COAL LIQUEFACTION AND GAS CONVERSION CONTRACTORS' REVIEW CONFERENCE

TITLE: Development of Alternative Fuels and Chemicals From Synthesis Gas

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Institution/Organization: Air Products and Chemicals, Inc.
Allentown, PA 18195

Contract Number: DE-AC22-91PC90018

Period of Performance: 1991 - 1993

Objective: The principal objective of this program is to investigate potential technologies for the conversion of synthesis gas derived from coal and other fossil energy sources, to oxygenated fuels, hydrocarbon fuels, fuel intermediates and octane enhancers. The most promising technologies will be demonstrated at DOE's Slurry Phase Alternative Fuels Development Unit (AFDU) in LaPorte, Texas.

ABSTRACT

Air Products and Chemicals, Inc. (APCI) has progressed into the third year of a four-year Alternative Fuels program with the DOE. In the past two years, a number of new process technologies that convert coal-derived syngas to liquid fuels have been demonstrated at DOE's Alternative Fuels Development Unit (AFDU), located at LaPorte, Texas. The demonstrations required a scale-up of different technologies derived from bench-scale investigations of slurry-phase processes to a 22.5" (ID) diameter slurry bubble column.

A single-step slurry-phase process for coproduction of dimethyl-ether (DME) and methanol, important fuels and chemical building-blocks, was demonstrated at the AFDU in 1991. Combining three reversible actions - methanol synthesis, methanol dehydration and water-gas shift reactions in a single reactor drives each reaction thermodynamically by removing its inhibiting products as reactants in the subsequent reaction. Substantial increase in per-pass syngas conversion (by at least 30% at commercial space velocities) was demonstrated by mixing a small amount of dehydration catalyst with a methanol catalyst.

A new slurry-phase, water gas shift process was demonstrated at the AFDU in the spring of 1992. Hydrogen generation via water-gas shift is important for complete conversion of coal-derived CO-rich syngas to liquid fuels. Many catalysts, such as copper-based methanol catalyst and iron-based Fischer-Tropsch (F-T) catalysts possess shift activity in addition to their primary fuel producing activity; others such as cobalt-based F-T catalyst, do not. Those catalysts which lack shift activity can be combined in a physical mixture with a shift catalyst to enhance syngas conversion in hydrogen deficient systems. The demonstration indicated good catalyst activity and excellent bubble column performance.

Slurry-phase Fischer-Tropsch technology was demonstrated at the AFDU in the summer of 1992. This run was sponsored by a number of industrial participants (Air Products, Exxon, Shell, Statoil and UOP), in addition to DOE. The 19-day run addressed scale-up issues such as catalyst activation, reactor performance and hydrodynamics. Stable catalyst productivity, expected hydrodynamic behavior and isothermal reactor operation were obtained, and correlation between laboratory autoclave and AFDU bubble column data was excellent.

UNITED STATES ENERGY INDEPENDENCE THROUGH THE PROCESSING OF FOSSIL FUELS

"THE LPMEOH AND ALTERNATIVE FUELS ORCHESTRA"

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LIQUID PHASE METHANOL AND ALTERNATIVE FUELS

The Path to Clean Burning Oxygenated Fuels

1981 First LPMEOH Contract begins (LP-I), basic R & D

1983 5 TPD pilot plant constructed at LaPorte, Texas

1984 1st Operating Campaign
Proof-Of-Concept

1985 2nd Operating Campaign (LP-II)
Defined process capabilities, catalyst life

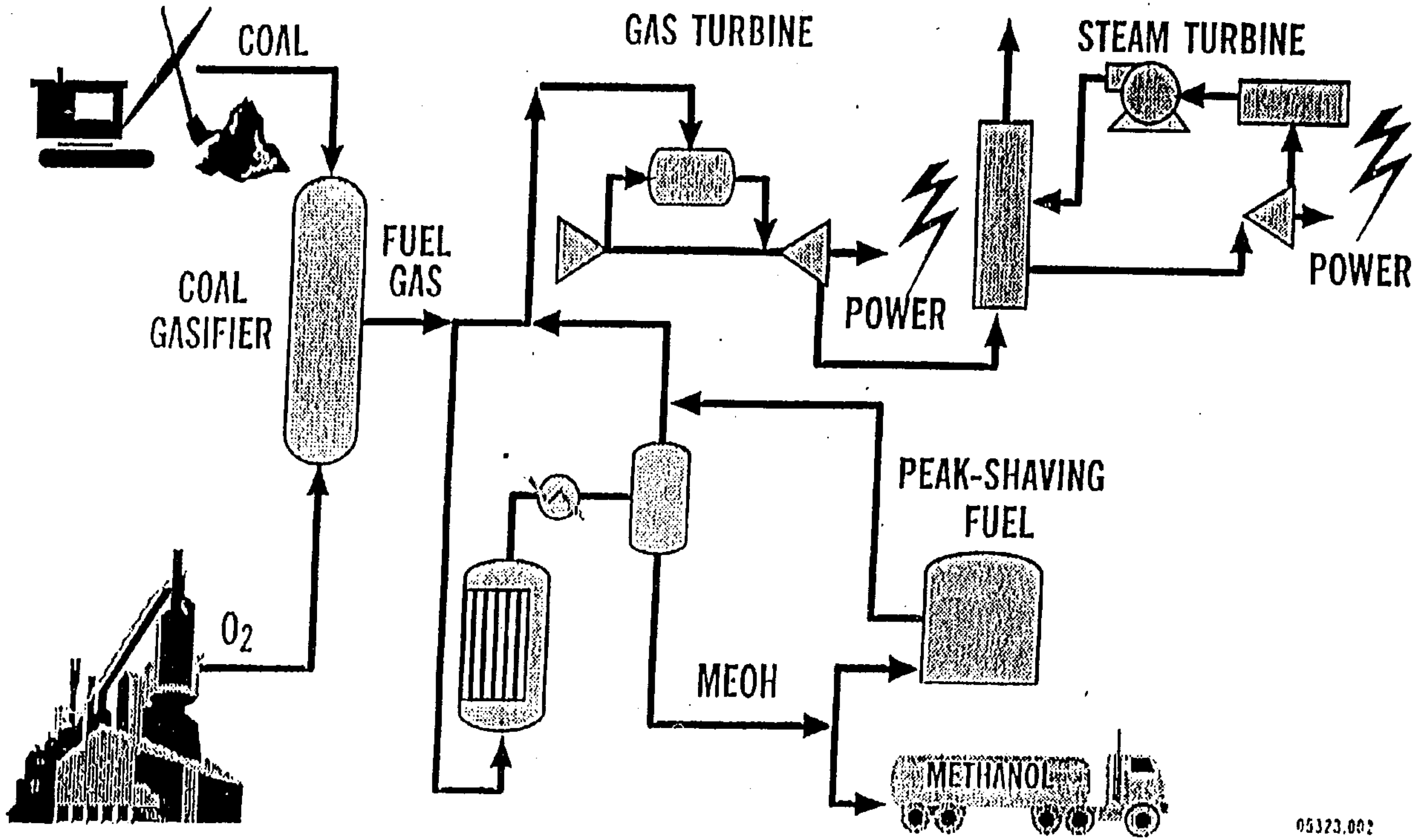
1988 – 89 3rd Operating Campaign (LP-III)
Commercially attractive, aggressive conditions
Up to 13 TPD

1990 – 96 Selected for negotiation under Clean Coal Technology Program to commercialize Liquid Phase Methanol Process at an appropriate third party site.

