Report 14

CATALYST PARAMETRIC STUDIES

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INDIRECT LIQUEFACTION CATALYST PROCESS STUDIES

To investigate the effects of process variables on catalyst activity, selectivity, and stability in various areas of indirect liquefaction catalyst and reactor development.

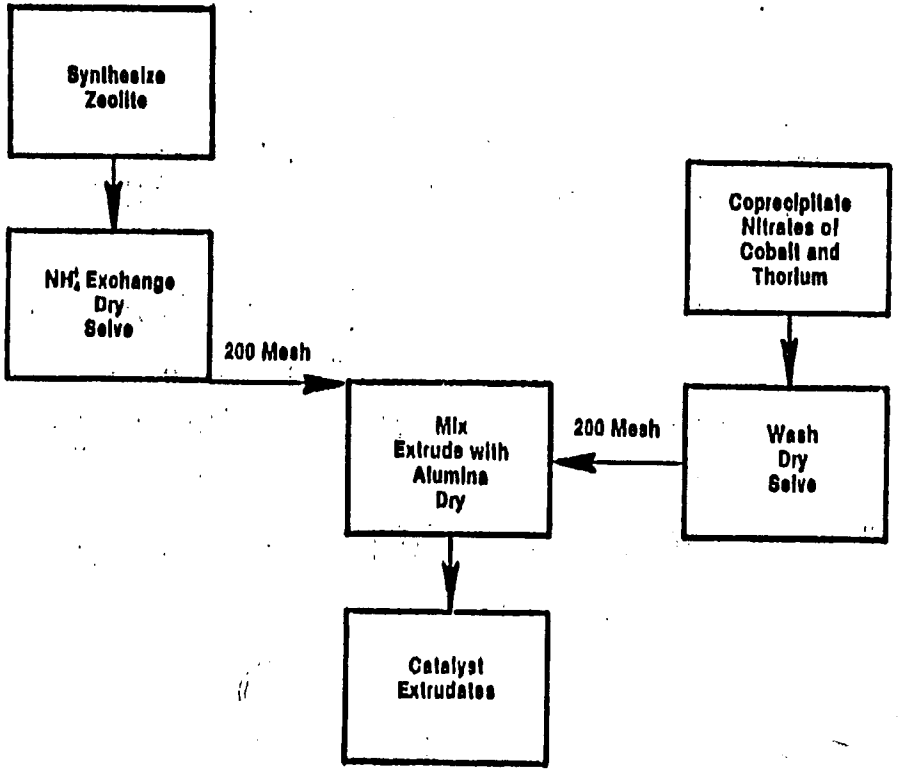
→ Activity 1: Bifunctional Zeolite Catalyst Investigation

