

LIQUID PHASE METHANOL UPDATE

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ABSTRACT

The U.S. DOE and Air Products and Chemicals, Inc. are now somewhat over halfway through a 42-month R&D program to prove the feasibility of the Liquid Phase Methanol (LPMeOH) technology. The program began in September 1981. Chem Systems Inc., inventor of the LPMeOH technology, is performing as a key subcontractor in the program. Cost sharing participants are DOE, Air Products, Fluor Engineers, Inc. and the Electric Power Research Institute. LPMeOH technology has the potential to be a lower-cost conversion route to methanol-from-coal than current gas-phase processes. Laboratory work to date shows LPMeOH technology particularly suited to coal-derived synthesis gas rich in carbon monoxide because: it is capable of processing feed gas of varying CO and H₂ contents; it can achieve high CO conversion per pass; and it permits effective recovery of heat liberated during reaction. In this program, a DOE-owned skid mounted process development unit was transferred from Chicago, refurbished, expanded for service as the LPMeOH Process Development Unit (PDU), and has been relocated to Air Products' LaPorte, TX facility. Synthesis feed gas from the facility will be used to test the unit beginning late this year. A liquid-fluidized (ebullated bed) mode and a liquid-entrained (slurry) mode will be tested. The PDU operation is supported by an extensive 42-month laboratory program, conducted principally at Chem Systems' labs, with a complementary research effort at Air Products. Chem Systems is providing technical management for the project. Air Products is providing overall program management and is responsible for engineering design, construction, and operation.

In the bench scale effort of the laboratory support program, new baseline data was established for gas phase and liquid phase methanol synthesis. CO conversion and methanol specific productivity in the liquid phase are comparable to the gas phase at matching conditions. Optimum in-situ reduction conditions for slurry powders have been identified which give performance very similar to gas phase reduction. Several commercial catalyst powders achieve acceptable liquid phase performance. Of the 28 new slurry catalysts prepared in this program, 3 have recently advanced from gas phase to liquid phase screening. Autoclave life tests were initially affected by the trace contaminants iron carbonyl and organic chloride; these are strong poisons of methanol synthesis catalysts. Tests in support of the LaPorte PDU design demonstrated that hot (350°C) alpha-alumina provided an effective guard bed against iron carbonyl. In the laboratory systems, ambient activated carbon has been effective. With strong guard measures in place, liquid phase life data from the autoclaves has been encouraging. CO-rich gas was run in the autoclave in excess of 1500 hours, and balanced gas in excess of 1000 hours. Activities were

stable with a very slow rate of decline. The slow liquid phase deactivation is less than expected for gas phase synthesis with dilute balanced gas.

In the Lab PDU effort, modifications to the Fairfield unit to allow either ebullated or slurry operation were completed. A second ebullated test was performed with an improved catalyst and with CO-rich gas. Catalyst activity maintenance over the 500 hour run was excellent but there is still an apparent catalyst attrition problem. Another catalyst candidate is presently under test. The first Lab PDU slurry run was recently accomplished with an 18 wt% loading. The early interpretation of the data suggests PDU performance similar to the autoclave (i.e., good mass transfer, mixing). With balanced gas at 1000 psig, 250°C, very high methanol specific productivities were achieved, up to 55 g mole/hr-kg = 1.8 kg/hr-kg at a space velocity of 22,000 l/kg-hr. Gas holdup at superficial gas velocities up to 0.23 ft/sec. appears to be lower than expected from cold flow tests.

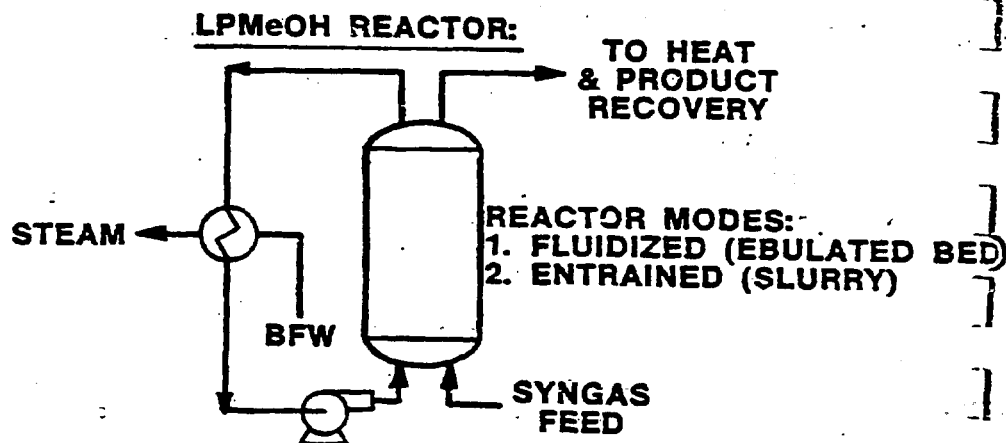
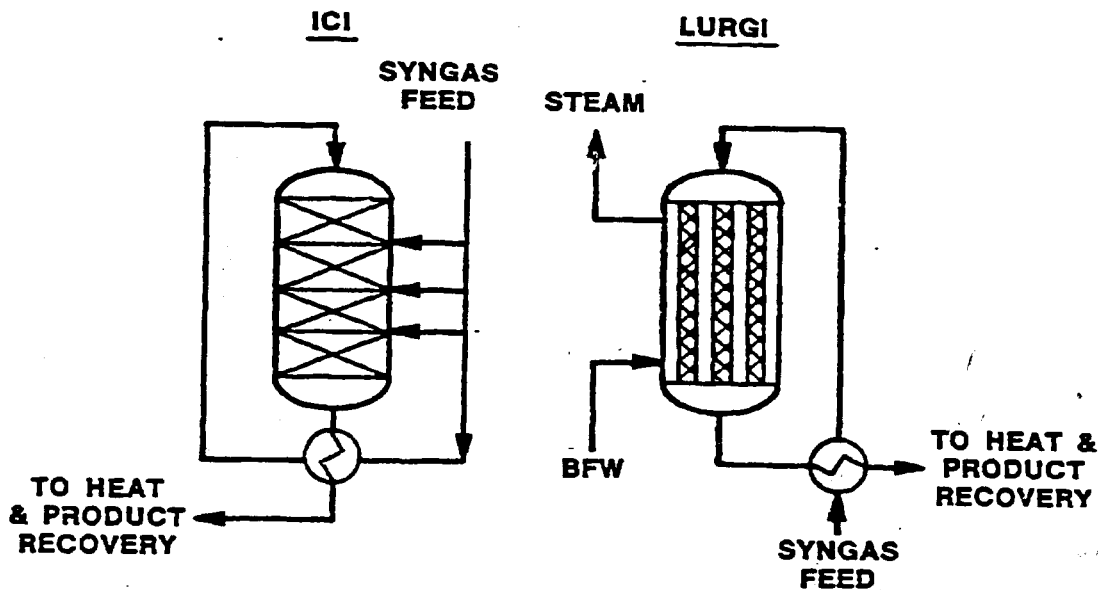
In the fundamental modeling effort, the slurry reactor has been described as a back flow cell model. Intrinsic rate constants were back calculated from autoclave data. Mass transfer is calculated from the $k_L a$ correlation of Akita and Yoshida, using the gas holdup determined in cold flow tests. When applied to the recent Lab PDU slurry run, the model provides a remarkably good fit of the balanced gas data at both 1000 psig and 500 psig.

The LaPorte PDU engineering is now complete and intense activity is underway at the site. Mechanical work is 95% complete and instrument/electrical work is 60% along. Integrated shakedown will begin in November. The ebullated operating campaign will start in December, with the slurry mode to follow in the spring of 1984.

LIQUID PHASE METHANOL UPDATE

- INTRODUCTION
- TECHNICAL CHALLENGES
 - BENCH SCALE - RESULTS AND INTERPRETATION
 - LAB PDU - RESULTS AND INTERPRETATION
 - FUNDAMENTAL MODELING PROGRESS
- SUMMARY AND PERSPECTIVE
- LAPORTE PDU ENGINEERING STATUS

REACTOR SCHEMATICS **CONVENTIONAL MeOH REACTORS:**



LPMeOH TECHNICAL MOTIVATION

LIQUID, AGITATED MEDIUM

1. LARGE HEAT SINK TO CONTROL REACTION TEMPERATURE
2. POTENTIAL FOR BROADER CATALYST COMPOSITIONS (SLURRY)



- LOW TEMPERATURE RISE
- HIGH CONVERSION PER PASS
- LOW RECYCLE RATE
- POTENTIAL TO ACCEPT LOW H_2/CO FEED

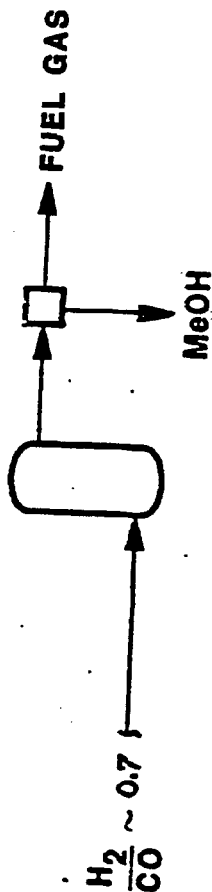
APPLICATIONS

1. METHANOL + FUEL GAS (COAL GASIF. COMBINED CYCLE)
2. ALL-METHANOL

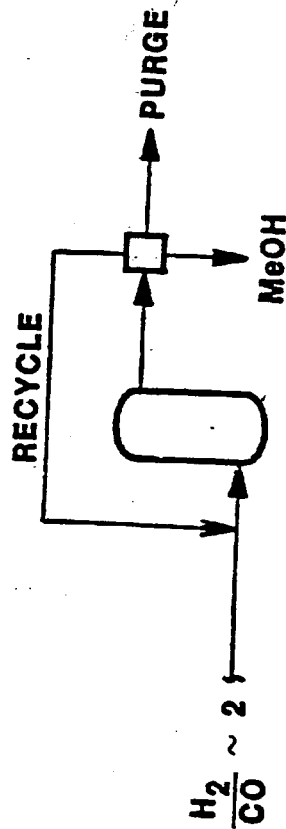
APPLICATIONS

1. METHANOL + FUEL GAS (COAL GASIF. COMBINED CYCLE)
2. ALL-METHANOL

1. SINGLE PASS
LPMeOH W.
CGCC POWER
 - NO SHIFT
 - NO CO₂ REMOV.



2. CONVENTIONAL
MeOH SYNTHESIS



LPM_{MeOH} PROJECT DESCRIPTION

OBJECTIVE

- DEMONSTRATE TECHNICAL FEASIBILITY OF LPM_{MeOH} PROCESS AT PDU SCALE

~ 1 MM SCFD

~ 5 TPD MeOH

STRATEGY

- UTILIZE EXISTING CHICAGO LPM PDU (LIQUID-FLUIDIZED)
- RELOCATE, REFURBISH, INSTALL AT LAPORTE SYNGAS FACILITY
- OPERATE LIQUID-FLUIDIZED (EBULLATED BED) MODE
- CONCURRENT WITH ABOVE, DEVELOP NEW CATALYSTS/ DATA BASE FOR LIQUID-ENTRAINED (SLURRY) MODE
- MODIFY PDU FOR LIQUID-ENTRAINED OPERATION
- OPERATE LIQUID-ENTRAINED (SLURRY) MODE

LPMeOH PROJECT DESCRIPTION (CONT.)

DURATION

- 42 MONTHS (1 OCTOBER 1981 - 1 APRIL 1985)

PARTICIPANTS

- DOE
- AIR PRODUCTS
- CHEM SYSTEMS
- EPRI
- FLUOR

LAPORTE LPM_{OH} PDU PRINCIPAL FEED GAS COMPOSITIONS

(TEXACO GASIFIER)

METHANOL + FUEL GAS COPRODUCTS

UNBALANCED TYPE
REACTOR FEED

H ₂	34.8 MOLE %
CO	51.2
CO ₂	13.1
CH ₄ , C ₂ H ₆	0.1
N ₂ , Ar, INERTS	<u>0.8</u>
TOTAL	100.0
H ₂ /CO	0.68
<u>H₂</u>	0.49
(CO+1.5CO ₂)	
<u>(H₂-CO₂)</u>	0.34
(CO+CO ₂)	

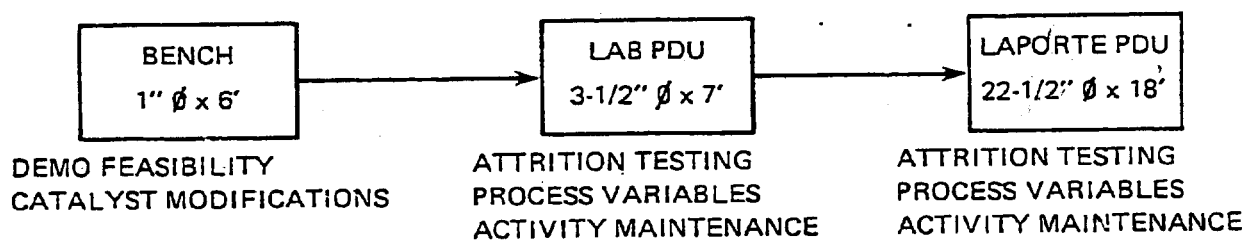
LAPORTE LPM₂OH PDU PRINCIPAL FEED GAS COMPOSITIONS (CONT.)

