight forward. On the other hand, the slurry F-T reactor is unconventional and involves complicated transport phenomena. A mathematical model of such a system would be extremely useful in aiding the design and the operation of the reactor. For the rest of this presentation the emphasis will be on the description and application of a preliminary slurry F-T reactor mathematical model. Slide #9 shows the major transport phenomena involved in such a three-phase catalytic reaction system. A reactant in a gas bubble must be diffused through the gas film adjacent to the gas-liquid interface, then through the

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liquid film there, then through the bulk liquid, and then through the liquid film adjacent to the liquid-catalyst interface. In the catalyst phase, the reactant is finally converted to F-T products. The resistances for these transports and the conversion are represented by the equations given on Slide #9. The nomenclatures are given in Appendix A. Typical values of these resistances in (sec) are given directly underneath these equations. These values were obtained with the assumptions of 0.7 mm gas bubble size and 2.5 mm catalyst size. The total resistance is simply a summation of all these resistances. The resistance values indicate that the major ones are contributed by the mass transfer across the liquid film at the gas-liquid interface and the catalytic conversion in the catalyst. For simplicity, only these two resistances are considered in the current model.

Slide #10 summarizes the major assumptions for the current model. They are similar to those adopted by others for more detailed models described in open literature. These assumptions will be examined and the critical ones will be eliminated in the future. For the moment, the single component first-order kinetics makes the analysis simple. This assumption is reasonable when the conversion is low and when the feed  $H_2/CO$  ratio is closed to the  $H_2/CO$  usage ratio. All other assumptions are rather conventional. Two extreme liquid mixing states were used in the current model to bracket the actual state of the

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liquid phase in a bubble-column, i.e., no-mixing and perfect-mixing in the axial direction.

Since the kinetic resistance is expected to be the major resistance in a slurry F-T system, kinetic rate constants for Fe-based slurry F-T catalysts were estimated from data in the open literature. Only bubble-column reactor data on Fe-catalyst were founded; they are summarized in Slide #11. References of these data are given as Appendix B. There are three things on this slide that should be emphasized. The first data set is from Koelbel's Rheinsprussen demonstration plant which has a large size reactor (1.29m inside diameter). The data from Schlesinger are for fused-Fe catalyst, all others involved precipitated-Fe catalysts. The Kunugi data were obtained using a relatively low catalyst loading. All these data contain the mass-transfer resistance which must be separated out before the kinetic rate constant can be estimated. Assuming an axially non-mixing liquid phase, the current model was used for the mass-transfer resistance. The kinetic rate constants were then determined and are summarized in Slide #12. Note that the assumption of non-mixing liquid phase may not be proper for the first data set because a large reactor may allow a substantial axial dispersion of the liquid phase. If one assumes that the liquid phase is perfectly-mixed in the axial direction, the estimated kinetic rate constant will be more than double the value given on Slide #12. Further investigation of this set of data is needed. The



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kinetic rate constant estimated from Schlesinger's data is relatively low. The fused-Fe catalyst used there may be less active than the precipitated-Fe catalysts given on this slide. Kunugi's catalyst has a very high activity level. It is not clear if this high activity is the result of a better catalyst or of a low catalyst loading. If we adopt the kinetic rate constants from Koelbel and Ralek (1980) and Mitra and Roy (1963), the precipitated-Fe catalysts will have a kinetic rate constant of about 0.85-1.1 mL liquid/s-gFe. A value of 1.1 is adopted for the current model calculations.

Slide #13 shows the model equations for the case of non-mixing liquid phase. The nomenclature is given in Appendix A. The LHS of the first equation represents the disappearance of  $H_2$  over a differential height of the bubble-column; while the RHS of the equation represents its disappearance due to both diffusion across the liquid film at the gas-liquid interface and the catalytic conversion. The second equation relates the  $H_2$  concentration in the gas phase to the  $H_2$  conversion. By substituting the second equation into the first equation, the resulting differential equation on  $H_2$  conversion is integrable in a closed-form.