1990 – 93 Alternative Fuels Contract: New Oxygenated Fuels Directly from LPMEOH Technology
R & D with Process Demonstration at LaPorte Facility

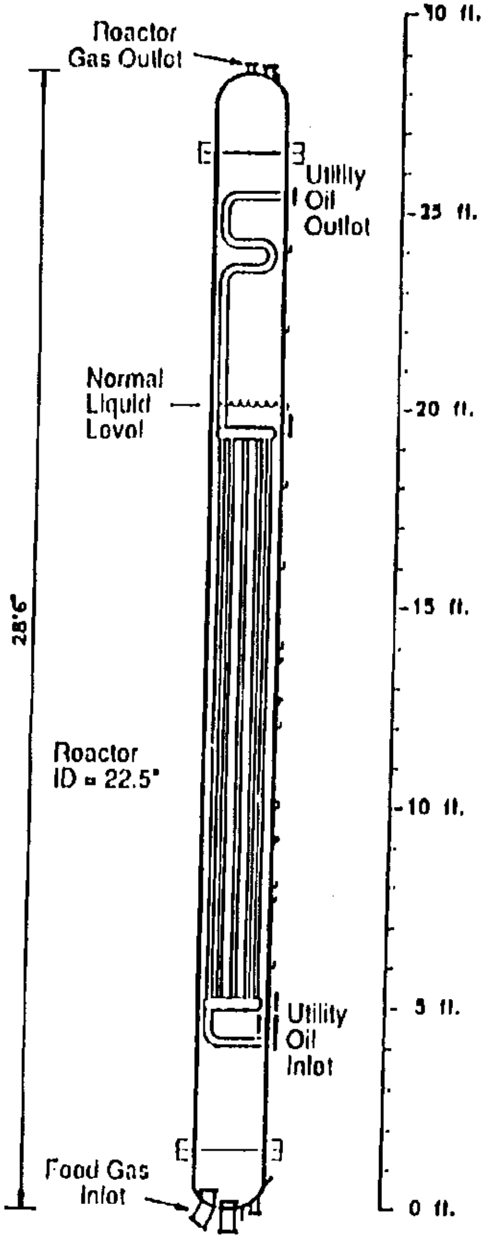
- *1991* One-step synthesis of Dimethyl Ether (DME) demonstrated at LaPorte
- *1991* New isobutanol catalyst developed
- *1992* Demonstration of Liquid Phase Shift (LPS) at LaPorte
- *1992* Slurry Phase Fischer-Tropsch successfully demonstrated at LaPorte: significant private sector participation.

POWER AND COPRODUCT METHANOL FROM COAL GASIFICATION COMBINED CYCLE (CGCC)



ESTIMATED COMPOSITION OF METHANOL FROM LPMEOH DEMONSTRATION PROJECT AT TEXACO COOL WATER PROJECT

Composition (wt%)	Beginning of Catalyst Life (BOL)	End of Catalyst Life (EOL)
Methanol	97.106	97.675
Dissolved gasses	0.090	0.090
Water	0.343	0.580
Dimethyl Ether	0.002	0.002
Methyl Formate	1.181	0.909
Methyl Acetate	0.138	0.049
Ethanol	0.582	0.308
n-Propanol	0.217	0.116
sec-Butanol	0.023	0.017
Isobutanol	0.034	0.000
n-Butanol	0.124	0.064
Isopentanol	0.034	0.000
1-Pentanol	0.068	0.041
Oil	0.150	0.150
Total Alcohols	98.096	98.221
Other Alcohols	1.080	0.546
Other Alcohols & Ethers	1.082	0.547
Molecular Weight	32.35	32.08
Reid Vapor Pressure	5.4	5.4
Density at 25°C	0.7989	0.7949