ALL-METHANOL PRODUCTS

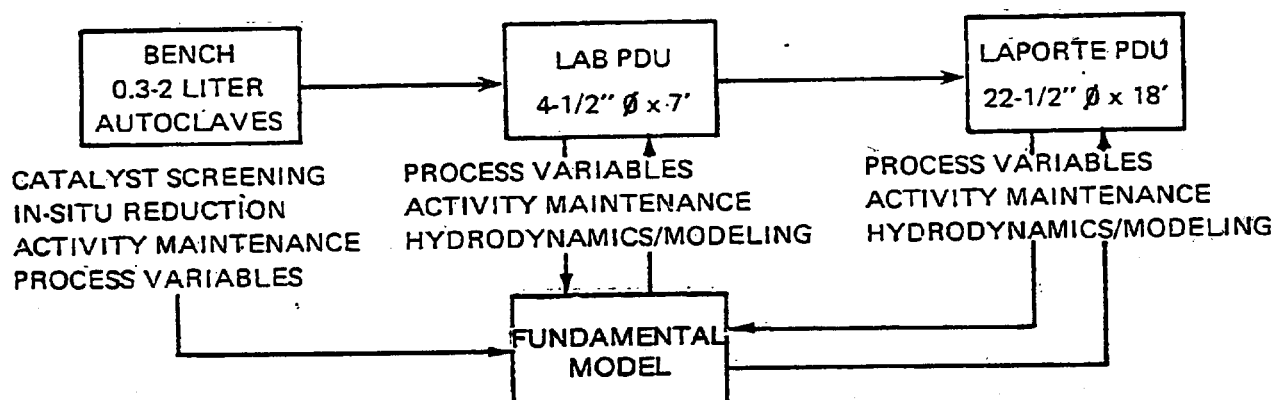
	SHIFTED FRESH FEED	BALANCED TYPE REACTOR FEED
H ₂	66.4 MOLE %	54.9 MOLE %
CO	30.7	18.8
CO ₂	2.0	4.9
CH ₄ , C ₂ H ₆	0.1	2.1
N ₂ , Ar, INERTS	<u>0.8</u>	<u>19.3</u>
TOTAL	100.0	100.0
H ₂ /CO	2.16	2.92
<u>H₂</u>	1.97	2.10
(CO+1.5CO ₂)		
<u>(H₂-CO₂)</u>	1.97	2.11
(CO+ CO ₂)		

LPMech TECHNOLOGY DEVELOPMENT

LIQUID-FLUIDIZED (EBULLATED BED) REACTOR 1975-1983



LIQUID-ENTRAINED (SLURRY) REACTOR 1979-1983



LABORATORY AUTOCLAVE PROGRAM

**OBJECTIVE: EXPLOIT SLURRY SYSTEM ON CATALYST ACTIVITY,
SELECTIVITY, LIFE ISSUES**

**COMPARE GAS PHASE TO LIQUID PHASE
OPERATION**

SCREEN COMMERCIAL CATALYSTS

SCREEN NEW EXPLORATORY CATALYSTS

OPTIMIZE REDUCTION TECHNIQUES

**CONDUCT PROCESS VARIABLE SCANS AND LIFE
TESTS**

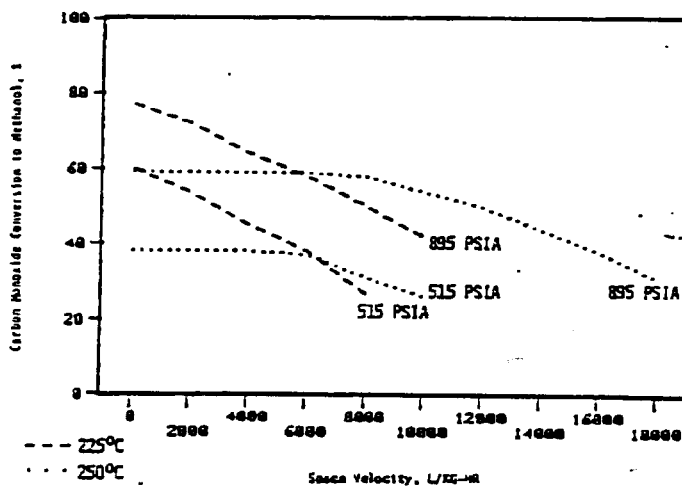
USE DATA TO MODEL PROCESS

CATALYST ACTIVITY IN APCI GAS PHASE SCREENING REACTOR

FEED GAS = 55% H₂/19% CO/5% CO₂/N₂

CATALYST = F50/4E75-01

REACTOR LOAD = 3 gm (AS OXIDE)



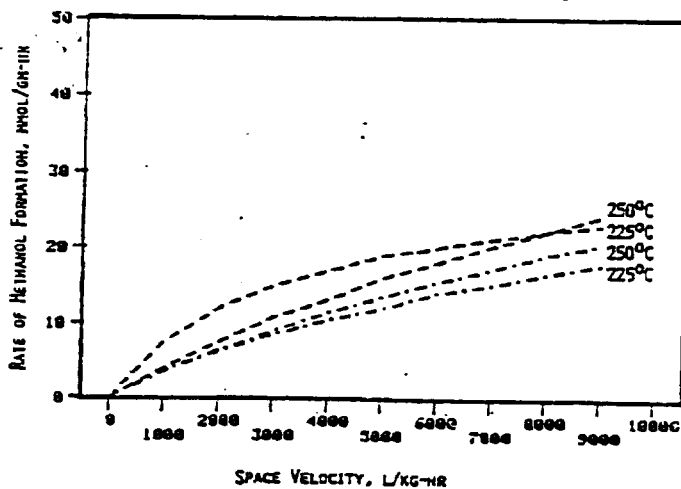
EFFECT OF GAS COMPOSITION APCI GAS PHASE SCREENING REACTOR

FEED GAS = 55% H₂/19% CO/5% CO₂/N₂

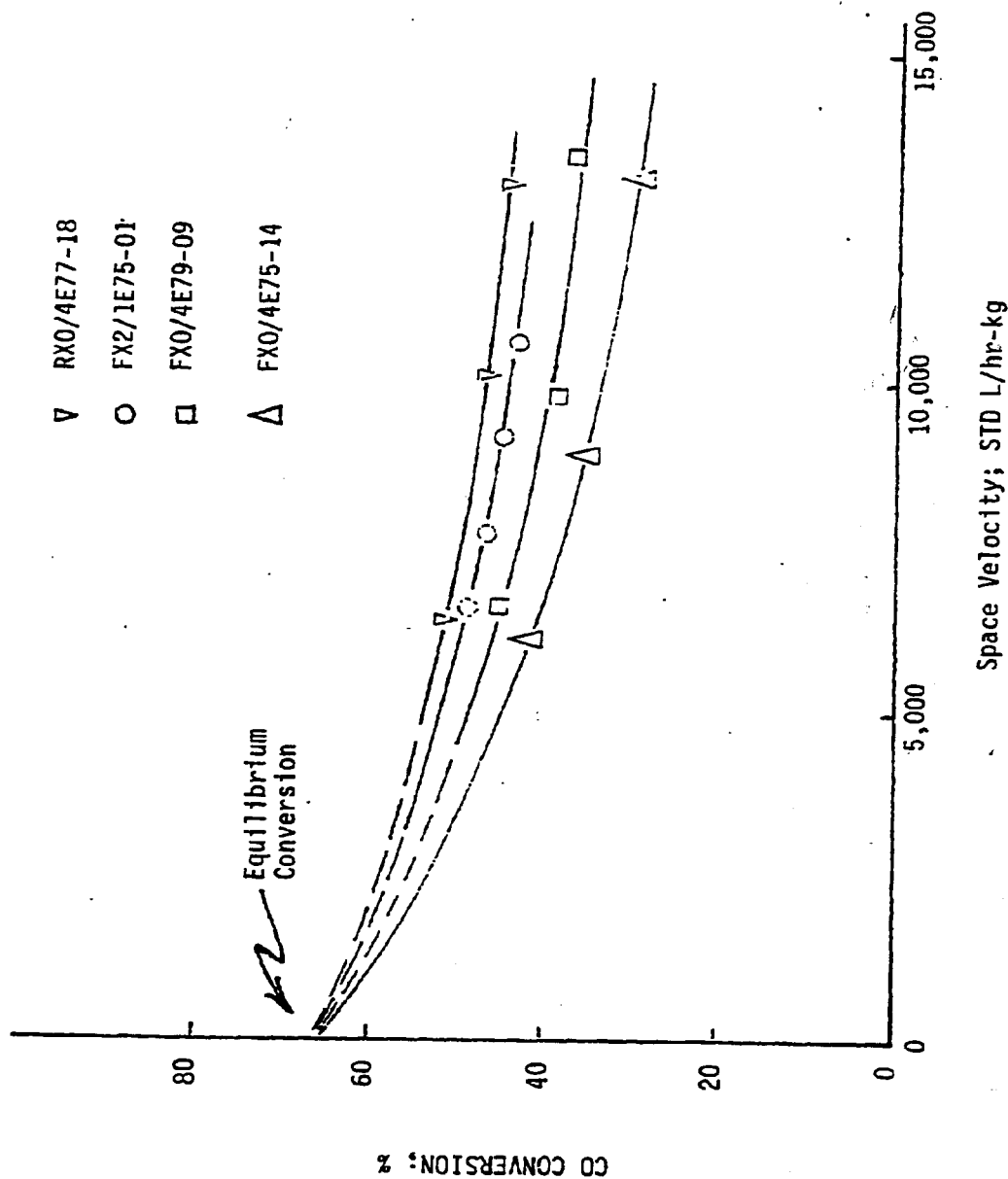
FEED GAS = 35% H₂/50% CO/13% CO₂/N₂

CATALYST = F50/4E75-01

PRESSURE = 515 PSIA (3500 KPA)



CO CONVERSION VS. S. ACE VELOCITY - BALANCED GAS AT 250°C; 7000 kPa IN FREEZENE-100



SOME NEW APCI LPMeOH CATALYST POWDERS

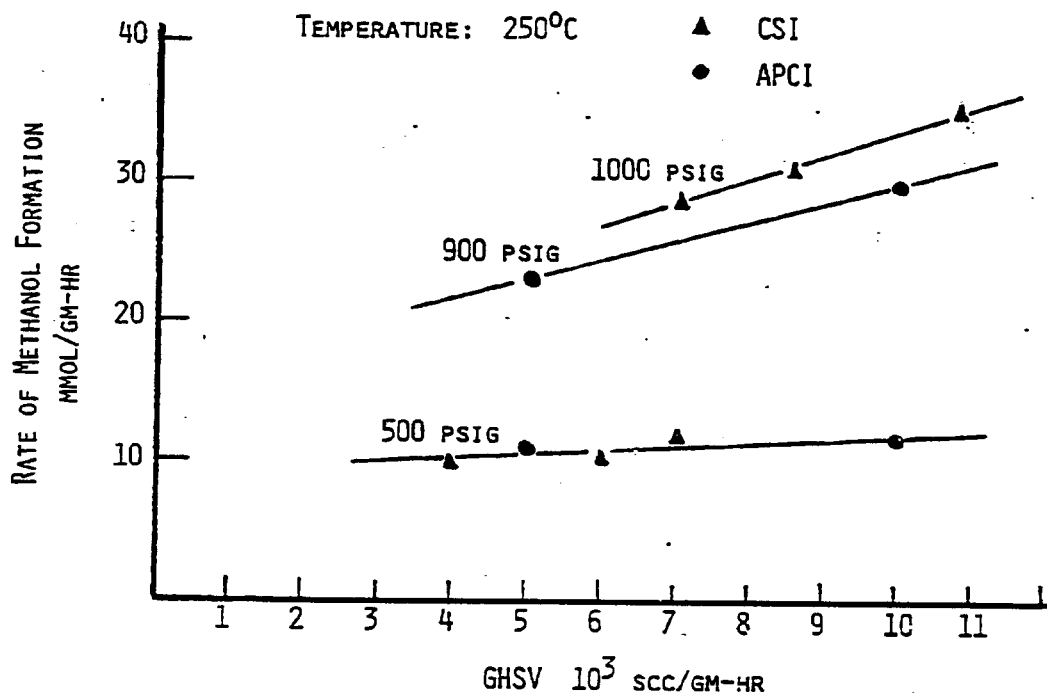
CATALYST PREP NO.	COMPOSITION	MeOH YIELD*, m.mol/gm-hr
ICI Commercial	Cu/Zn/Al ₂ O ₃	18.6
66	Cu/Zn/Al ₂ O ₃ (Stilles)	14.6
56	Cu/Zn/Cr ₂ O ₃	Nil
50	Cu/Zn (Binary)	0.7
60	Cu/Zn/Boron	7.8
63	Cu-Zn-Al Raney (stored)	1.0
75	Cu-Zn/Al Raney (fresh)	6.0
70	Ni-Boride	0.05 (25.8 CH ₄)

*Gas-Phase Screening @ 500 psig, 225°C, 5000 l/hr-kg.
Balanced Gas: 55% H₂, 19% CO, 5% CO₂, 21% N₂