Slides #14 and 15 show some results using the current model. Slide #14 shows the effect of the kinetic rate and the liquid phase mixing on the  $H_2$  conversion. An active catalyst is essential to obtain a high conversion within a reasonable reactor

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height. Furthermore, the states of the liquid mixing in the axial direction will drastically reduce the conversion for the same reactor volume at the high conversion region. The last slide (Slide #15) shows the effect of the bubble size on the H<sub>2</sub> conversion. In order to achieve 90% conversion, the column height has to increase by 30-40% if the gas bubble size increases by four times. Also shown on this slide are the calculated results for infinite catalyst activity. These results are the best one can achieve by improving the catalyst.

APPENDIX A, NOMENCLATURE

A	Column cross-sectional area, (cm <sup>2</sup> )
a <sub>c</sub>	Catalyst particle external surface area per slurry volume, $6C_{\text{cat}}(1-v)/\rho_c d_c$ , (cm <sup>2</sup> solid-liquid area/mL slurry).
a <sub>g</sub>	Gas bubble interfacial area, $6\epsilon_g/d_B$ , (cm <sup>2</sup> gas-liquid area/mL expanded slurry)
C <sub>cat</sub>	Catalyst loading, (gCat/mL liquid)
C <sub>Fe</sub>	Iron loading, (gFe/mL liquid)
C <sub>Hg</sub>	Gas phase H <sub>2</sub> concentration, (mol/mL gas)
C <sub>Hg</sub> <sup>*</sup>	C <sub>Hg</sub> in equilibrium with C <sub>HL</sub> , (mol/mL gas)
C <sub>HL</sub>	Liquid phase H <sub>2</sub> concentration, (mol/mL liquid)
D <sub>R</sub>	Reactor diameter, (cm)
d <sub>B</sub>	Bubble diameter, (cm)
d <sub>c</sub>	Catalyst particle diameter, (cm)
K <sub>H</sub>	H <sub>2</sub> solubility coefficient, C <sub>Hg</sub> <sup>*</sup> /C <sub>HL</sub> , (mL liquid/mL gas)
k <sub>H</sub> <sup>0</sup>	Intrinsic kinetic rate constant for H <sub>2</sub> conversion, $r_H/(1-\epsilon_g)(1-v)C_{\text{HL}} C_{\text{Fe}}$ , (mL liquid/s-gFe)
k <sub>c</sub>	Liquid-particle mass transfer coefficient, (cm/s)
k <sub>g</sub>	Gas side mass transfer coefficient, (mL gas/s-cm <sup>2</sup> gas-liquid area)
k <sub>l</sub>	Liquid side mass transfer coefficient, (mL liquid/s-(cm <sup>2</sup> gas-liquid area))
L	Bubble column length, (cm)
N <sub>H</sub>	H <sub>2</sub> molar flow rate, (mol/s)
P	Pressure, (MPa)
R <sub>c</sub>	H <sub>2</sub> transport resistance, from bulk liquid phase to liquid-solid interface, $K_H/k_c a_c (1-\epsilon_g)$ , (s)
R <sub>d</sub>	H <sub>2</sub> transport resistance from gas-liquid interface to bulk liquid phase, $K_H/k_l a_g$ , (s-mL expanded slurry/mL gas)

## Appendix A

$R_g$	Gas law constant, 8.2, (MPa-mL/mol-°K)
$R_k$	Kinetic resistance, $K_H/k_H^n C_{Fe}(1-\epsilon_g)(1-v)$ , (s-mL expanded slurry/mL gas)
$R_t$	H <sub>2</sub> transport resistance, from bulk gas phase to gas-liquid interface, $(k_g a_g)^{-1}$ , (s)
$r_H$	H <sub>2</sub> conversion rate, (mol/s-mL expanded slurry)
$T$	Temperature, (°K)
$v$	Volumetric fraction of catalysts in slurry, $\rho_s w / (\rho_L + w(\rho_s - \rho_L))$ , (mL catalyst/mL slurry)
$w$	Weight fraction of catalysts in slurry, (gCat/g slurry)
$X_H$	H <sub>2</sub> conversion
$Y_H$	H <sub>2</sub> mole fraction
$Z$	Reactor vertical distance from its entrance, (cm)

### Greek Letters

$\beta$	CO/H <sub>2</sub> mole ratio in F-T reaction
$\gamma$	Moles product per mole of H <sub>2</sub> converted in F-T reaction
$\epsilon_g$	Gas hold-up, (mL gas/mL expanded slurry)
$\rho_c$	Catalyst particle density, (gCat/mL catalyst particle)
$\rho_L$	Liquid density, (g/mL liquid)
$\rho_s$	Catalyst solid density, (gCat/mL catalyst solid)

### Superscripts

$e$	At reactor exit
$i$	At reactor inlet

APPENDIX B, LITERATURE

Kolbel, H., Ackerman, P., and Engelhardt, F., Proc. Fourth World Petroleum Congress, Section IV/C, p. 227, Carlo Colombo Publishers, Rome (1955).