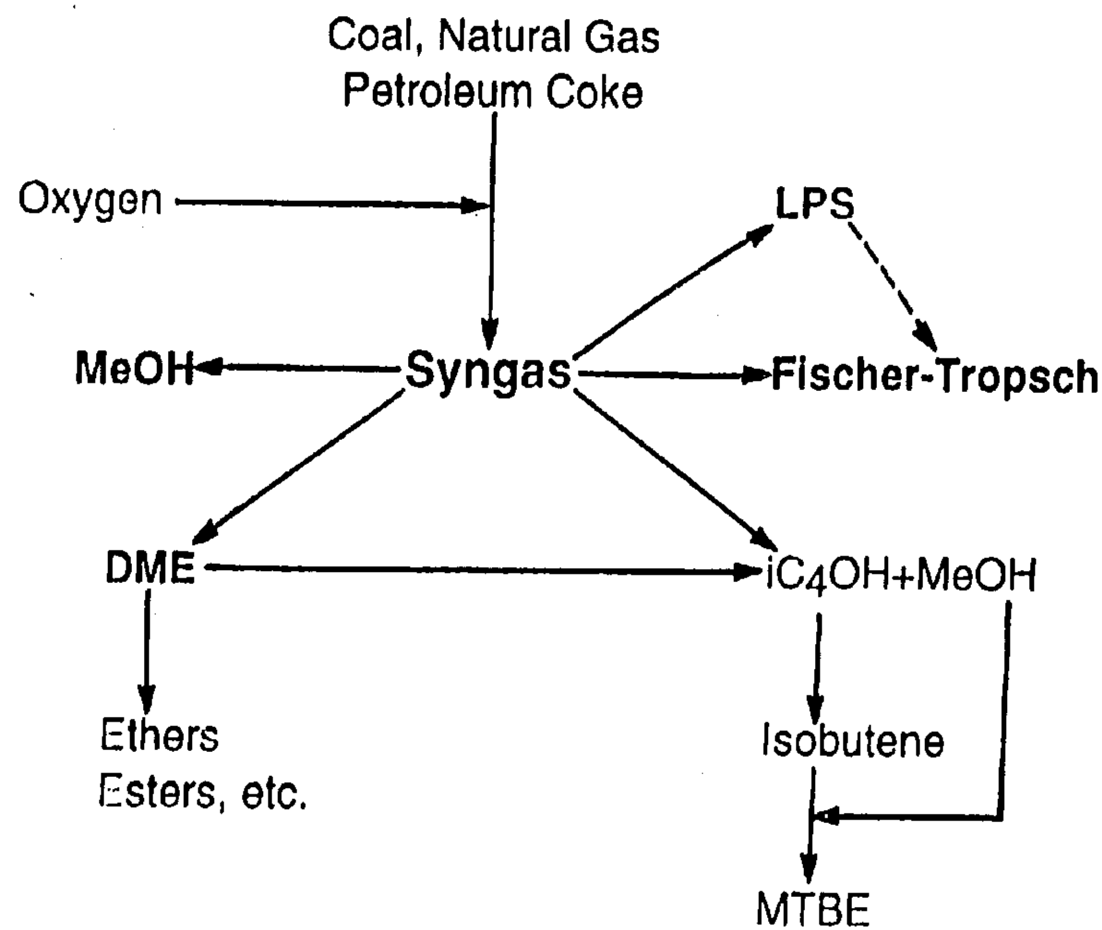


LaPorte AFDU Reactor

Demonstrated Range of Operating Variables

		Minimum	Typical	Maximum
Reactor Pressure,	psia	500	750	900
	kPa	3,500	5,300	6,300
Reactor Temperature,	°F	428	482	545
	°C	220	250	285
Space Velocity,	Sl/hr-kg cat. ox.	2,000	10,000	17,500
Superficial Inlet Gas Velocity,	ft/sec	0.13	0.50	0.72
Catalyst Loading,	wt% ox.	20	35	50
Slurry Level,	% of normal	64	100	100
	L/D	6.8	10.6	10.6
Feed Gas Composition				
H_2/CO Ratio		0.49	0.69	3.94
CO_2 Concentration,	mol %	0.94	13.0	18.1
H_2O Concentration,	mol %	--	--	1.82
Methanol Production Rate,	TPD	1.4	10.0	12.8

SYNGAS TO FUELS AND CHEMICALS



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DME PROCESS CHEMISTRY

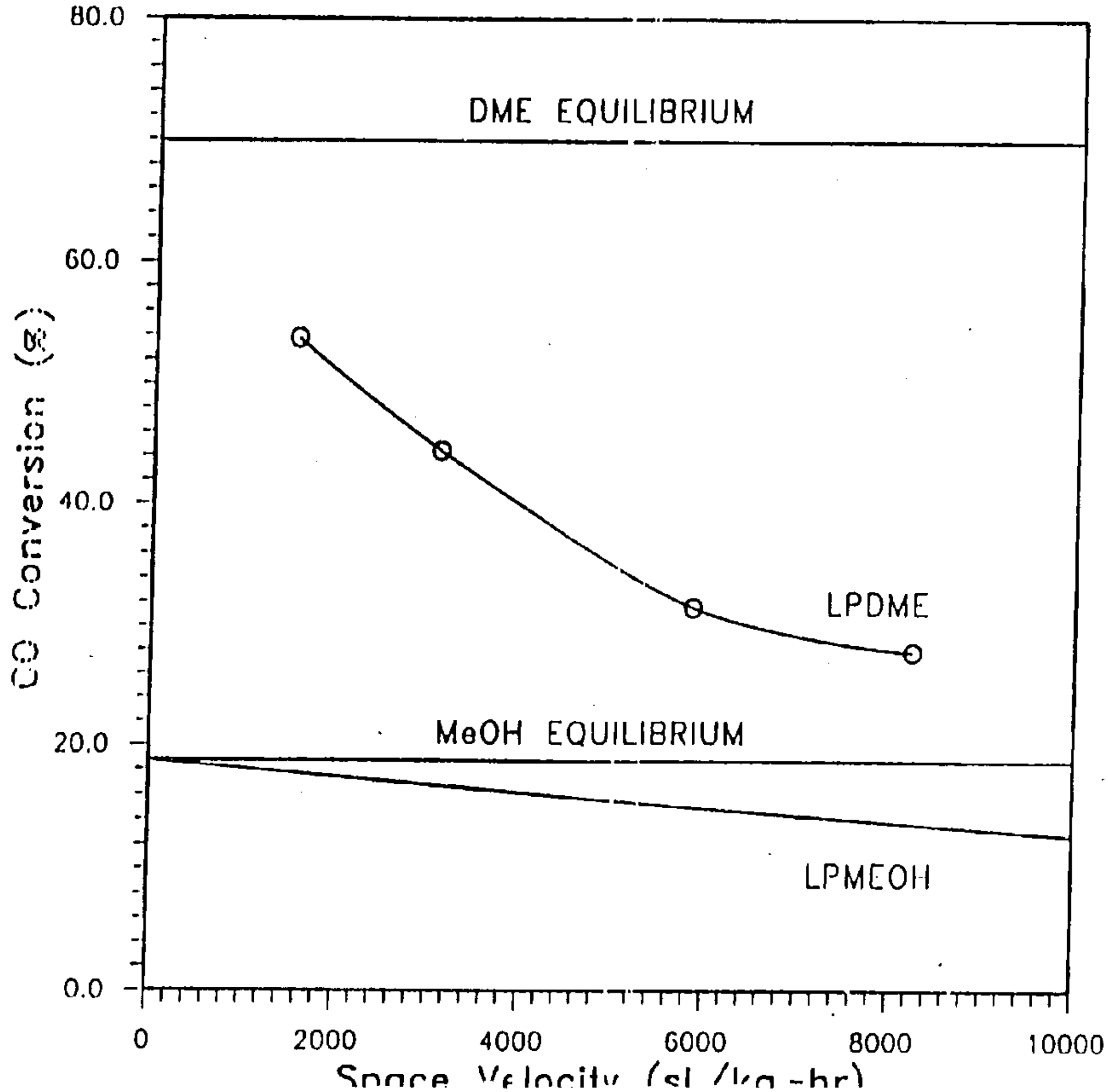
		HEAT OF REACTION AT 298^{o}K, (KCAL/GMOLE)
WATER-GAS SHIFT:	$x\,CO + x\,H_2O \Longleftrightarrow x\,CO_2 + x\,H_2$	- 9.8
MEOH SYNTHESIS:	$y\,CO + 2y\,H_2 \Longleftrightarrow y\,CH_3OH$	- 21.7
MEOH DEHYDRATION:	$2\,CH_3OH \Longleftrightarrow CH_3OCH_3 + H_2O$	- 4.7