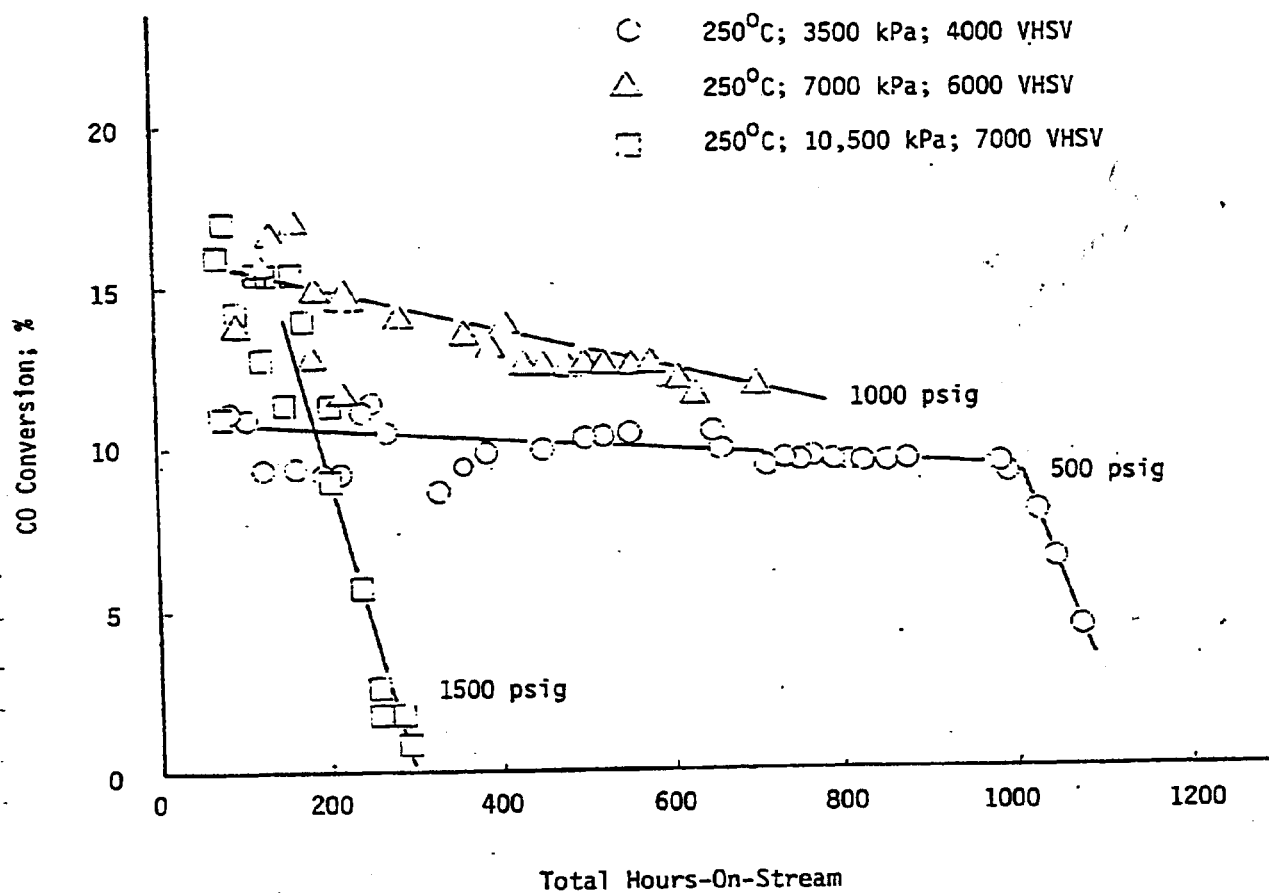
APCI STIRRED AUTOCLAVE

CROSS-CHECK WITH CSI AUTOCLAVE:

- SAME BASELINE COMMERCIAL CATALYST (F50/4E75)
- GAS PHASE REDUCTION
- BALANCED GAS, 55% H₂/ 19% CO/5% CO₂/21% N₂
- 15 WT% SOLIDS
- 30 DAYS OPERATION

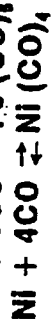
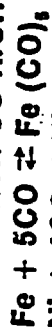


CO Conversion Vs. Total Hours on Stream for Catalyst F50/4E75-01; In-Situ Reduction in Freezeze-100



CARBONYLS AT LAPORTE

- CONCERN WITH CO RICH GAS (UNBALANCED CASE)



- POTENTIAL IMPACT
 - LINE CORROSION
 - CATALYST POISONING

INDUSTRIAL EXPERIENCE

LIMITED TO GAS PHASE SYNTHESIS

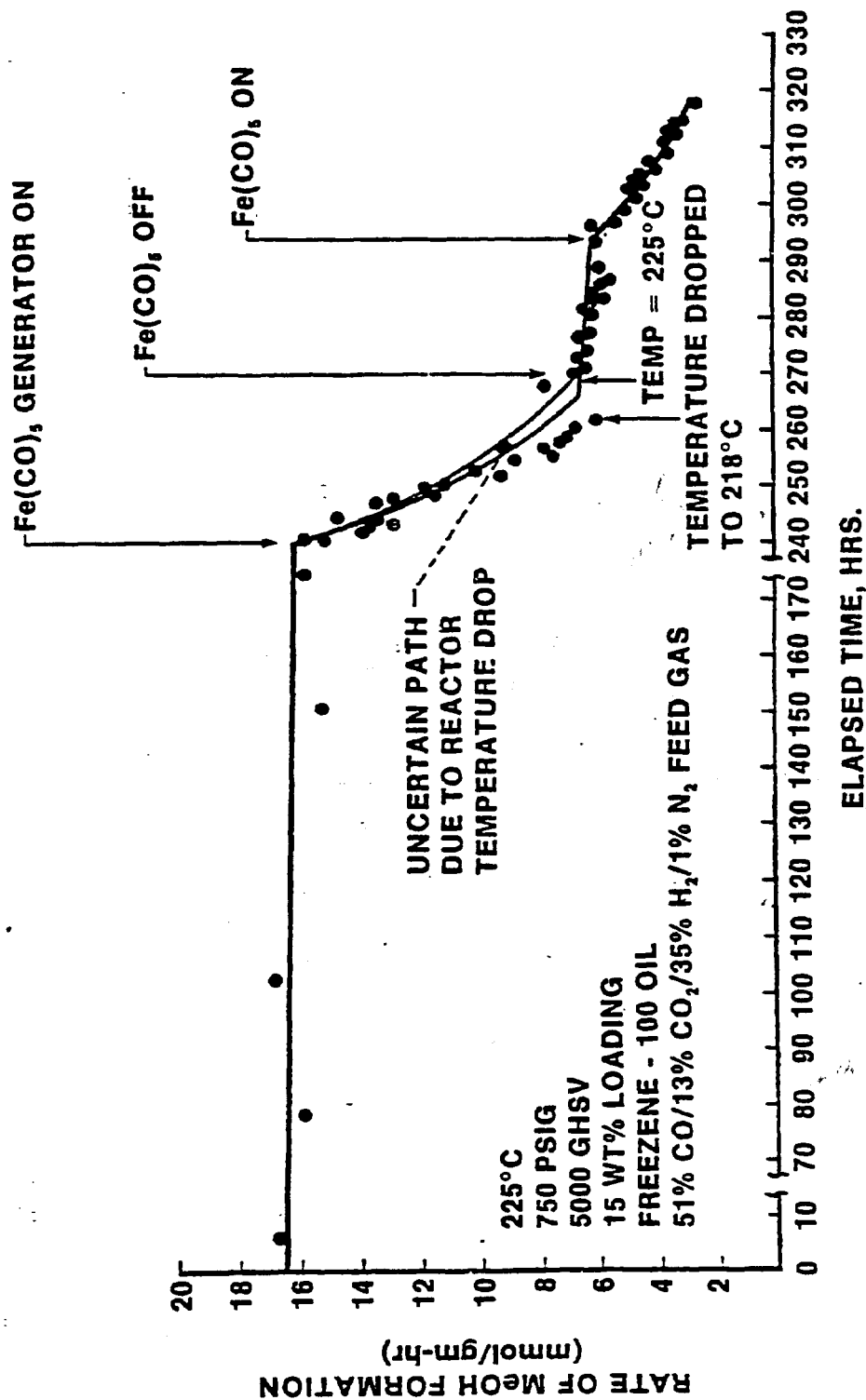
SIGNIFICANT IN HIGH PRESSURE MeOH

- CATALYST DEACTIVATION
- METHANATION

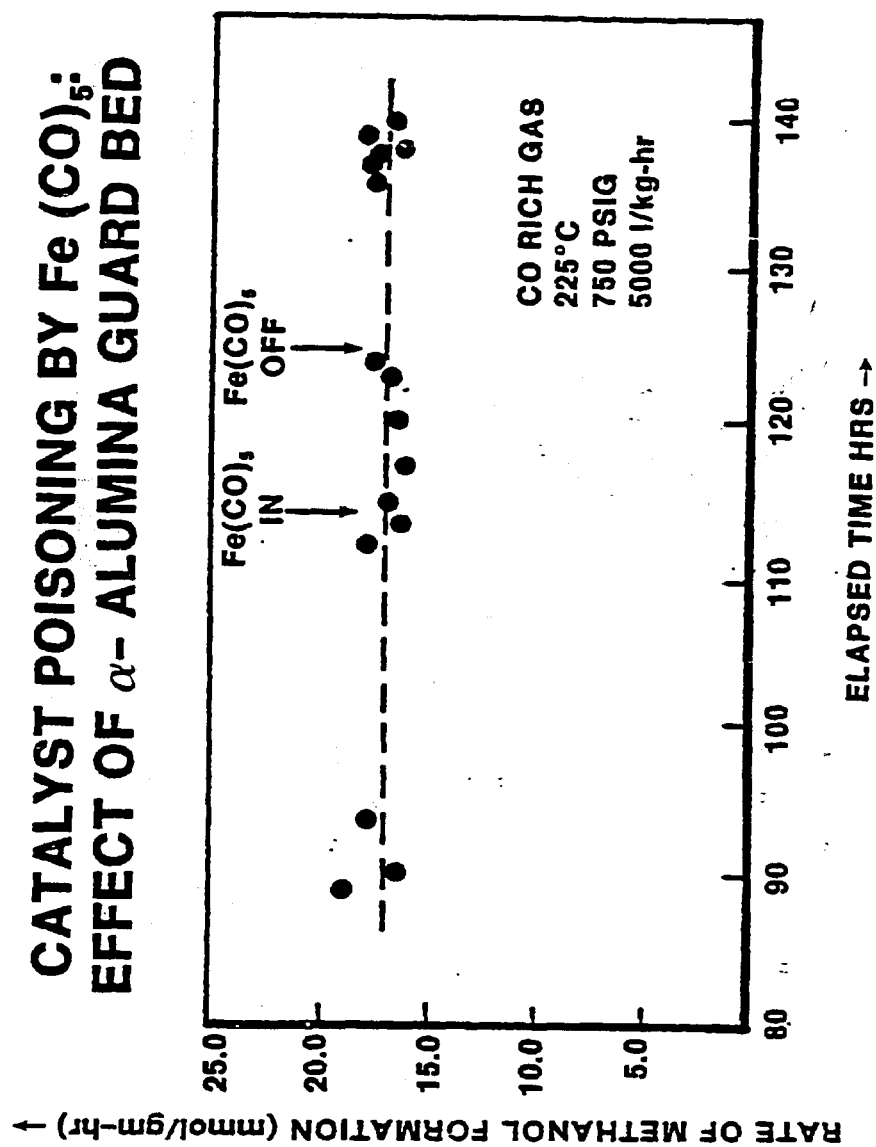
CORRECTIVE ACTION

- IMPROVED STEELS/COPPER LINING
- ACTIVATED CARBON
- MAINTAIN HIGH CO STREAMS AT T°F
WHERE $200^\circ > T > 600^\circ$

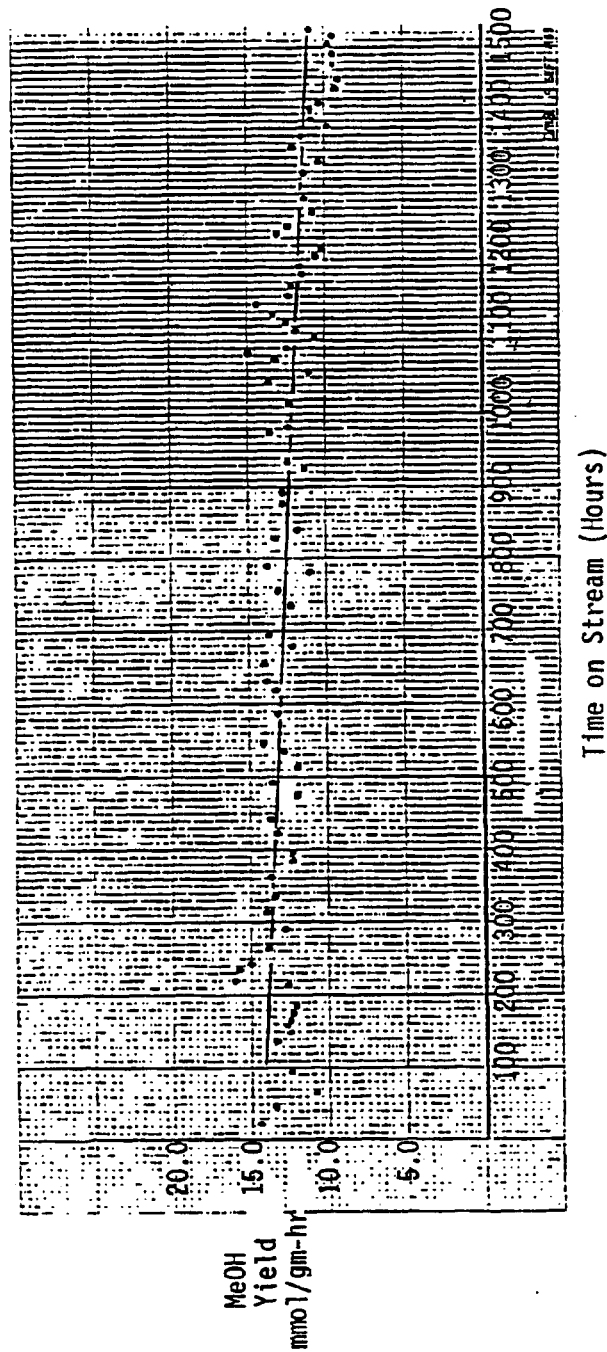
CATALYST POISONING STUDIES: EFFECT OF $\text{Fe}(\text{CO})_5$ COMMERCIAL CATALYST