Kolbel, H., and Ralek, M., Cat. Rev. Sci. Eng., 21, 225 (1980).

Kunugi, T., Sakai, T., and Negishi, N., Sekiyu Gakkai Shi, 11, 636 (1968).

Mitra, A., and Roy, A., Indian Chemical Engineer, 127 (1963).

Schlesinger, M., Benson, H., Murphy, E., and Storch, H., Ind. Engng. Chem., 46, 1322 (1954).

Slide #1

**CONTRACT TITLE**

**Slurry Fischer-Tropsch / Mobil Two-Stage Process of Converting Syngas to High Octane Gasoline (DE-AC22-80 PC 30022).**

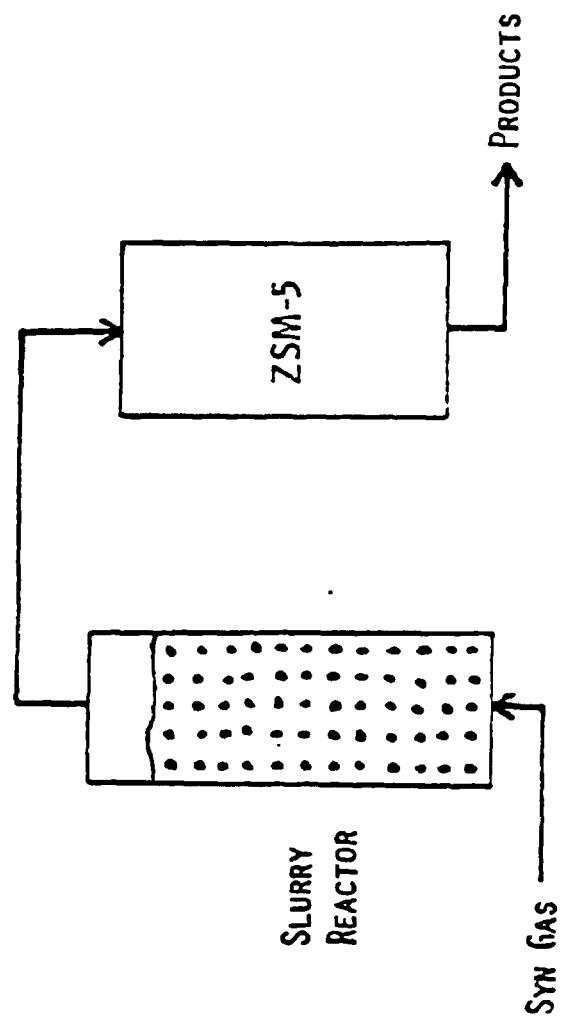
**Contract Period: October 1, 1980 - April 1, 1983.**

**OVERALL OBJECTIVE**

**To Develop a Two-Stage Slurry Fischer-Tropsch / ZSM-5 Process for Direct Conversion of Syngas to High Octane Gasoline.**

Slide #2

**TWO-STAGE PROCESS FOR CONVERSION  
OF SYNTHESIS GAS TO GASOLINE**



**FIRST STAGE      SECOND STAGE**  
**(FISCHER-TROPSCH SYNTHESIS)    (PRODUCT UPGRADING)**

## STATUS OF PROJECT

- Design Phase of the Bench Scale Pilot Plant is Complete
- Shop Fabrication of BSU Components Has Begun
- Purchase Orders of All Major BSU Components Have Been Issued
- A Preliminary Mathematical Model of the Slurry F-T Bubble Column is Being Developed