NET REACTION: $(x+y)\,CO + (2y-x)\,H_2 \Longleftrightarrow CH_3OCH_3 + x\,CO_2 + (y-2)\,CH_3OH + (1-x)\,H_2O$

- REACTION SYNERGY: INCREASE THERMODYNAMIC EQUILIBRIUM CONVERSION

FIGURE 4

Comparison of LFDME and LPMEOH
(Texaco Gas, 250 C, 5.27 MPa)



PRINCIPAL APPLICATIONS FOR DME PRODUCT

CGCC:	HIGHER SYNGAS CONVERSION TO LIQUIDS. MORE STORABLE FUEL FOR PEAK-SHAVING APPLICATION.
TRANSPORTATION FUELS:	IGNITION PROMOTER IN M-100 APPLICATIONS. (Methanol Replacement for Diesel)
AEROSOLS:	MARKET DEVELOPING; EUROPEAN INTEREST STRONGER THAN IN U.S.
FEEDSTOCK FOR OTHER FUELS AND CHEMICALS:	ALTERNATIVE TO MEOH AS A CHEMICAL BUILDING BLOCK (e.g., Simplifies Mobil's MTG Process). Concept: DME + unreacted synthesis gas may be better than MEOH or DME alone.

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LIQUID PHASE SHIFT PROCESS

<u>WATER-GAS SHIFT REACTION:</u>

$CO + H_2O \Longleftrightarrow CO_2 + H_2$ ΔH @ 523°K = - 9.4 KCAL/GMOLE

<u>APPLICATIONS:</u>

- ABILITY TO EFFECTIVELY PROCESS CO-RICH GAS.

  EXAMPLE - REFORMER OPERATIONS IN AMMONIA PLANT. OFFERS AN EFFECTIVE ALTERNATIVE TO THE CONVENTIONAL TWO-STEP WGS BY AVOIDING FISCHER-TROPSCH PRODUCT FORMATION IN HTS.

- PROVIDE SHIFT ACTIVITY IN SLURRY PHASE.

  EXAMPLES - ALCOHOL SYNTHESIS AND FISCHER-TROPSCH SYNTHESIS. MIXING SHIFT CATALYST WITH PRIMARY CATALYST IN SLURRY SHIFTS THE CO-RICH FEED TOWARDS STOICHIOMETRICALLY REQUIRED COMPOSITION (H_2:CO = 2).

LIQUID PHASE SHIFT DEMONSTRATION (APRIL 1992)

<u>OBJECTIVES:</u>

- DEMONSTRATE TECHNICAL FEASIBILITY OF THE LPS PROCESS
- PROVIDE BASIS FOR FUTURE CO-CATALYST INVESTIGATIONS

<u>RUN CONDITIONS:</u>

CATALYST USED = BASF K3-110, COPPER-BASED COMMERCIAL LOW TEMPERATURE SHIFT CATALYST
CATALYST CHARGE = 254 KG (560 LB)
REACTOR TEMPERATURE = 251°C (483°F)
REACTOR PRESSURE = 308 - 450 PSIG
RATE OF STEAM ADDITION ADJUSTED TO ACHIEVE A DESIRED H_2:CO RATIO IN EFFLUENT (TYPICALLY 1:1 OR 2:1)

LPS DEMONSTRATION RESULTS
(REACTOR TEMPERATURE = 483°F)

FEED GAS COMP. ($H_2/CO/CO_2/N_2$) (MOLE%)	H_2:CO RATIO IN REACT. EFFLUENT	PRESS. (PSIG)	SPACE VEL., SL/KG-HR	H_2O:CO RATIO IN REACT. INLET	WATER CONV. (%)	FRACT. OF EQUL. H_2O CONV
TEXACO (37/50/12.7/0.3)	1:1	450	11,200	0.15	84.4	0.87
TEXACO	2:1	445	10,800	0.48	80.4	0.84
SHELL (31/66/2.7/0.3)	1:1	430	6,900	0.31	97.1	0.99
SHELL	2:1	430	6,600	0.54	95.0	0.98
H2 LEAN (1/71/14/14)	2:1	390	6,300	0.75	88.8	0.92
POX (61/37/1.7/0.3)	13:1	310	6,300	1.45	55.4	0.86
POX	40:1	365	4,800	1.85	50.8	0.97

LIQUID PHASE F-T DEMONSTRATION (AUGUST 1992)

<u>SPONSORSHIP:</u>

DOE, AIR PRODUCTS, EXXON, SHELL OIL, STATOIL & UOP.