CATALYST POISONING BY $\text{Fe}(\text{CO})_5$: EFFECT OF α -ALUMINA GUARD BED



MeOH PRODUCTIVITY WITH TIME **CSI AUTOCLAVE: CO-RICH, 250°C, 750 PSIG,** **15 WT% CATALYST**

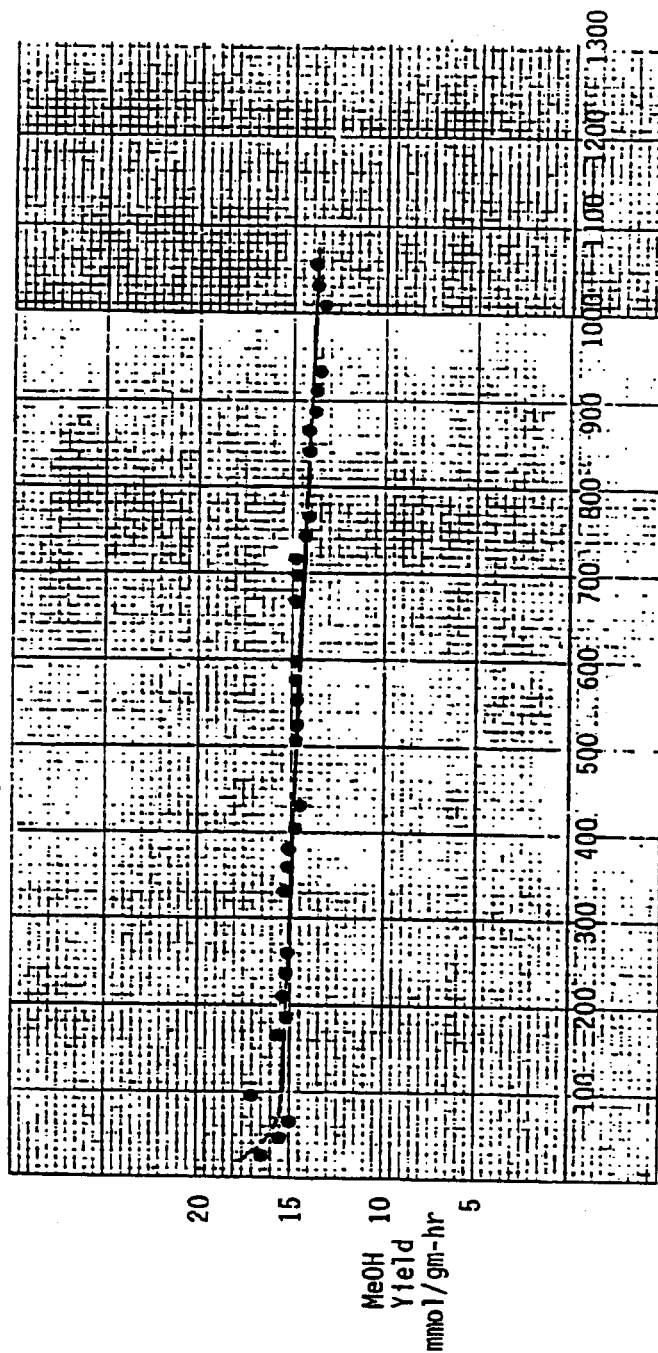


LIQUID PHASE

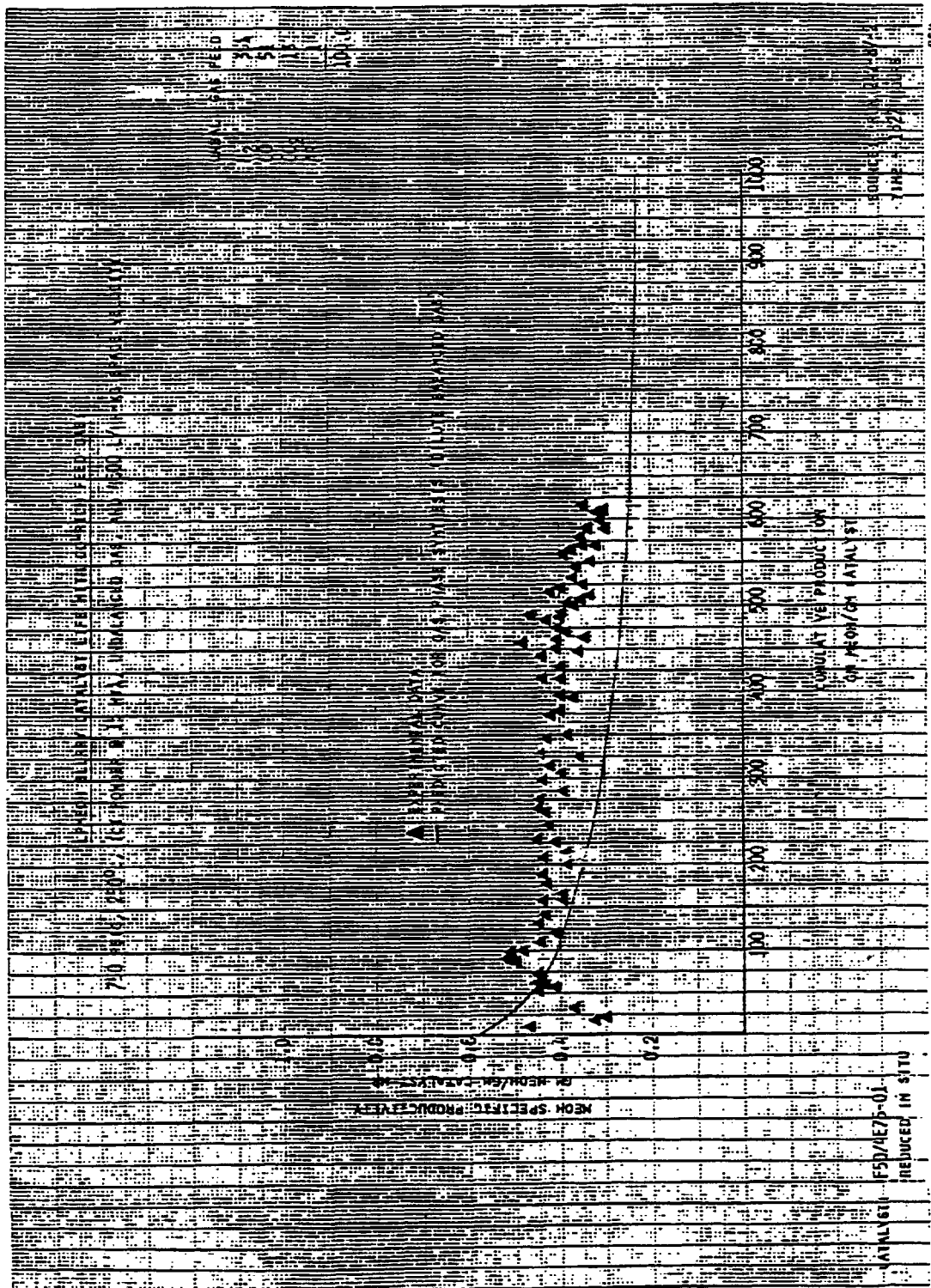
Balanced Gas: 15 wt% F50/4E75-01

250°C, 750 psig, 5000 GHSV

Methanol Productivity with Time

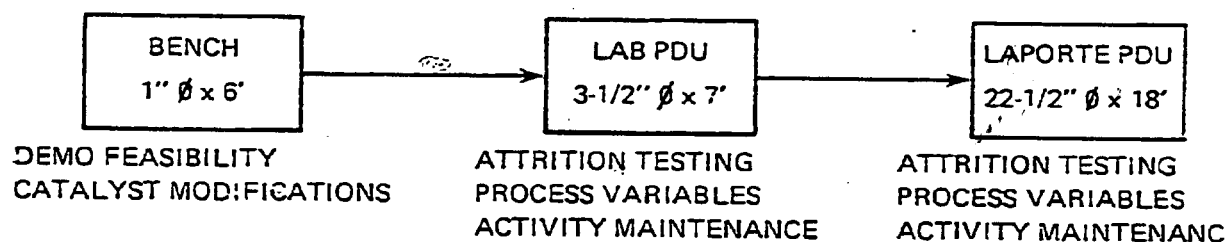


Time on Stream (Hours)

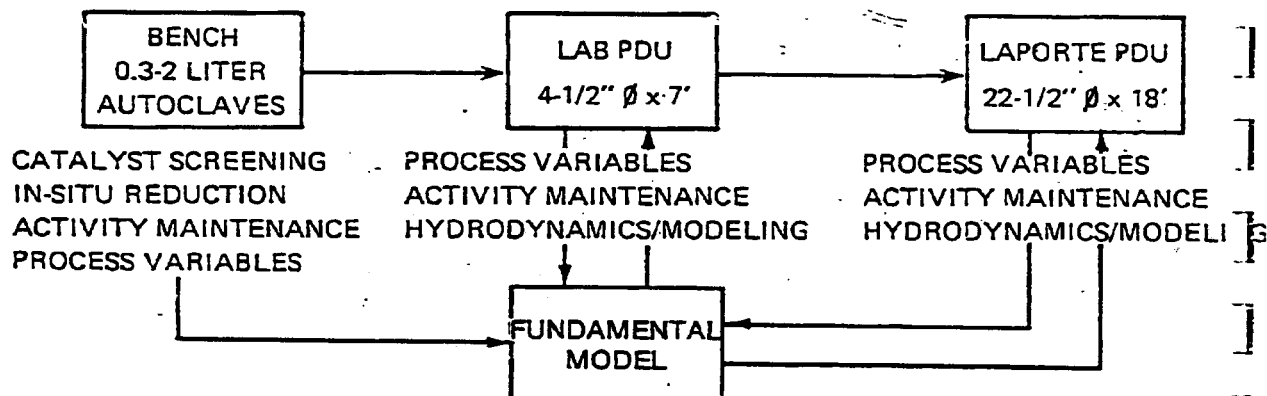


LPM₂OH TECHNOLOGY DEVELOPMENT

LIQUID-FLUIDIZED (EBULLATED BED) REACTOR 1975-1983



LIQUID-ENTRAINED (SLURRY) REACTOR 1979-1983

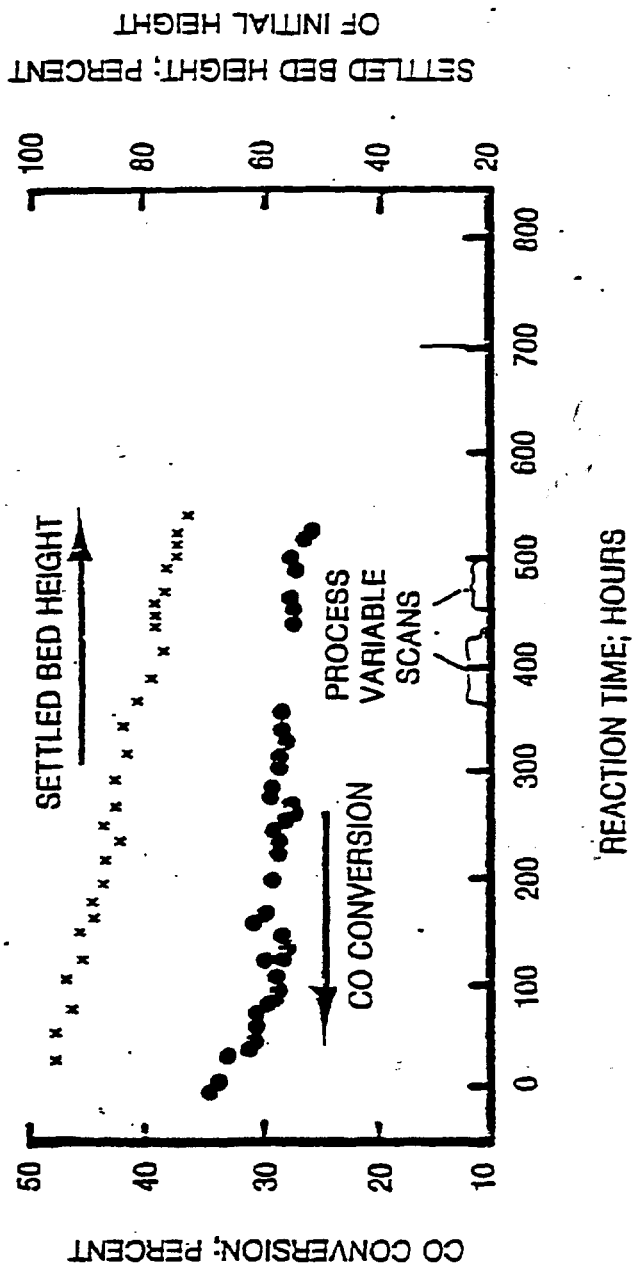


OBJECTIVES OF LAB PDU PROGRAM

- **DEMONSTRATE EBULLATED AND SLURRY MODES AT A SCALE INTERMEDIATE TO LAPORTE**
 - **EBULLATED FACES CATALYST ATTRITION AND ACTIVITY ISSUES**
 - **SLURRY FACES CATALYST LOADING AND ACTIVITY ISSUES**