Activity 2: Three-Phase Catalyst Study

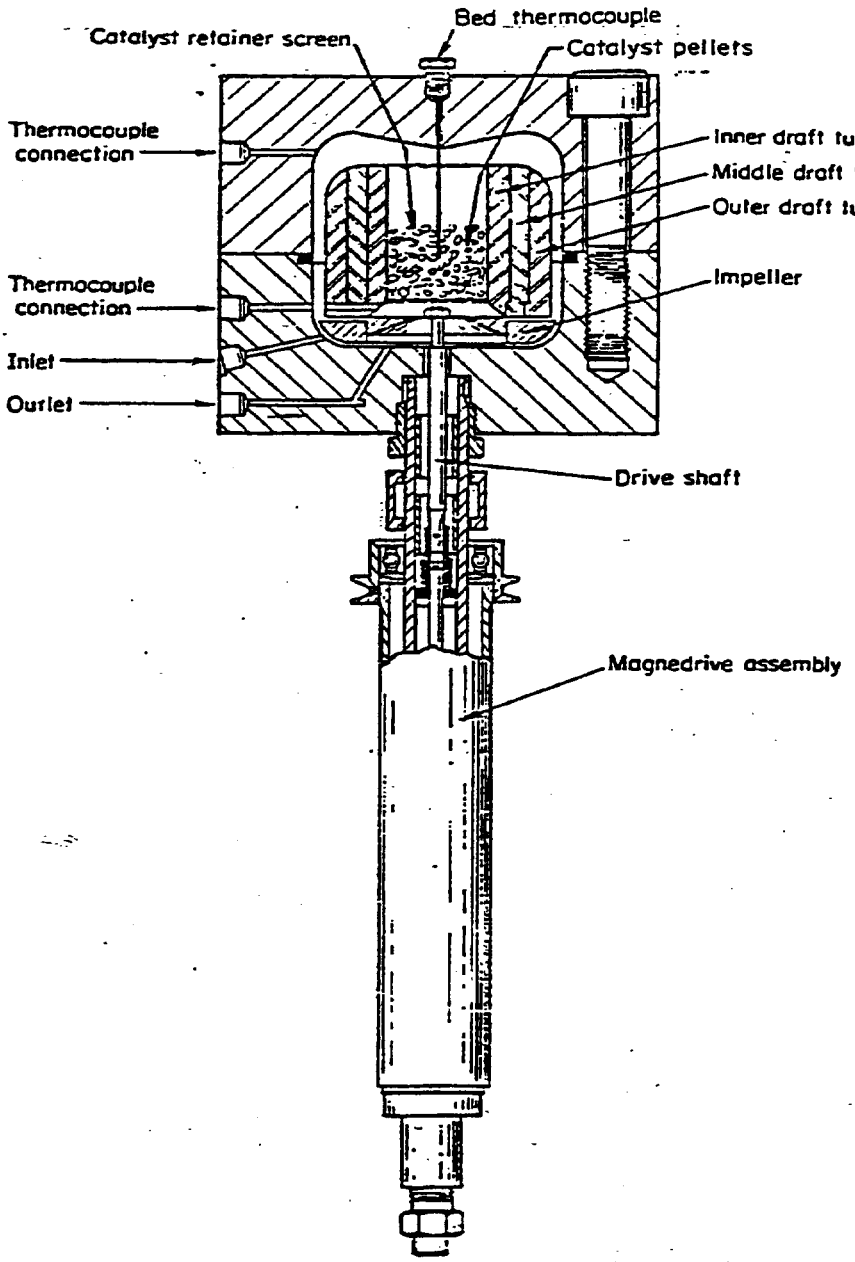
Activity 3: PETC-UOP Cooperative Effort