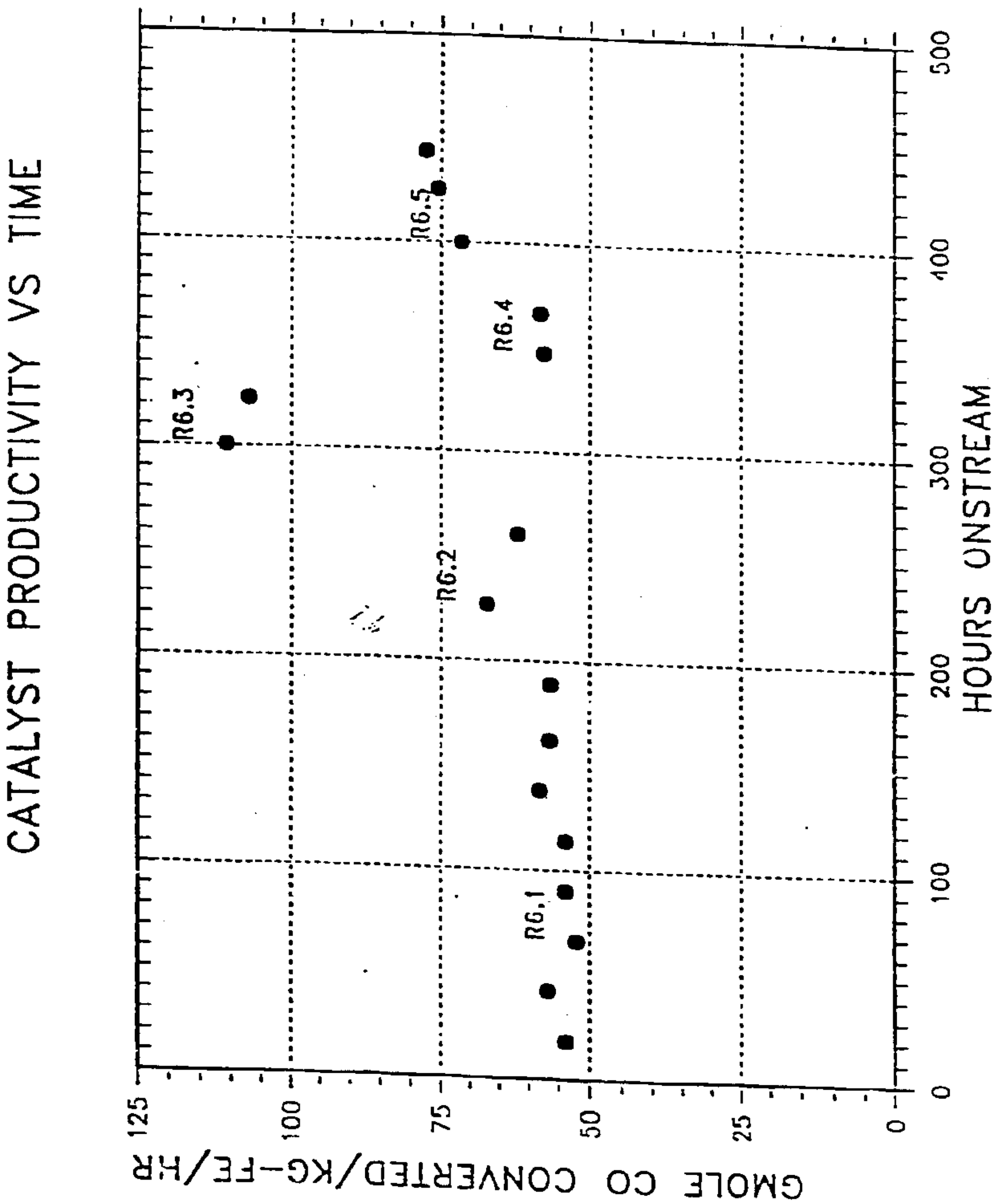
<u>OBJECTIVES:</u>

TO DEMONSTRATE F-T TECHNOLOGY AT A PILOT SCALE (0.7 T/D PRODUCT) IN A BUBBLE COLUMN REACTOR AND ADDRESS SCALE-UP ISSUES SUCH AS:

- CATALYST ACTIVATION
- CATALYST PERFORMANCE
- HYDRODYNAMICS

<u>CRITERIA OF SUCCESS IDENTIFIED BY PARTNERS AS:</u>

- HIGH NUMBER OF DAYS ON-STREAM
- GOOD CATALYST ACTIVITY - CO CONVERSION AT LEAST 50%
- STABLE REACTOR PERFORMANCE
- GOOD CORRELATION BETWEEN BUBBLE COLUMN AND AUTOCLAVE



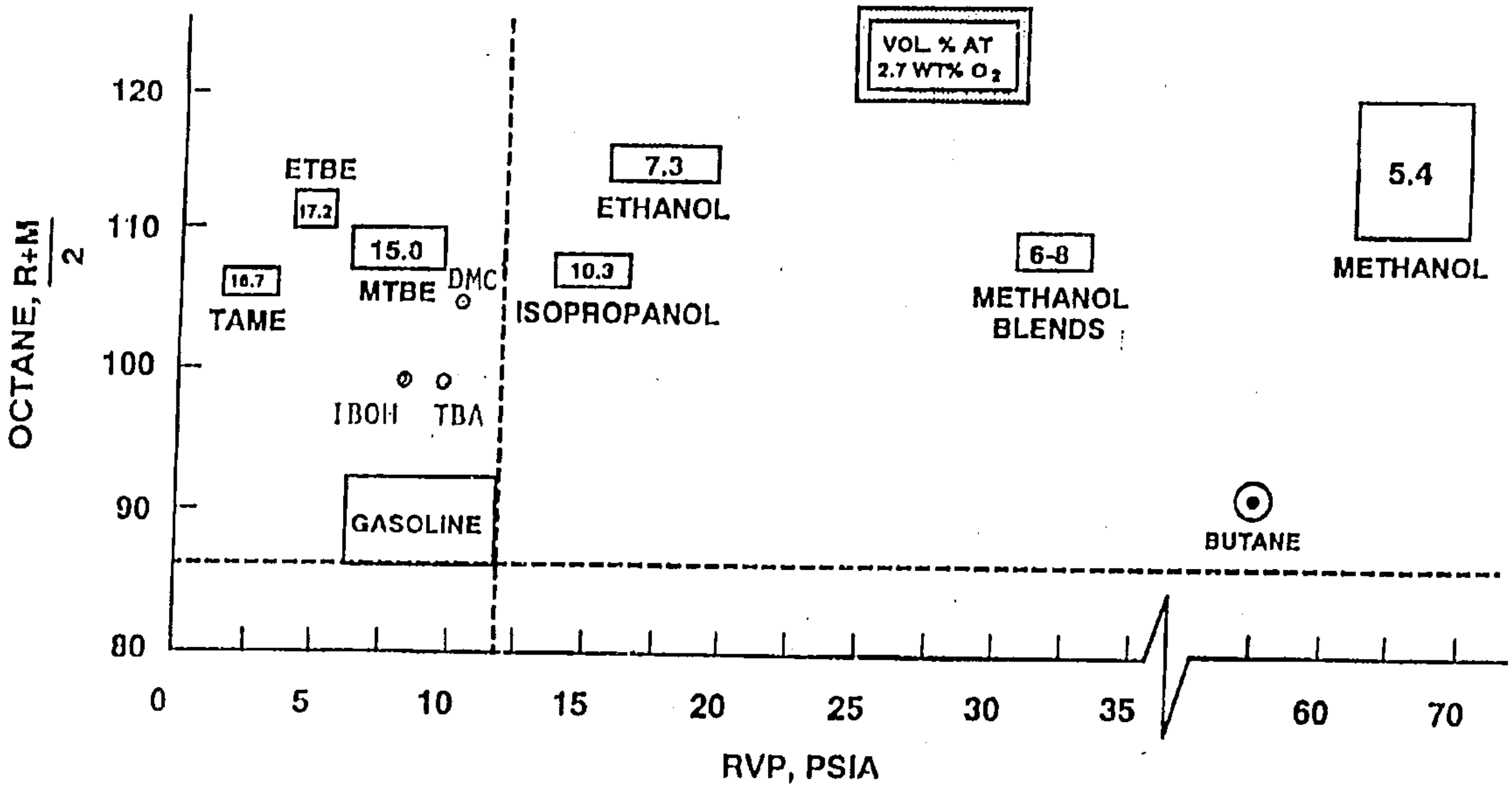
CATALYST PRODUCTIVITY VS TIME
GMOLE CO CONVERTED/KG-FE/HR
HOURS ONSTREAM
0
25
50
75
100
125
0
100
200
300
400
500
R6.1
R6.2
R6.3
R6.4
R6.5

SUMMARY OF F-T RESULTS

- DEMONSTRATED LIQUID PHASE F-T TECHNOLOGY AT PILOT SCALE. ACHIEVED SUCCESSFUL CATALYST ACTIVATION AND OBTAINED STABLE CATALYST PRODUCTIVITY.
- ATTAINED ISOTHERMAL REACTOR OPERATION AND OBTAINED EXPECTED HYDRODYNAMIC BEHAVIOR. CONTINUOUS 19-DAY AFDU OPERATION WAS ACHIEVED.
- BUBBLE COLUMN PERFORMANCE COMPARABLE TO CSTR.
- AS ANTICIPATED, CATALYST-WAX SEPARATION REQUIRES FURTHER DEVELOPMENT.