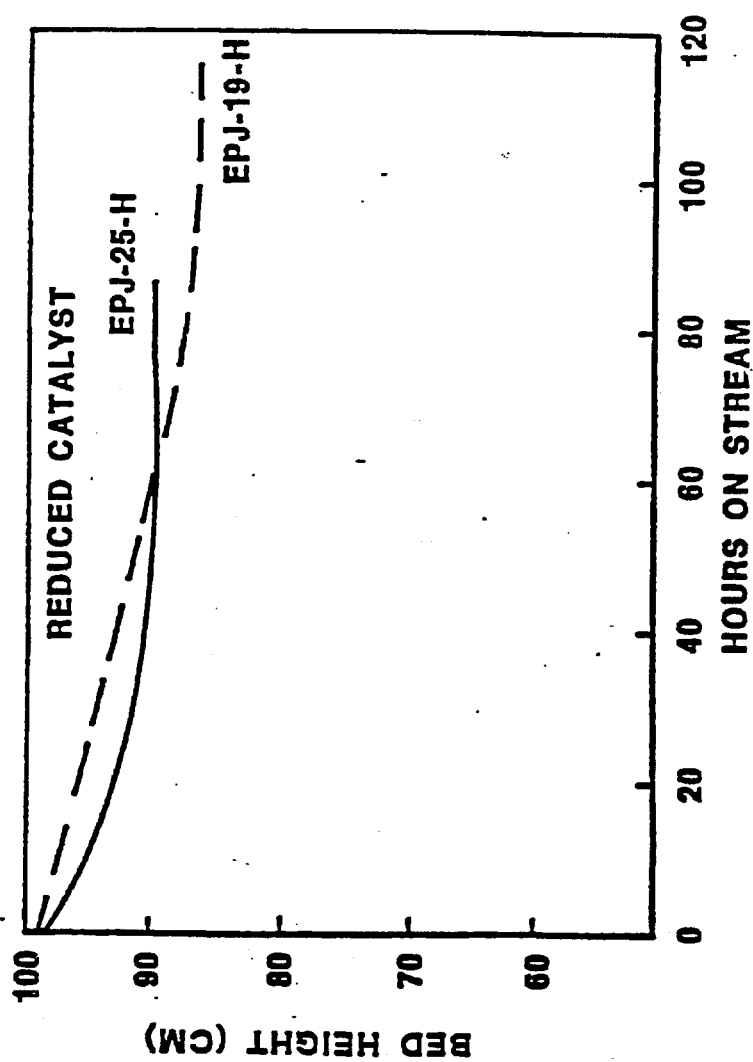
CATALYST ACTIVITY AND ATTRITION IN CSI LIQUID-FLUIDIZED LAB PDU

2/1 H₂/CO FEED GAS WITH 10% CO₂
250°C, 7000 kPa
3000 L/HR. - Kg CAT APPARENT SPACE VELOCITY
3.8 CM/SEC. SUPERFICIAL LIQUID VELOCITY



IRI COLD-FLOW TESTS

WET SETTLED BED HEIGHT COMPARISON

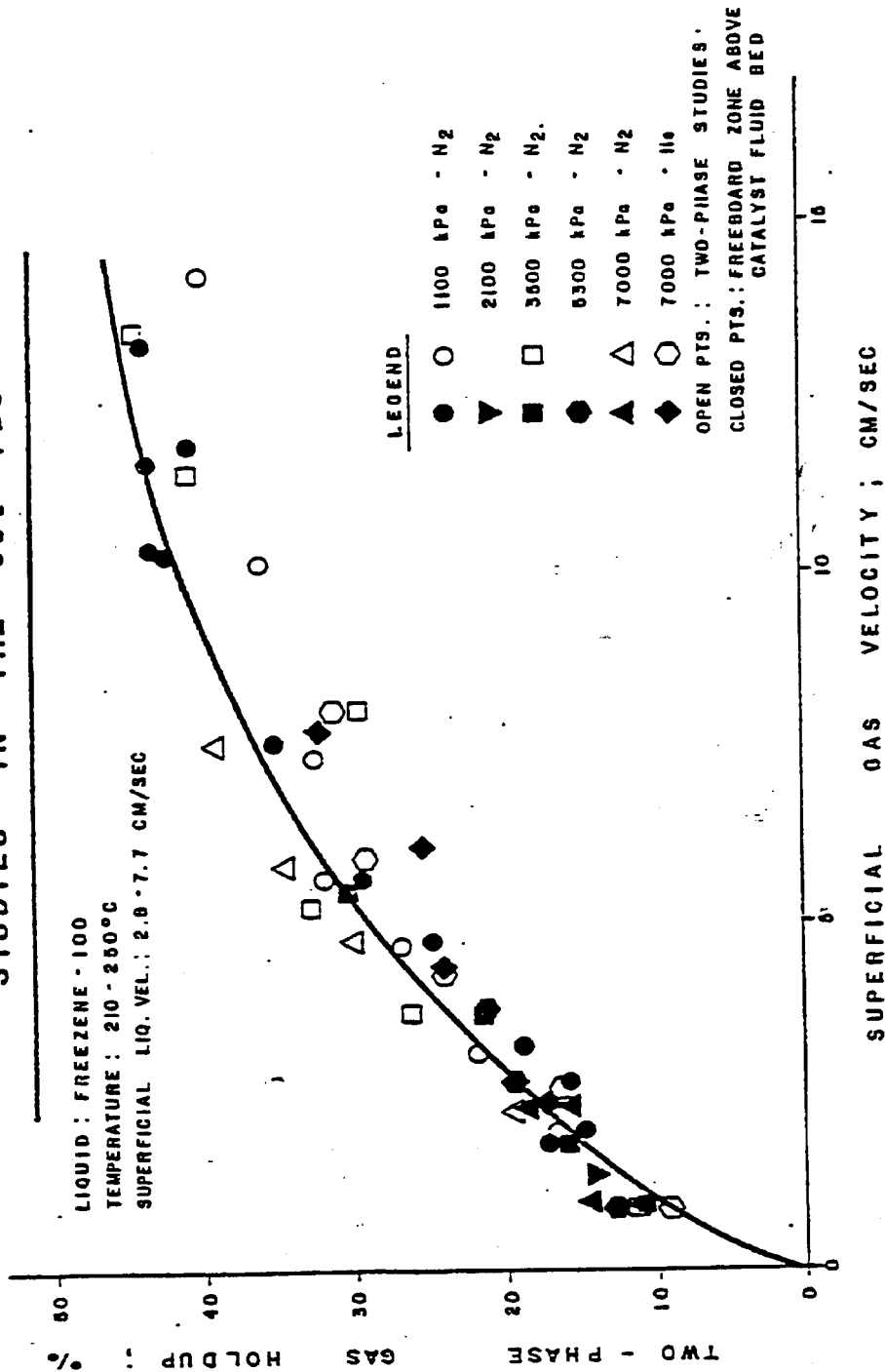


HRI COLD-FLOW TESTS ON EBULLATED CATALYST CANDIDATES

CONCLUSIONS : EPJ 19-H AND EPJ 25-H

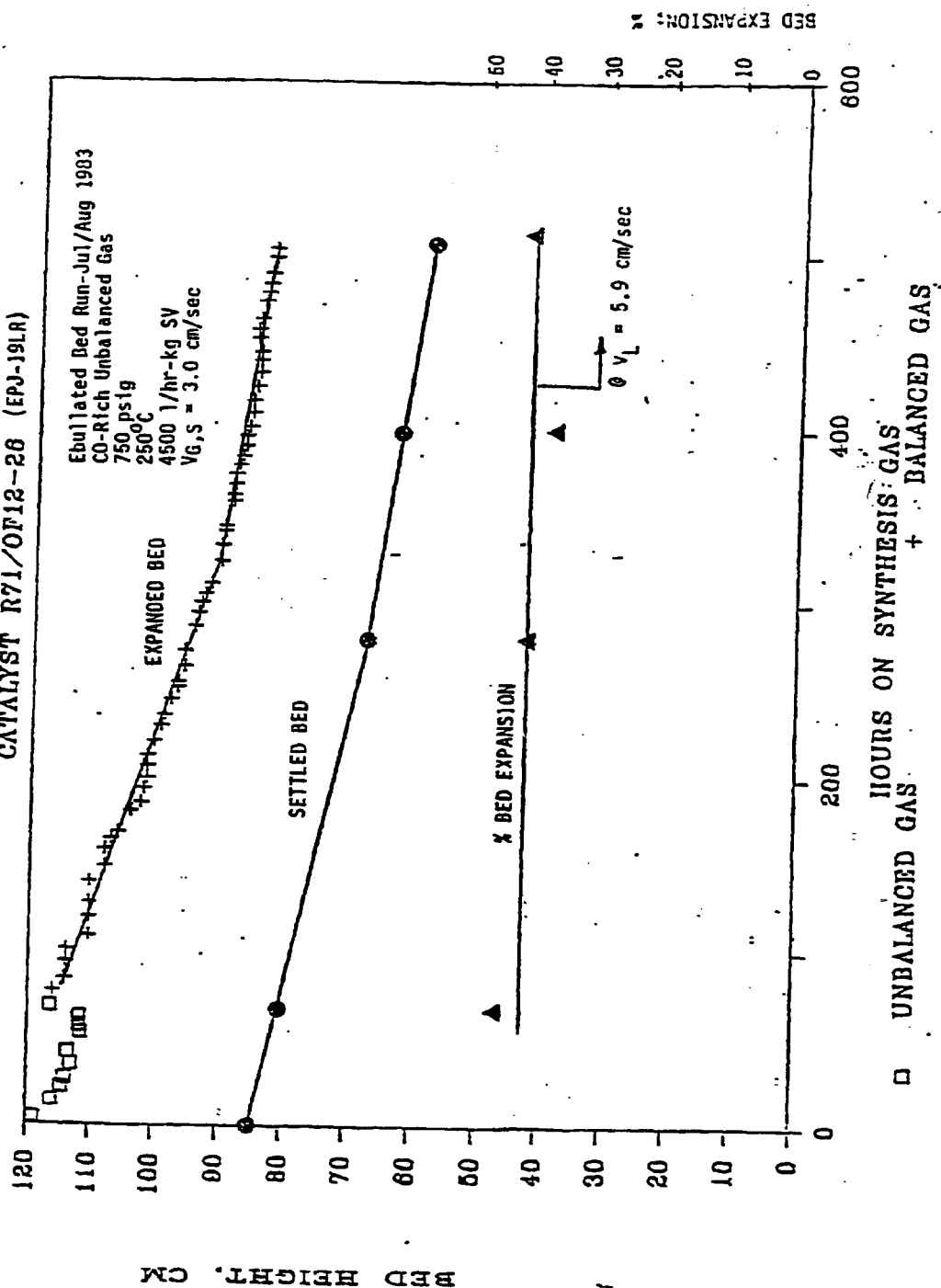
- COMPARABLE AND ACCEPTABLE ATTRITION RATES
0.5 WT% PER DAY
- FINES GENERATION PREDOMINATE
LOW STEADY STATE CARRYOVER RATE
- UNIFORM BED DENSITY FOR 19-H
SLIGHT DENSITY GRADIENT FOR 25-H
- DECREASE IN CATALYST LENGTH SEEN
NO CHANGE IN DIAMETER

GAS HOLDUP DATA DURING EXPANSION STUDIES IN THE CSI PDU



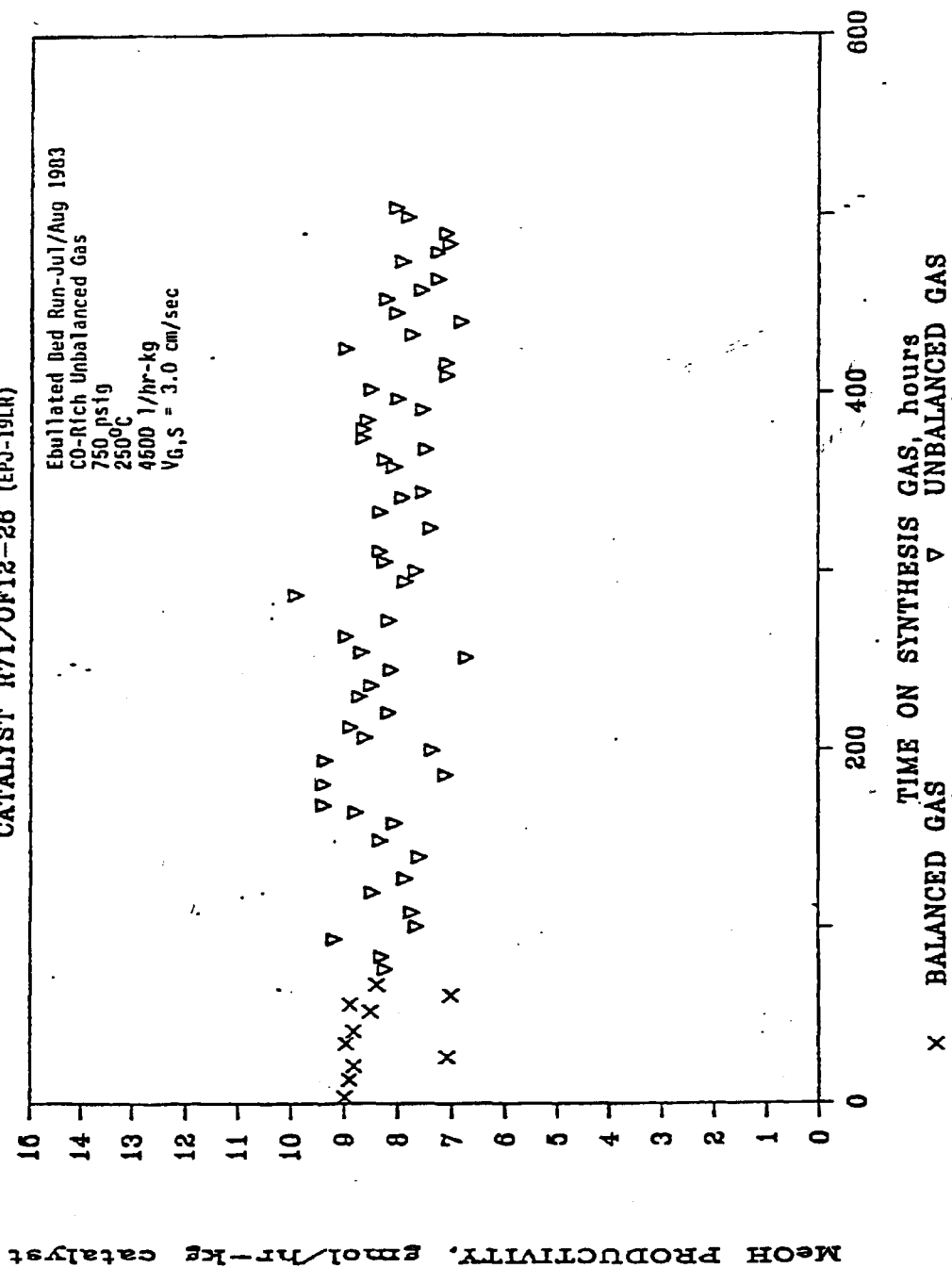
CSI LAB, PDU RUN

CATALYST R71/OF12-26 (EPJ-19LR)