Activity 4: Automation of Bench Reactor Units

PREPARATION OF COBALT-THORIA-ZSM-5 CATALYST



DSI/979



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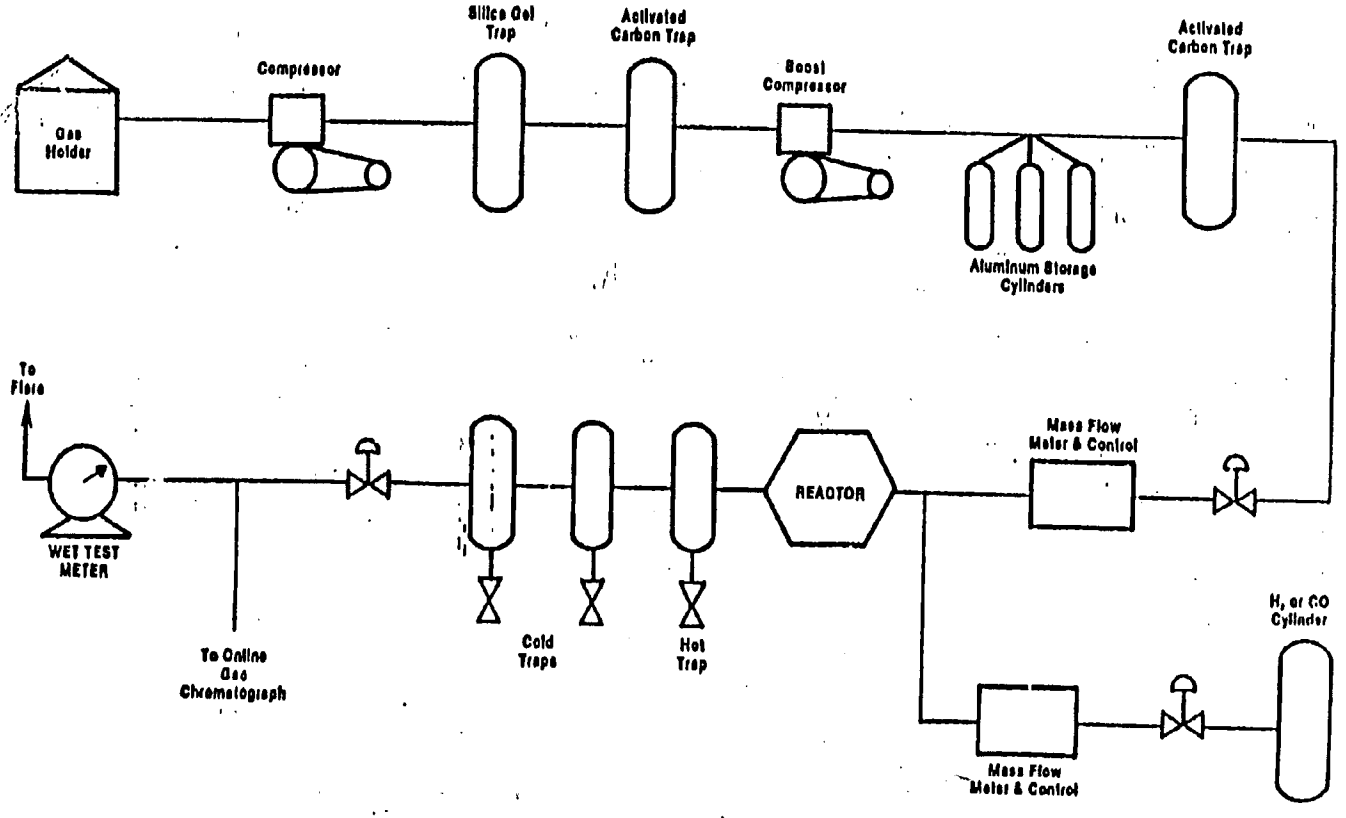
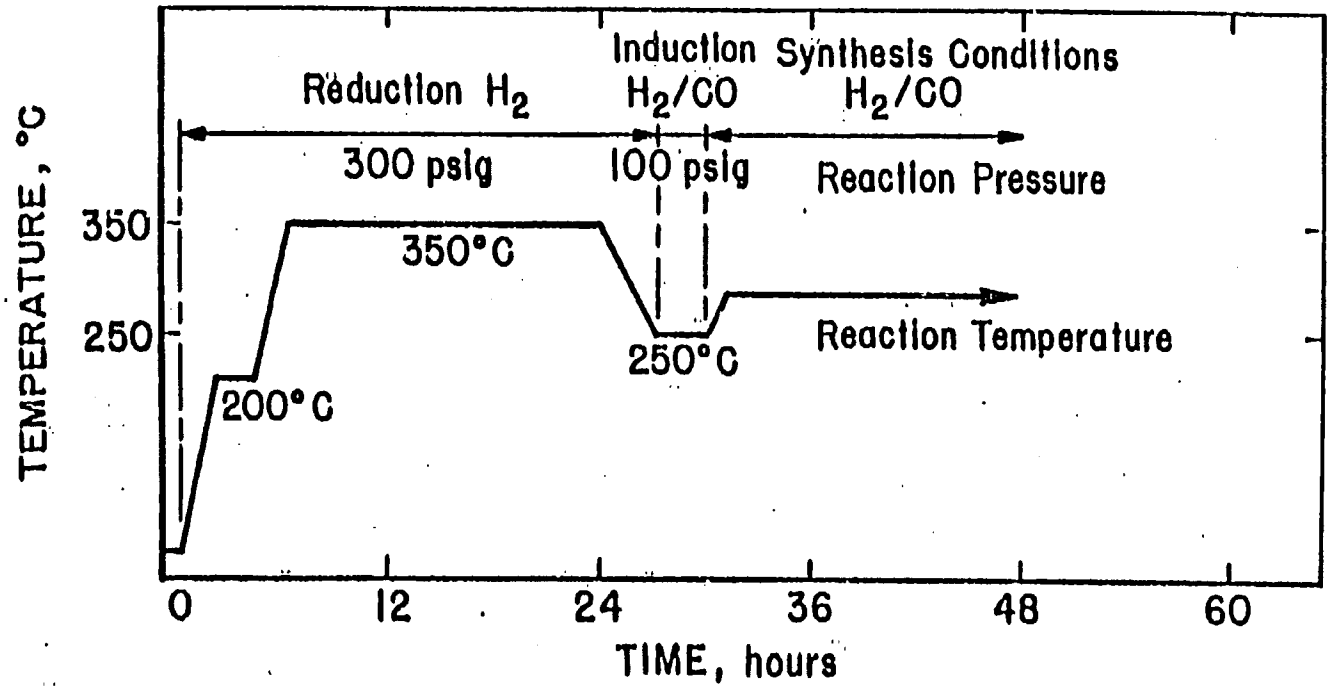
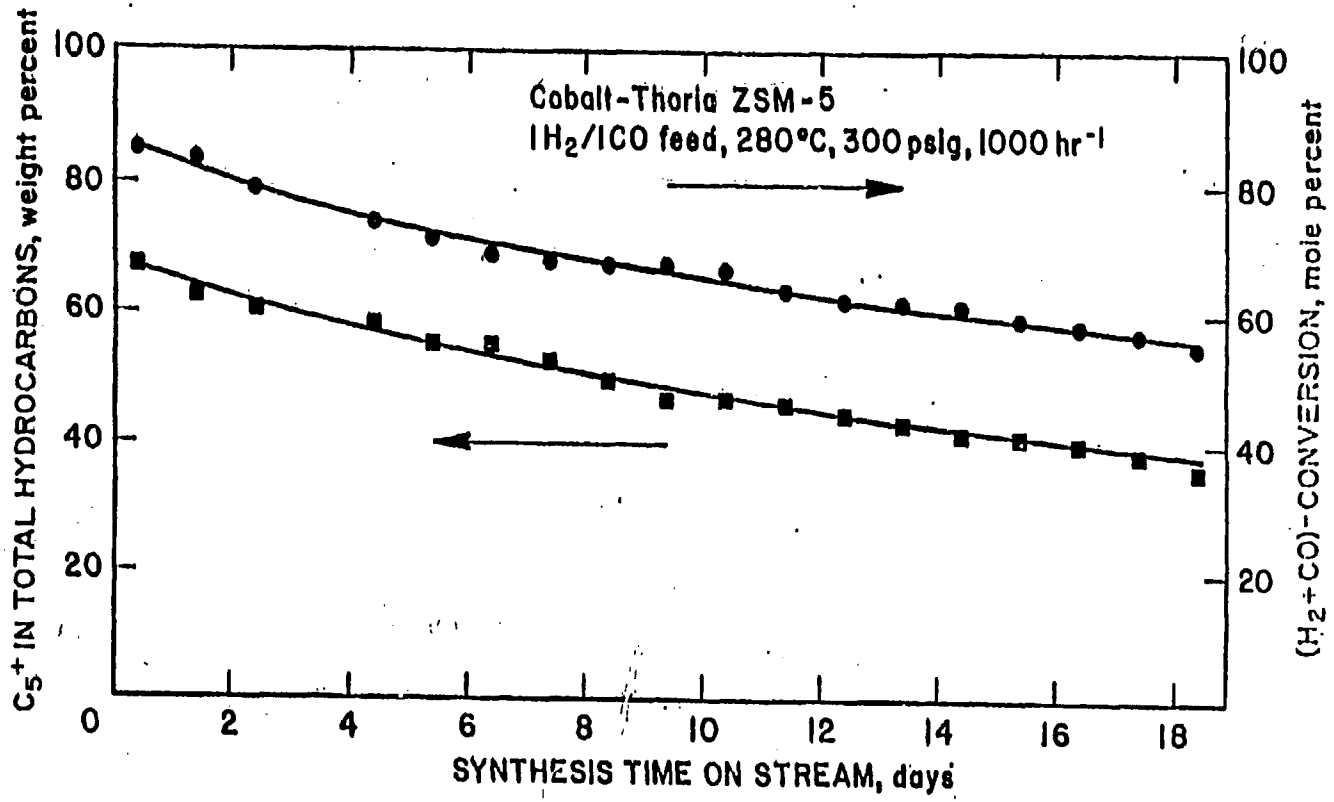