Exhibit 1

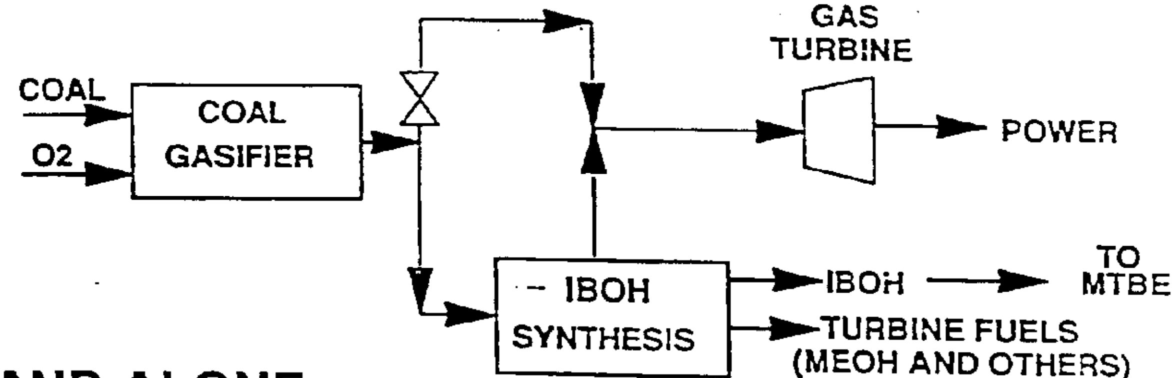
Blending Properties of Various Oxygenates



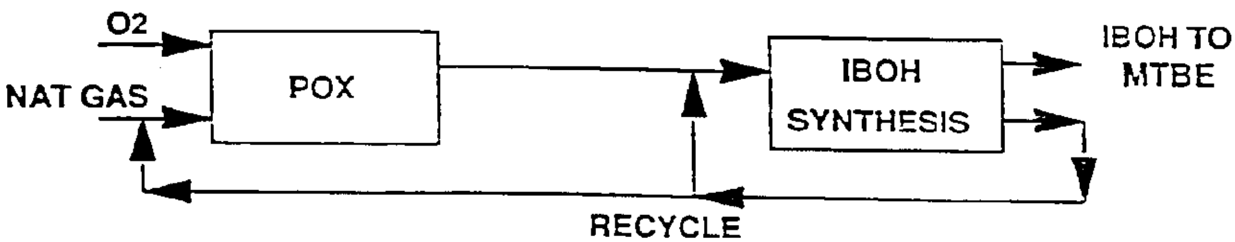
CHEM SYSTEMS

- MTBE DEMAND TO EXHAUST DOMESTIC BUTANE SOURCES
- FOREIGN SOURCED MTBE WILL DOMINATE U.S. SUPPLY
- COAL AND NATURAL GAS ROUTES TO MTBE NEEDED FOR ENERGY INDEPENDENCE