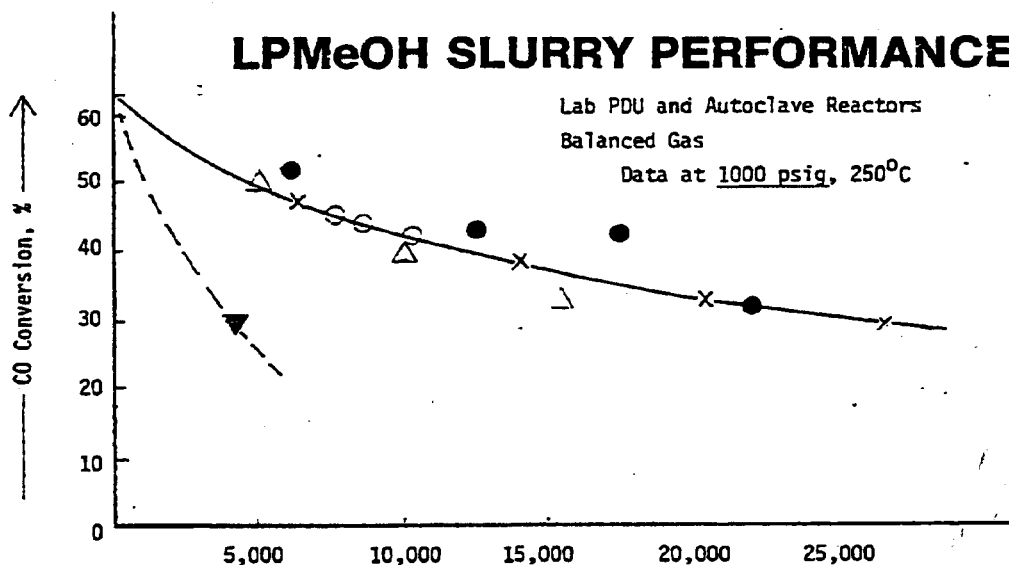


LAPORTE BATCH CHECK IN CSI LAB PDU

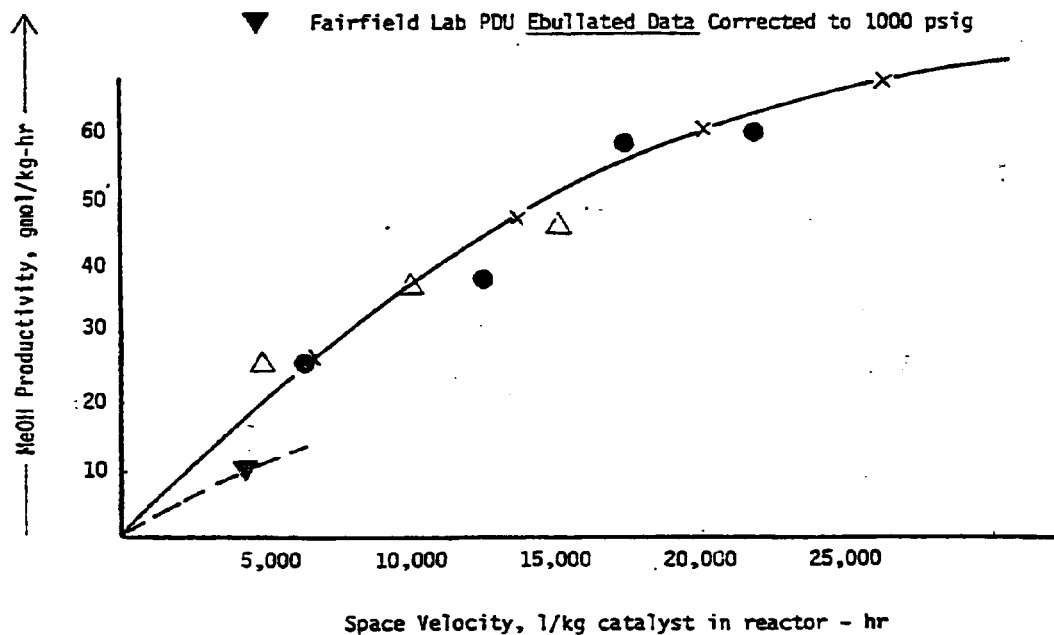
CATALYST R71/OF12-26 (EPJ-19LR)



LPM₂OH SLURRY PERFORMANCE



- Fairfield Lab DPU Data, Using Measured ϵ_g to Calculate Catalyst in the Reactor
- CSI 2-liter Autoclave data
- △ APCI 1-liter Autoclave data
- x Model Prediction for Lab PDU
- ▼ Fairfield Lab PDU Ebullated Data Corrected to 1000 psig



LAB PDU - PRELIMINARY CONCLUSIONS

- EBULLATED STILL HAS CATALYST
ATTRITION QUESTION
- ACTIVITY MAINTENANCE IN EBULLATED
LOOKS GOOD
- NO EVIDENCE OF MASS TRANSFER
EFFECTS IN PDU

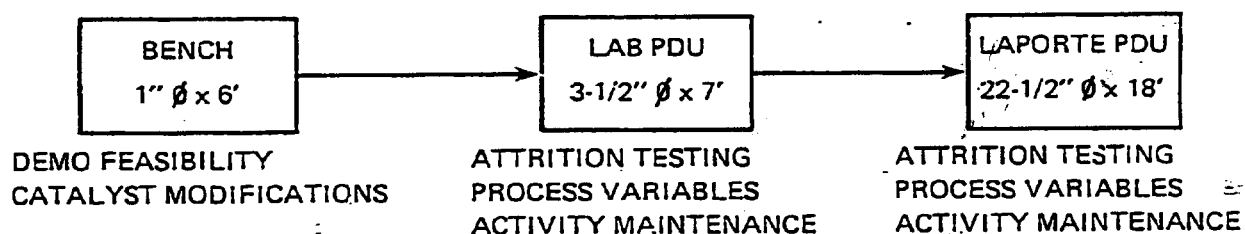
FURTHER LAB PDU

TEST OTHER EBULLATED CATALYST CANDIDATE
COMPLETE FURTHER SLURRY WORK

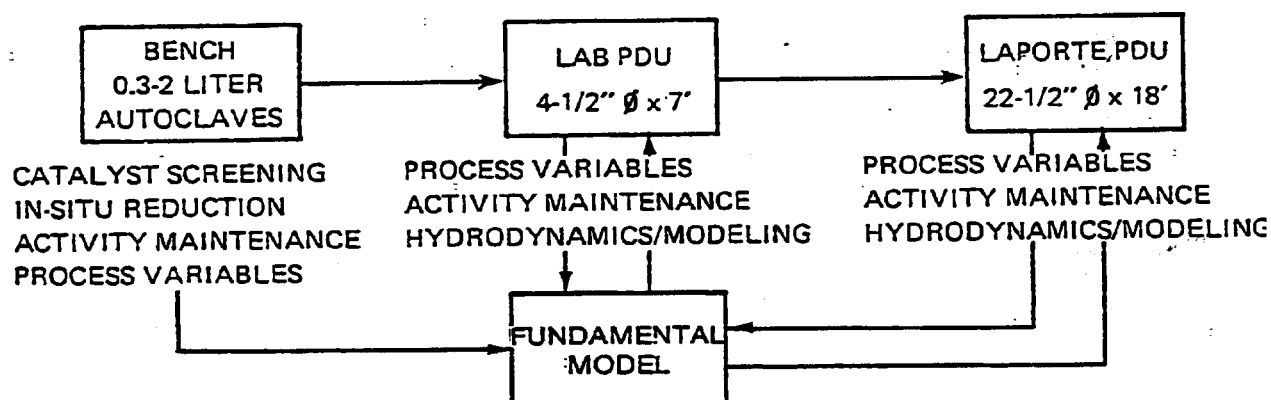
- > MAXIMIZE THROUGHPUT
- > MAXIMIZE SLURRY LOADING

LPM_eOH TECHNOLOGY DEVELOPMENT

LIQUID-FLUIDIZED (EBULLATED BED) REACTOR 1975-1983



LIQUID-ENTRAINED (SLURRY) REACTOR 1979-1983



MODELING PROGRAM

GOAL:

**CONSTRUCT A REALISTIC MATHEMATICAL MODEL WHICH
ALLOWS PREDICTION OF REACTANT CONVERSION AND
PRODUCT YIELD FOR A RANGE OF OPERATING CONDITIONS**

APPLICATIONS:

- **RECALCULATION OF PROCESS HEAT AND MATERIAL
BALANCES**
- **ASSIST IN DEFINING OPERATING CONDITIONS FOR LAPORTE**
- **USE IN COMMERCIAL LP MeOH DESIGN STUDIES AND
ONGOING ECONOMIC EVALUATIONS**

SLURRY REACTOR MODEL

THREE PHASES, MIXING BETWEEN PLUG FLOW AND PERFECTLY MIXED

- ~~DISPERSION~~ MODEL - CLOSER TO PLUG FLOW
- TANKS IN SERIES MODEL - CLOSER TO PERFECT MIXING

LAPORTE REACTOR PROBABLY CLOSER TO PERFECT MIXING
REACTOR VOLUME V DIVIDED INTO N EQUAL TANKS WHERE

$$\frac{1}{N} = 2\left(\frac{D}{VL}\right) - 2\left(\frac{D}{VL}\right)^2 (1 - e^{-VL/D})$$

WHICH FOR LARGE DISPERSIONS $N \rightarrow VL/2D$

V = SUPERFICIAL VELOCITY

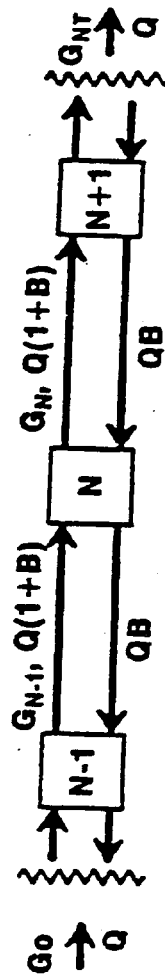
L = REACTOR LENGTH

D = DISPERSION COEFFICIENT

FOR MULTI-PHASE, NEED N FOR EACH PHASE

INTRODUCE BACKFLOW MODIFICATION

- USES A SINGLE NUMBER OF TANKS IN SERIES WITH N BASED ON THE LEAST DISPERSED PHASE
- MIXING OF OTHER PHASES DESCRIBED BY DIFFERENT DEGREES OF BACKFLOW, B

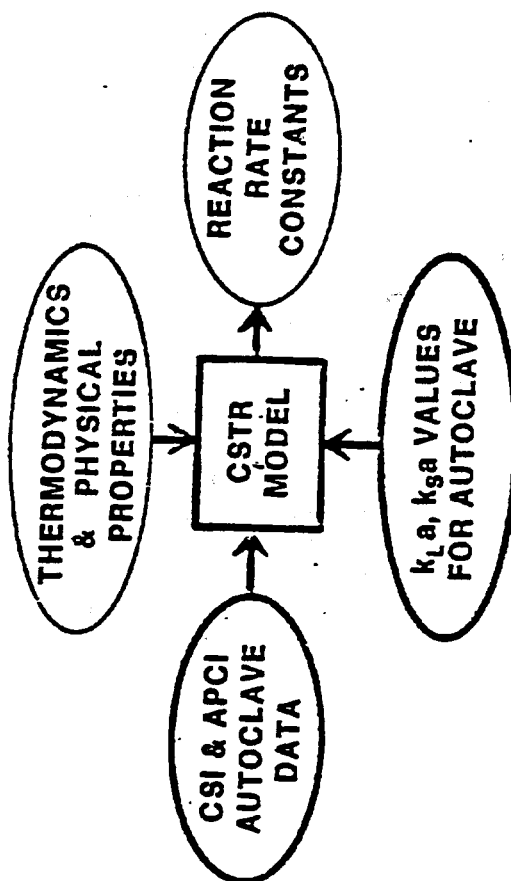


- CAN HAVE B FOR MORE THAN ONE PHASE, HENCE DESCRIBING DEGREES OF MIXING FOR ALL PHASES
- CURRENT MODEL DESCRIBES 7 TANKS IN SERIES WITH BACKFLOW RATIOS UP TO 10 AVAILABLE