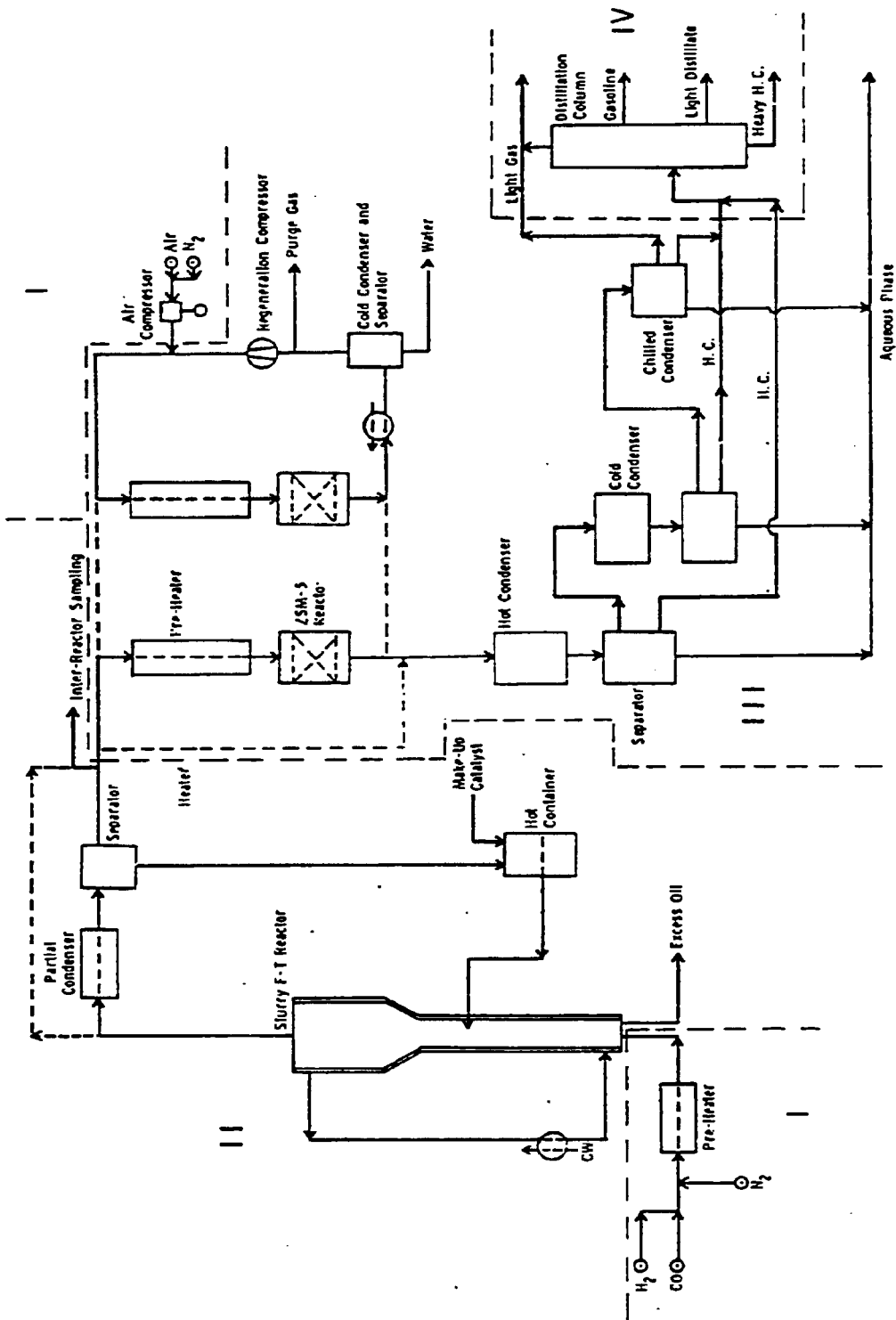
ADVANTAGES OF SLURRY F-T REACTOR

- Good Reactor Temperature Control
  - Less Carbon Formation
  - Less Methane and Ethane Formation
  - Low  $H_2$  / CO Feed
- High Single Pass Syngas Conversion
  - No Recycle Compression
  - More Efficient Reaction Heat Recovery
- High Tolerallon of Carbon Formation and Catalyst Disintegration