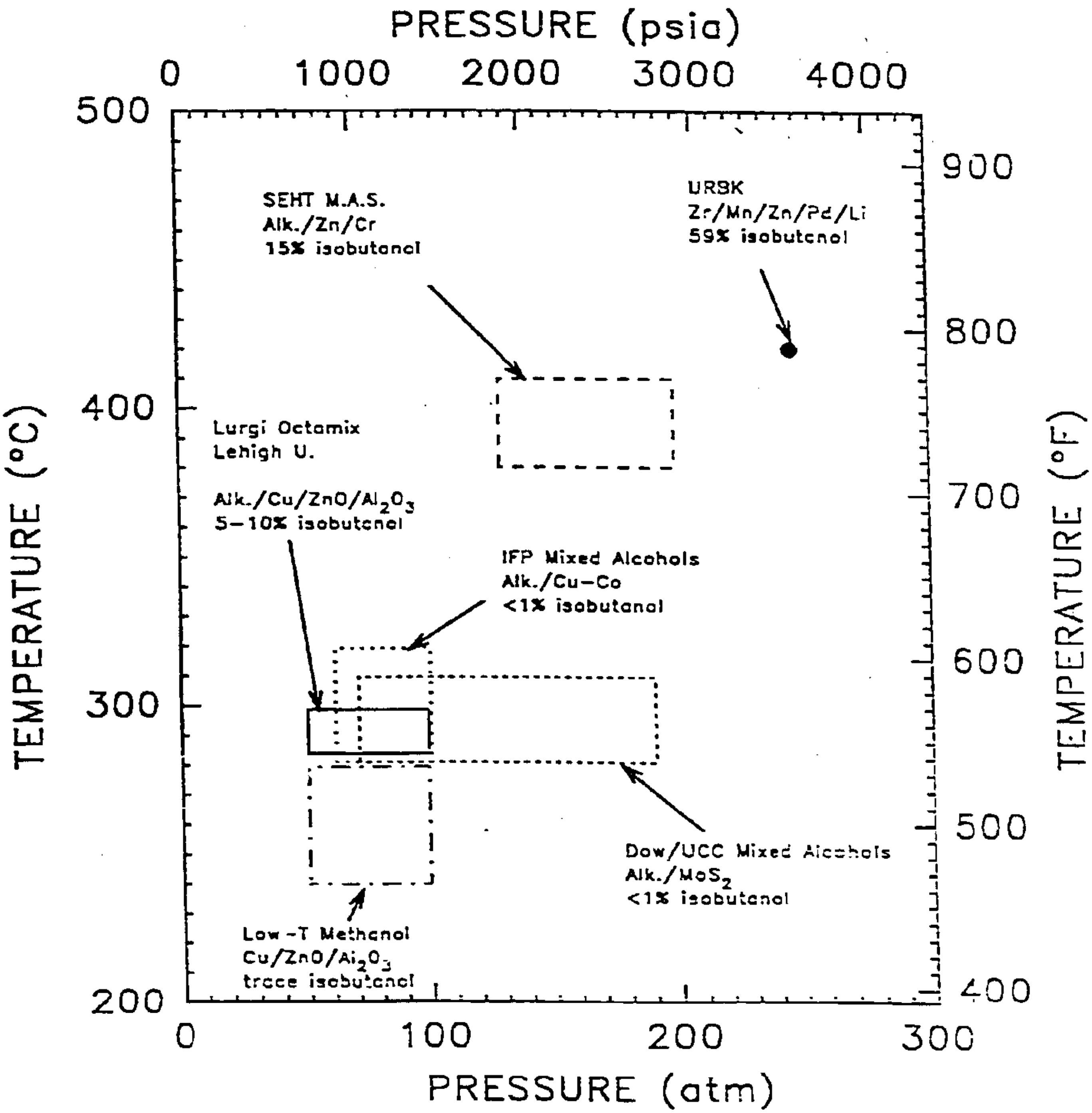
ADD-ON TO IGCC



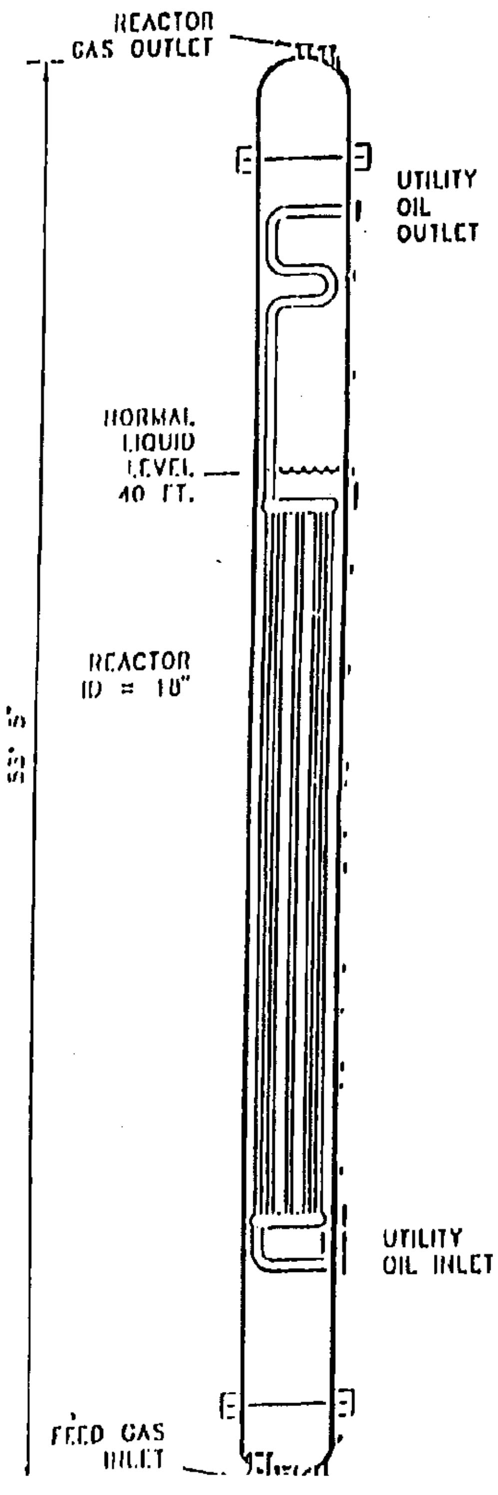
STAND ALONE NATURAL GAS BASED



Operating Temperature and Presssure Regimes for Mixed Alcohols Production Processes



TP_REGIM.SPG

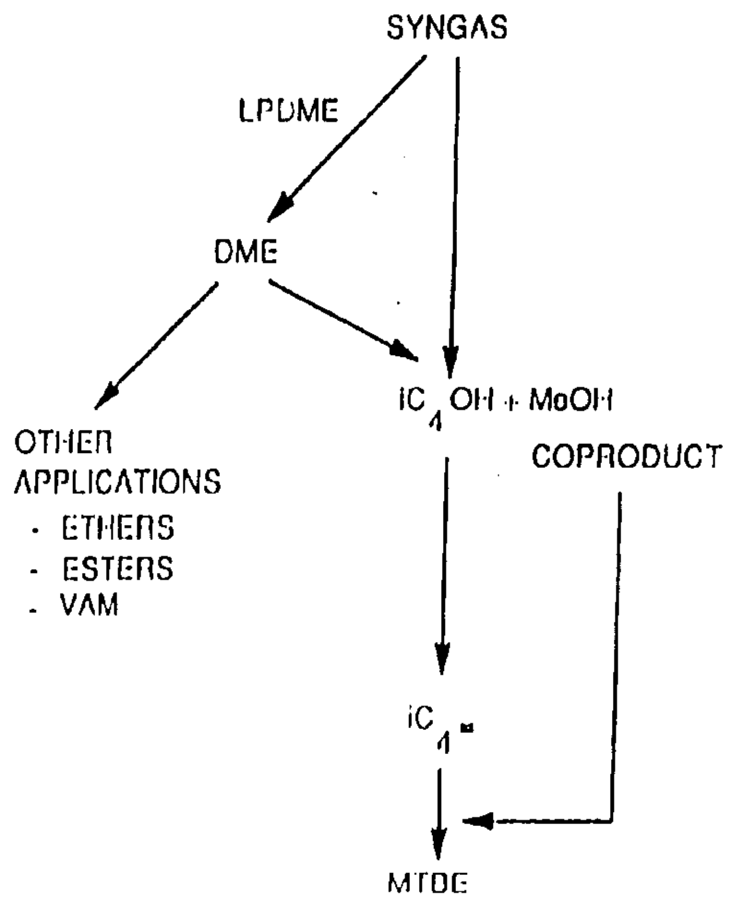


LaPorte - Alternative Fuels Development Unit (AFDU)