REACTION RATE DATA

CSI & APCI AUTOCLAVES: ADVANCE FUNDED WORK, CURRENT DOE CONTRACT

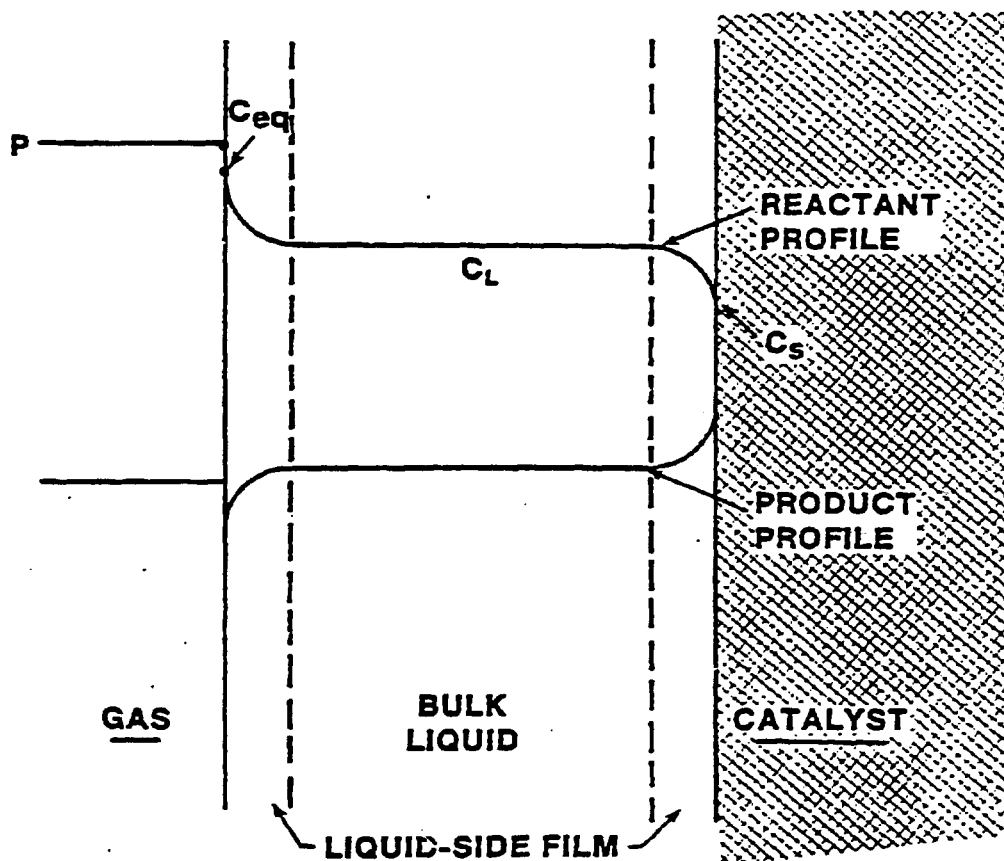
USE A CSTR MODEL TO DESCRIBE AUTOCLAVE OPERATION



ASSUMPTIONS

- WELL MIXED REACTOR
- NO INTRA PARTICLE DIFFUSION

CONCENTRATION PROFILES IN STIRRED AUTOCLAVE REACTOR



C_{eq} - LIQUID CONCENTRATION IN EQUILIBRIUM
WITH GAS

C_L - BULK LIQUID CONCENTRATION

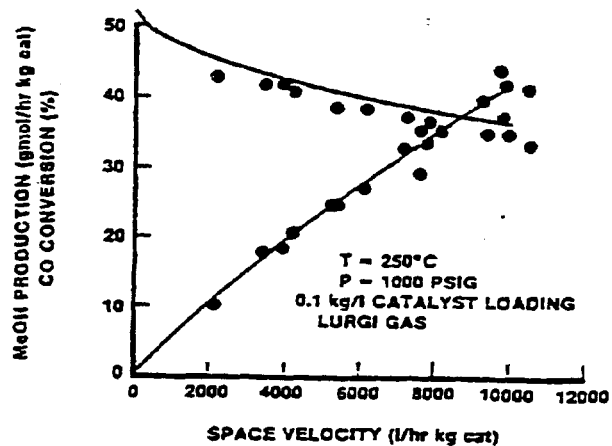
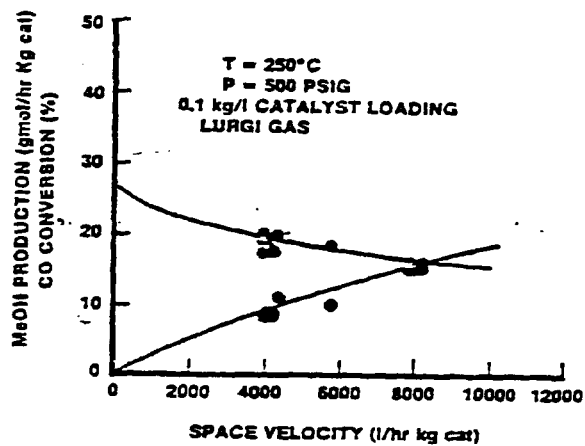
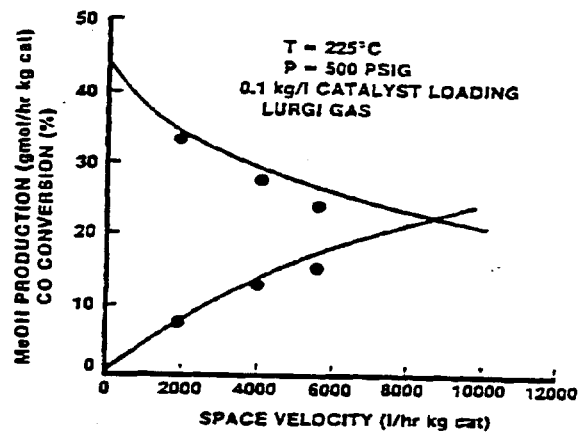
C_s = LIQUID CONCENTRATION AT CATALYST
SURFACE

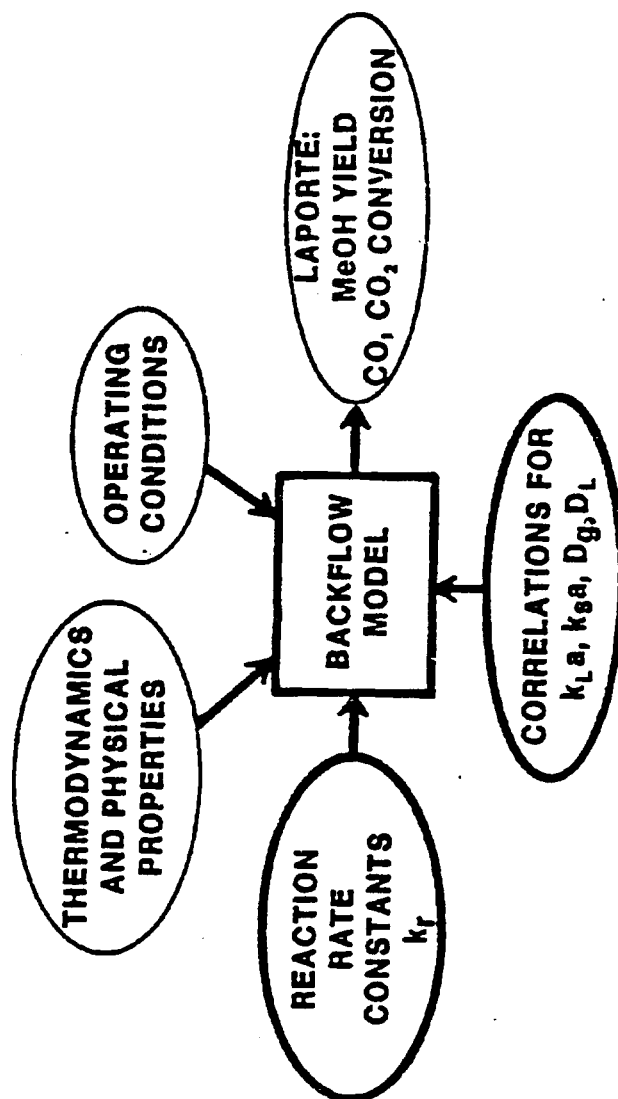
CALCULATION OF RATE CONSTANT

UNDER REACTION RATE CONTROL,

$$\begin{aligned}\text{RATE} &= k_L a (C_{eq} - C_L) \\ \text{(MEASURED)} &= k_{sa} (C_L - C_s) \\ &= k_r W_c (C_s - C_{seq})\end{aligned}$$

KNOWING $k_L a$, k_{sa} , A STEPWISE CALCULATION GIVES k_r
 k_{sa} CORRELATIONS AVAILABLE: NEED $k_L a$ DETERMINATION





NEED

- REACTION RATE CONSTANTS
- MASS TRANSFER COEFFICIENTS

LAPORTE PDU : $k_L a$ DETERMINATION

CORRELATIONS USED:

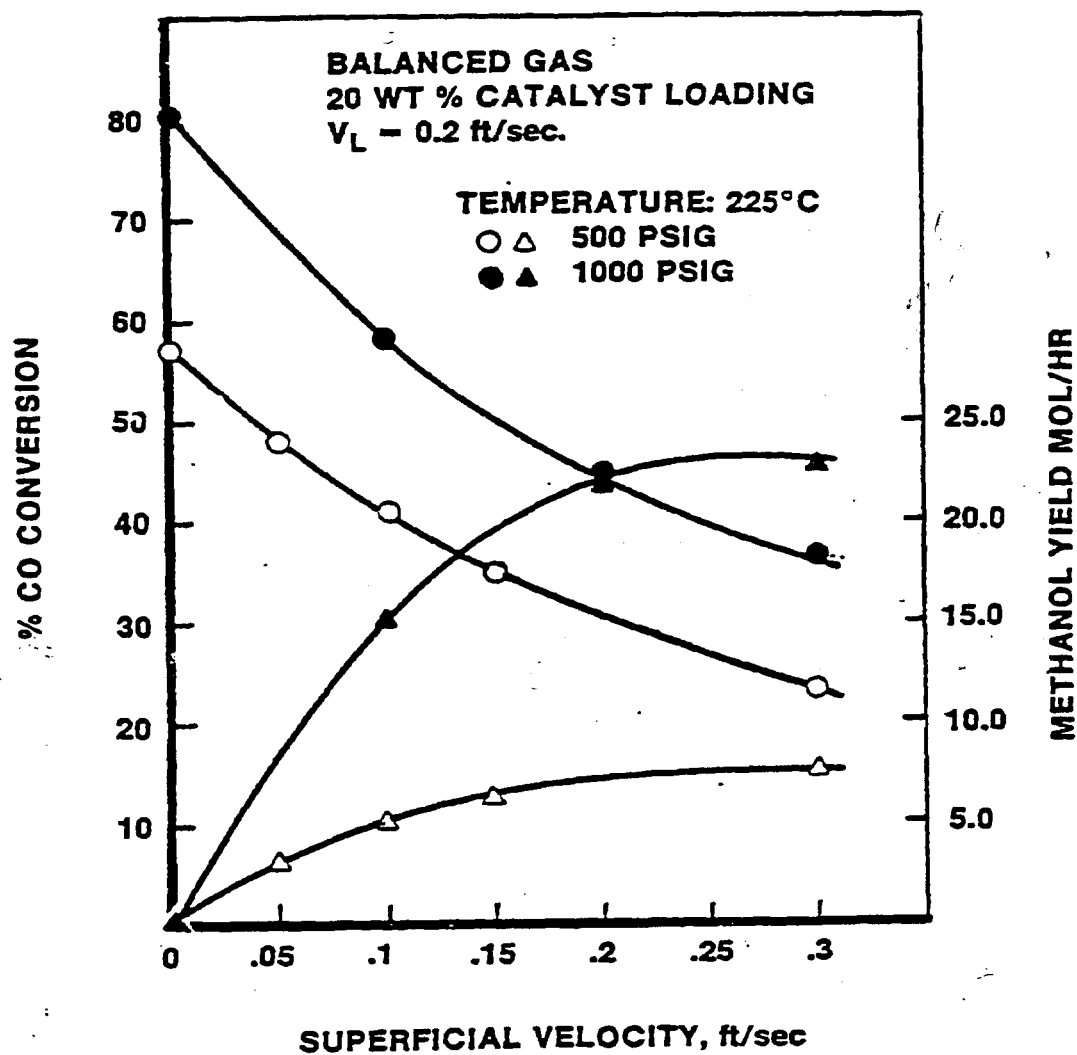
- AKITA AND YOSHIDA (1973) FOR k_{La} :

$$\frac{k_L a \cdot D_c^2}{D_i} = 0.6 \left(\frac{\nu_L}{D_i} \right)^{0.5} \cdot \left(\frac{g D_c^2 \rho_L}{\sigma} \right)^{0.62} \cdot \left(\frac{g D_c^3}{\nu_L^2} \right)^{0.31} \cdot (E_g)^{1.1}$$