## TWO-STAGE CONVERSION OF SYNTHESIS GAS

H <sub>2</sub> /CO	0.65
First Reactor Temp., °F	509
Second Reactor Temp., °F	672
Pressure, psia	200
Space Velocity, L/Hr/G Fe	3
H <sub>2</sub> + CO Conversion, Vol %	90
Hydrocarbon Dist., Wt %	
C <sub>1</sub>	8.5
C <sub>2</sub>	6.7
C <sub>3</sub>	8.3
C <sub>3</sub> - C <sub>4</sub>	3.3
i-C <sub>4</sub>	8.2
n-C <sub>4</sub>	7.2
C <sub>5</sub> <sup>+</sup> Gasoline	57.8
	<u>100.0</u>
C <sub>5</sub> <sup>+</sup> Gasoline:	
Aromatics, Wt %	33.2
95% Boiling Point, °F	371
Estimated Finished Gasoline, Wt % (10 RVP Including Alkylate)	65

SIMPLIFIED FLOW DIAGRAM OF TWO-STAGE PILOT PLANT FOR SYNTHESIS GAS CONVERSION



DESIGN BASIS OF THE TWO-STAGE SYNGAS  
CONVERSION BENCH-SCALE UNIT

<u>Reactor Dimensions</u>	<u>Normal</u>	<u>Design Range</u>
Slurry F-T Catalyst Bed	2" (ID) x 25' (L)	2" (ID) x 10-25' (L)
ZSM-5 Catalyst Bed	2" (ID) x 8" (L)	2" (ID) x 4-18" (L)

Material Balance Basis

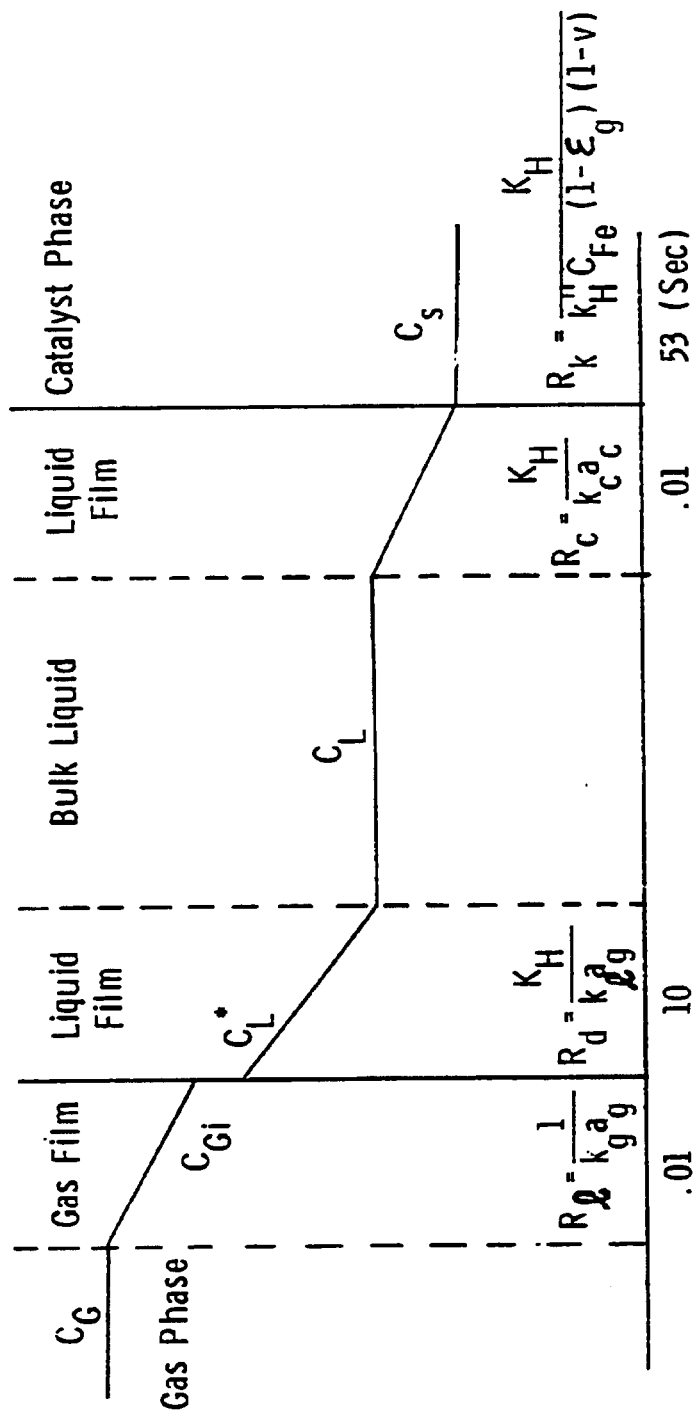
Syngas Feed Rate, SCFH	70	35 - 140
H <sub>2</sub> /CO Mole Ratio	0.67	0.5 - 2
H <sub>2</sub> + CO Conversion, Mole %	90	50 - 97