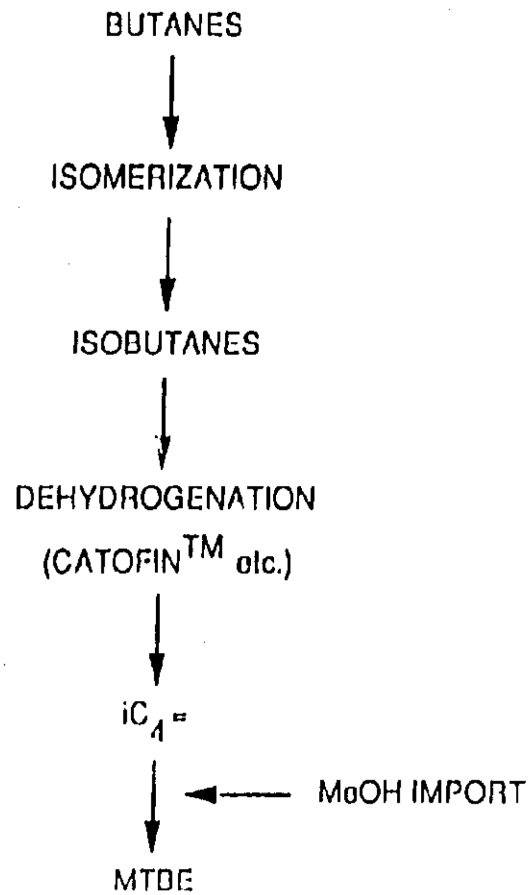
Pilot plant (operating cost ~ $20,000 per day)

- existing bubble column (900 psi, 300°C); 300 lb moles/hr. (13 TDMEOH)
    - removes 0.9 (3.3) MMBTU/hr.
- new reactor (1800 psi, 350°C); 600 lb moles/hr.
    - removes 2.8 MMBTU/hr.
- fully automated
- operator staff
- operating permits

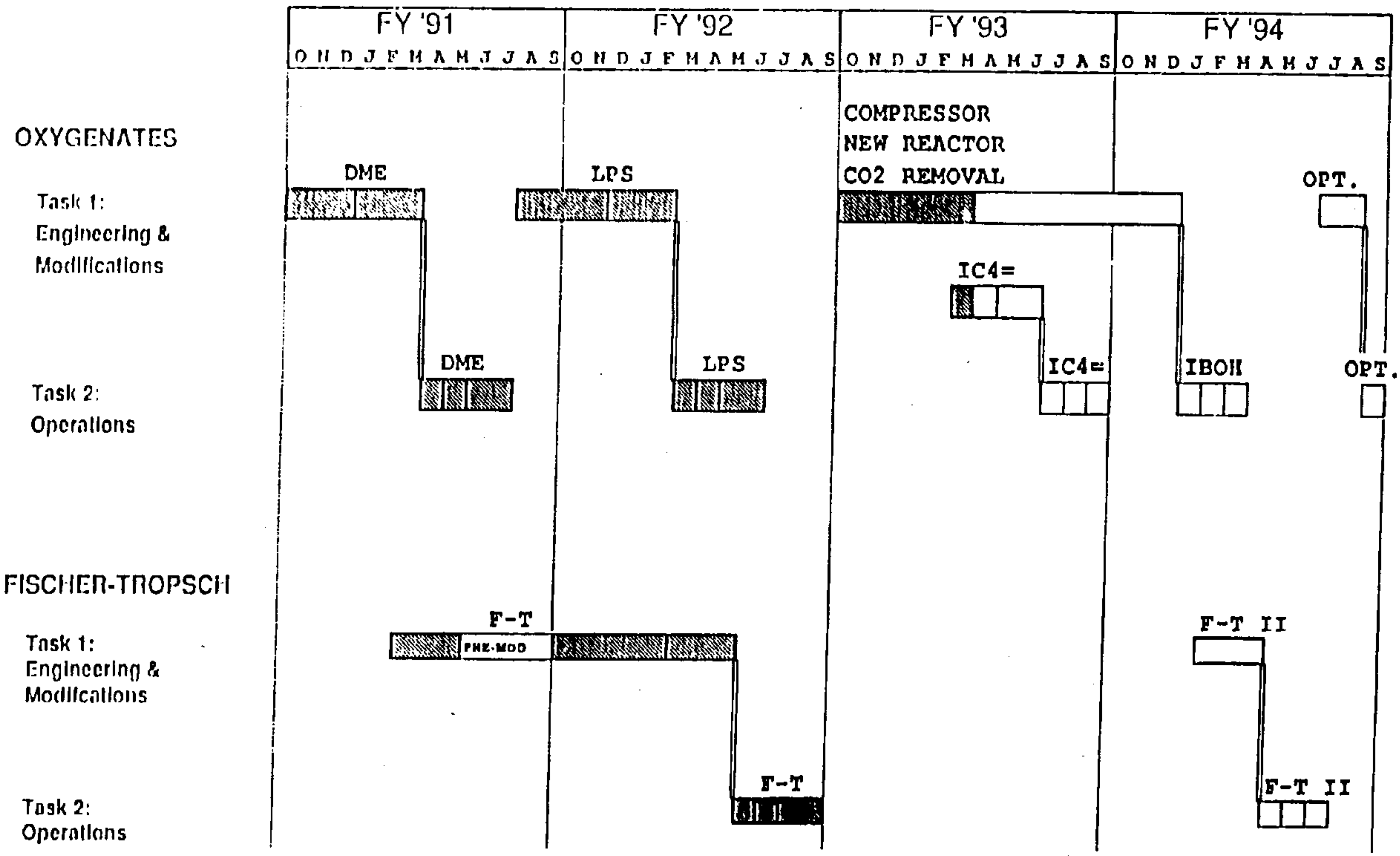
POTENTIAL ROUTE TO MTBE



EXISTING ROUTE



ALT. FUELS I



FY '91
FY '92
FY '93
FY '94
O N D J F M A M J J A S
OXYGENATES
Task 1: Engineering & Modifications
Task 2: Operations
FISCHER-TROPSCH
Task 1: Engineering & Modifications
Task 2: Operations
DME
LPS
COMPRESSOR
NEW REACTOR
CO2 REMOVAL
OPT.
IC4=
IBOH
F-T
PRE-MOD
F-T II

ALTERNATIVE FUELS AND CHEMICALS II

Starts: October 1, 1994

Duration: 5 Years (3 minimum)

Basis: New Routes to Fuels and Chemicals which reduce dependency on Imported Energy.

Feedstock:	Synthesis gas from Coal, Natural Gas, and Refinery Wastes.
Products:	Oxygenates: MTBE, mixed ethers, alcohols, olefins, acetyls, others? Hydrocarbons: (Fischer-Tropsch).
Technology:	Liquid Phase (Slurry), but not exclusively.

ALTERNATIVE FUELS AND CHEMICALS II (cont'd)

Program: Ongoing Laboratory R&D;

Air Products, Universities (Lehigh, Delaware, Aachen), Others?

LaPorte Operations;

2 or 3 per year

Supporting Programs:

- Reactor Design (Hydrodynamics)
- Syngas Clean-up
- Process and Economic Evaluations
- Product Testing
- Fischer-Tropsch Support