- SANGER AND DECKWER (1981) FOR k_{Sa} :

$$\frac{k_{Sdp}}{D_i} = 2 + 0.545 \left(\frac{\mu_L}{\rho_L D_i} \right)^{0.33} \cdot \left(\frac{g V_g d_p^4}{\nu_L^3} \right)^{0.264}$$

- THE GAS HOLD-UP, E_g , IS CALCULATED FROM CSI'S PDU RESULTS,
 $E_g = 0.5 (1 - \exp(-0.1735 V_g))$



LPMethOH SLURRY PERFORMANCE

Lab PDU and Autoclave Reactors
Balanced Gas
Data at 1000 psig, 250°C

CO Conversion, %

Time, min

Time (min)	CO Conversion (%)	Symbol
0	60	Start of Run
5000	29	▲
6000	49	△
7000	51	●
7500	46	×
8500	44	○
9500	43	○
10500	38	△
11000	41	○
13000	42	●
14500	37	×
18000	41	●
20500	32	×
22000	31	●
24500	28	×

Balanced Gas

Data at 1000 psig, 250°C

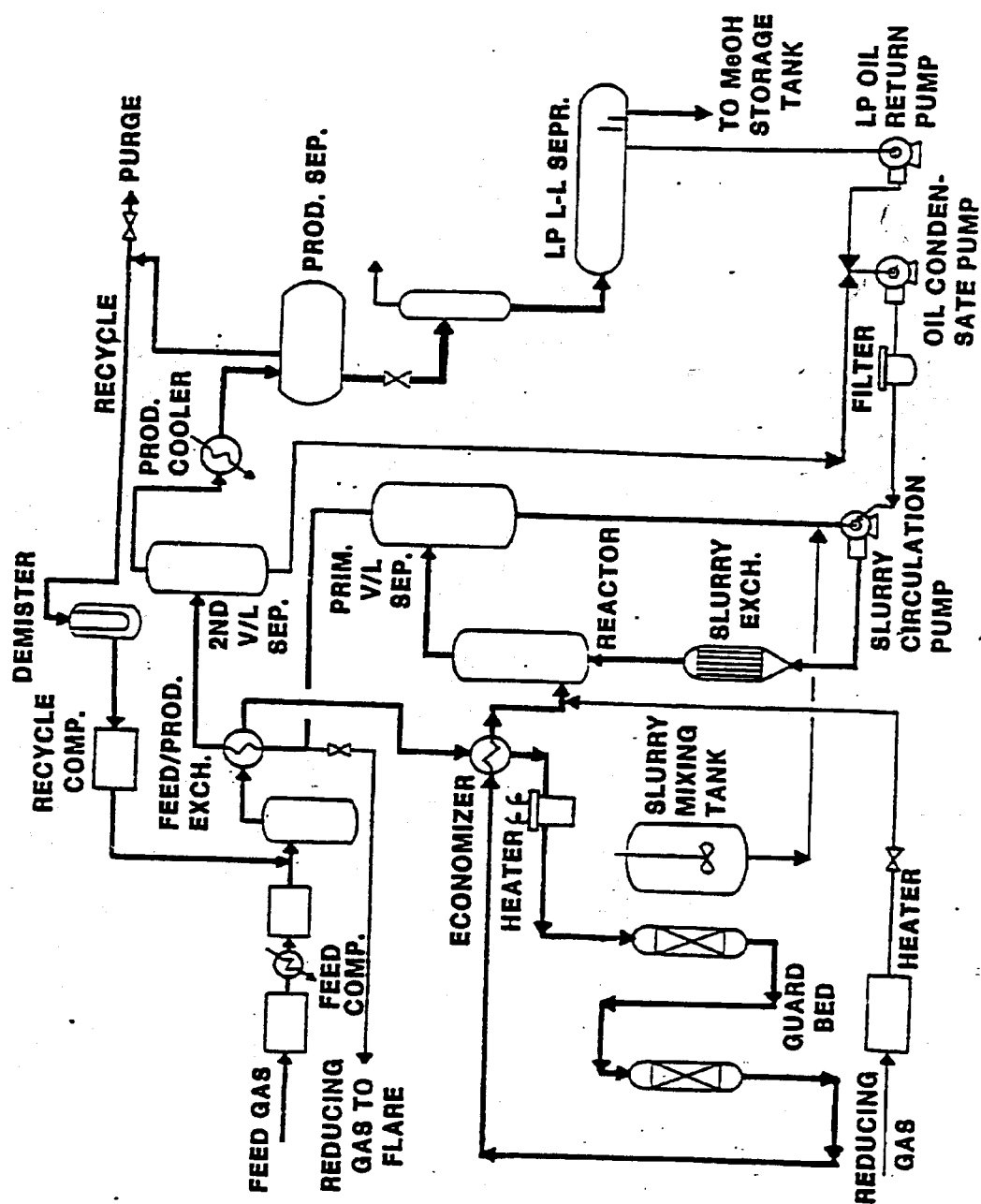
- Fairfield Lab DPU Data, Using Measured ϵ_g to Calculate Catalyst in the Reactor
- CSI 2-liter Autoclave data
- △ APCI 1-liter Autoclave data
- x Model Prediction for Lab DPU
- ▼ Fairfield Lab DPU Ebullated Data Corrected to 1000 psig

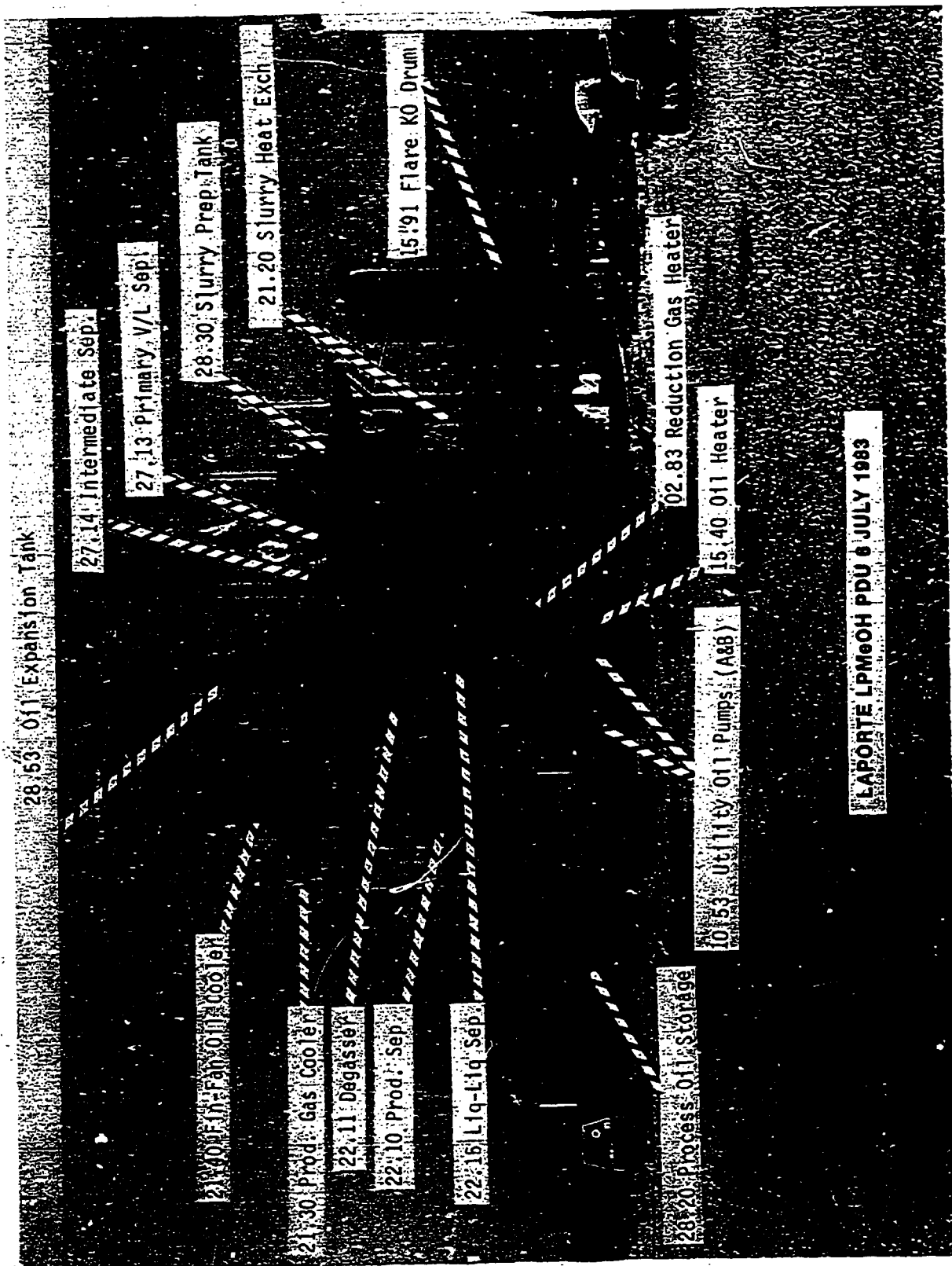


LAPORTE LPMeOH PDU ENGINEERING STATUS

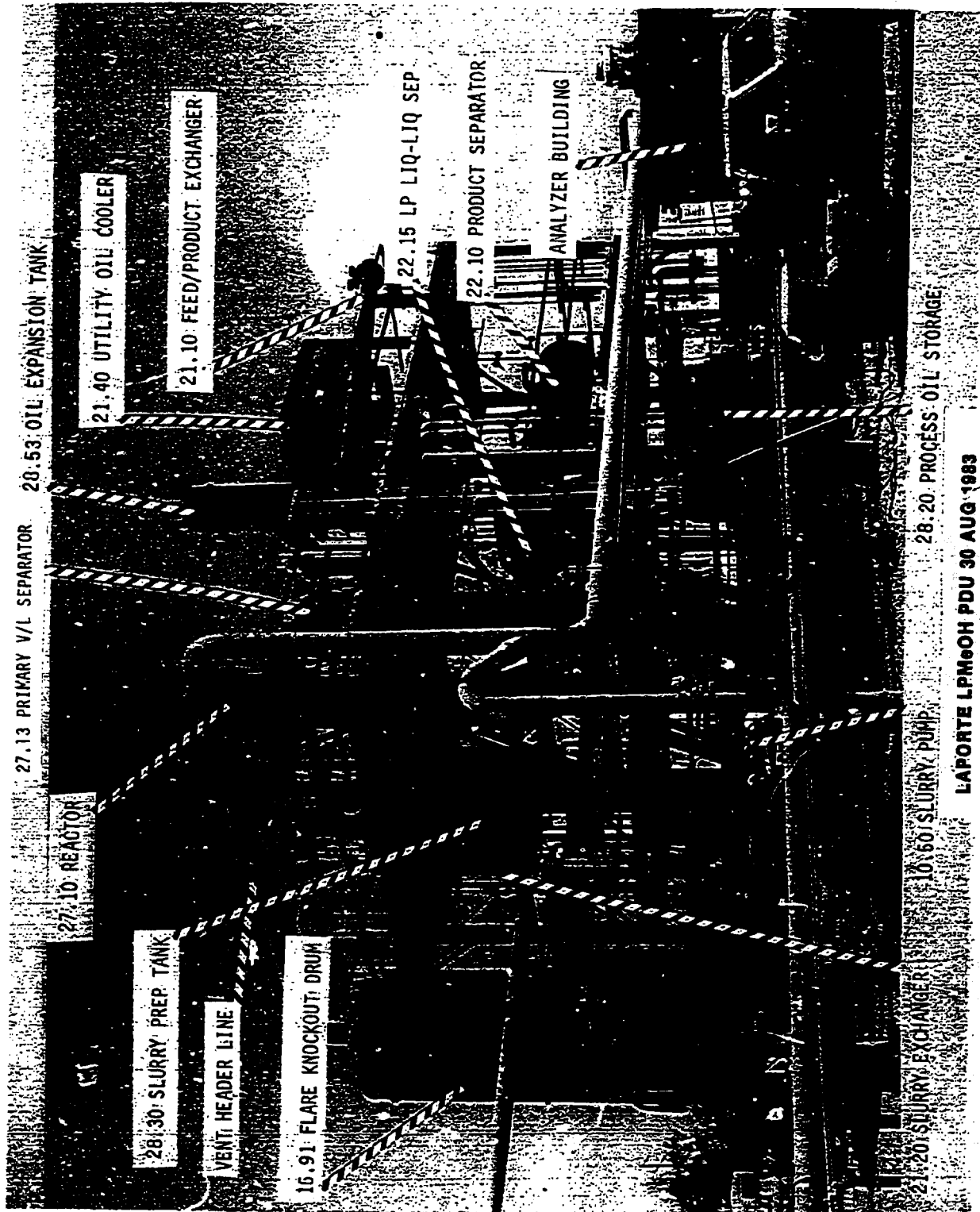
• LPM UNIT RELOCATION/ INSPECTION	COMPLETE
• PROCESS	COMPLETE
• EQUIPMENT	COMPLETE
• MECHANICAL	95% COMPLETE
• INSTRUMENTATION/ELECTRICAL	60% COMPLETE

SIMPLIFIED PROCESS FLOWSHEET FOR LAPORTE LP MeOH PDU





LAPORTE LPMEOH PDU 6 JULY 1983



LAPORTE LPM6OH PDU 30 AUG 1983