Slide #8

DESIGN BASIS OF THE TWO-STAGE SYNGAS  
CONVERSION BENCH-SCALE UNIT

<u>Slurry F-T Reactor</u>	<u>Normal</u>	<u>Design Range</u>
Inlet Temperature, °F	500	100 - 650
Exit Temperature, °F	500	420 - 650
Pressure, psia	200	100 - 600
GHSV (STP), Hr <sup>-1</sup>	128	64 - 256
Catalyst Load, Lbs	3.4	3.4 - 8.5
Reaction Heat Removal Rate, Btu/Hr	4,600	1,300 - 9,500
<u>ZSM-5 Reactor</u>		
Inlet Temperature, °F	600 - 750	600 - 850
Exit Temperature, °F	715 - 865	650 - 900
Pressure, psia	190	100 - 600
WHSV Based on Hydrocarbons	1.5	-
Catalyst Load, Lbs	0.5	0.25 - 1.2

MASS TRANSFER RESISTANCES IN A GAS-LIQUID-SOLID SYSTEM



## MAJOR MODEL ASSUMPTIONS

- Single Component ( $H_2$ ) Diffusion and First-Order Irreversible Kinetics With Respect to  $H_2$
- Constant Syngas Usage Ratio for All Syngas Conversion Levels at a Given  $H_2/CO$  Feed Ratio
- Isothermal Steady State Operation
- Plug-Flow in Gas Phase
- Constant Hydrodynamic Properties (Bubble Size, Gas Hold-Up, and Gas-Liquid Interfacial Area) Along the Column Height
- A 50% Molar Contraction in F-T Reaction

SELECTED F-T CONVERSION DATA IN BUBBLE-COLUMNS

<u>Sources / Catalysts</u>	<u>Temp. / Pres. (°C / MPa)</u>	<u>Reactor Dimension D<sub>R</sub> (cm) x L (cm)</u>	<u>Superficial Inlet Gas Velocity (cm/s)</u>	<u>Inlet H<sub>2</sub> / CO</u>	<u>Hydrogen Conversion</u>	<u>Catalyst Loading (Wt %)</u>
Koelbel et. al. (1955) / pptd Fe	268 / 1.2	129 x 770	9.5	0.67	86	28.4
Koelbel and Ralek, (1980) / pptd Fe	266 / 1.1	4.7 x 350	3.5	0.67	85	15.4
Schlesinger et. al. (1954) / Fused Fe	258 / 2.14	7.6 x 300	1.52	1.0	63.9	21.1
Mitra and Roy (1963) / Fe pptd on Kieselgur	260 / 1.12	5.0 x 300	1.48	1.33	89.7	17.0
Kunugi et. al (1968) / pptd Fe	266 / 1.03	5.0 x 550	4.0	0.59	80.8	4.8



ESTIMATED F-T KINETIC CONSTANTS ON Fe-CATALYSTS  
(NON-MIXING LIQUID PHASE MODEL)

Sources	Temperature (°C)	$k_H^*$	Kinetic Resistance as % of Total Resistance
Koebel et. al (1955)	268	0.931	0.92
Koebel and Ralek (1980)	266	1.12	0.80
Schlesinger et. al (1954)	258	0.203	0.84
Mitra and Roy (1963)	260	0.848	0.68
Kunugi et. al. (1968)	266	2.28	0.89

\* Intrinsic Kinetic Rate Constant Defined as  $R_H / (1 - \epsilon_A) C_{HL} C_{Fe}$ , (mL Liquid/s-gFe)

Slide # 13

MODEL EQUATIONS  
(NON-MIXING LIQUID)

$$N_H^i \frac{dX_H}{dz} = A (R_k + R_d) - I C_{Hg}$$

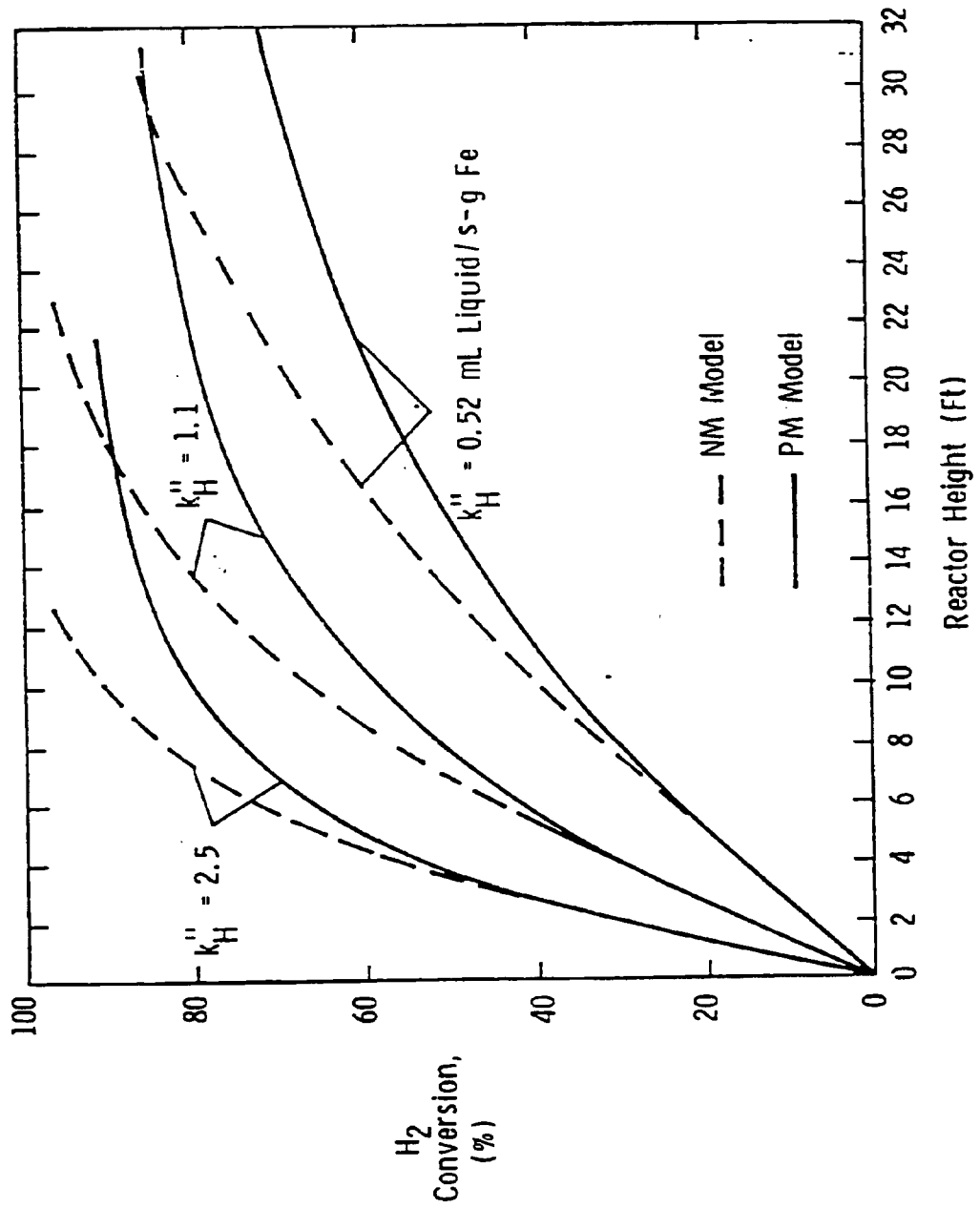
$$C_{Hg} = \frac{P y_H}{R_g T} = \frac{P y_H^i}{R_g T} \frac{1 - X_H}{1 + y_H^i (\gamma - 1 - \beta) X_H}$$

$$R_k = K_H / K_H'' C_{Fe} (1 - \epsilon_g) (1 - v)$$

$$R_d = K_H / K_H' a_g$$

Slide # 14

### EFFECT OF KINETIC RATE AND LIQUID PHASE MIXING ON H<sub>2</sub> CONVERSION



EFFECT OF BUBBLE SIZE ON H<sub>2</sub> CONVERSION