Gas Holder
Compressor
Silica Gel Trap
Activated Carbon Trap
Boost Compressor
Aluminum Storage Cylinders
Activated Carbon Trap
To Flare
WET TEST METER
To Online Gas Chromatograph
Cold Traps
Hot Trap
REACTOR
Mass Flow Meter & Control
Mass Flow Meter & Control
H, or CO Cylinder



ACTIVATION PROCEDURE FOR CATALYST

BSI-986


Cobalt-Thoria ZSM-5
1 H2/1CO feed, 280°C, 300 psig, 1000 hr-1
C5+ IN TOTAL HYDROCARBONS, weight percent
(H2+CO)-CONVERSION, mole percent
SYNTHESIS TIME ON STREAM, days
0
2
4
6
8
10
12
14
16
18
20
40
60
80
100

BSI-983

EFFECT OF DEACTIVATION

PROCESS CONDITIONS: 1 H_2/1 CO, 280°C, 300 psig, 1000 hr^{-1}

HOURS ON STREAM	33	201	417
(H_2 + CO) CONVERSION	83.8	67.9	56.6
H_2 CONVERSION	93.3	87.1	76.0
HYDROCARBON DISTRIBUTION, wt%			
CH_4	23.4	34.5	42.4
$C_2H_6 + C_2H_4$	3.9	5.4	6.1
$C_3H_8 + C_3H_6$	5.9	6.4	7.8
$C_4H_{10} + C_4H_8$	4.0	3.8	5.2
C_5^+ (Oil)	61.0	49.6	38.5
Wax	1.8	0.3	
LIQUID PRODUCT COMPOSITION, wt%			
AROMATICS	4	2	2
OLEFINS	76	83	80
SATURATES	20	15	18
WEIGHT FRACTION IN			
GASOLINE RANGE (BP < 204°C)	89	85	90
LIQUID YIELD, gm oil/gm cat·hr	0.13	0.08	0.05

DSI/975

EFFECT OF SUPPORT

PROCESS CONDITIONS: 1 H_2/1 CO, 280°C, 300 psig, 1000 hr^{-1}

SUPPORT	ZSM-5	ALUMINA
HOURS ON STREAM	33	33
(H_2 + CO) CONVERSION	83.8	80.5
H_2 CONVERSION	93.3	91.7
HYDROCARBON DISTRIBUTION, wt%		
CH_4	23.4	22.5
$C_2H_6 + C_2H_4$	3.9	4.1
$C_3H_8 + C_3H_6$	5.9	5.9
$C_4H_{10} + C_4H_8$	4.0	4.6
C_5^+	61.0	52.6
Wax	1.8	10.3
LIQUID PRODUCT COMPOSITION, wt%		
AROMATICS	4	2
OLEFINS	76	43
SATURATES	20	55
WEIGHT FRACTION IN GASOLINE RANGE (BP < 204°C)	89	68
LIQUID YIELD, gm oil/gm cat-hr	0.13	0.09

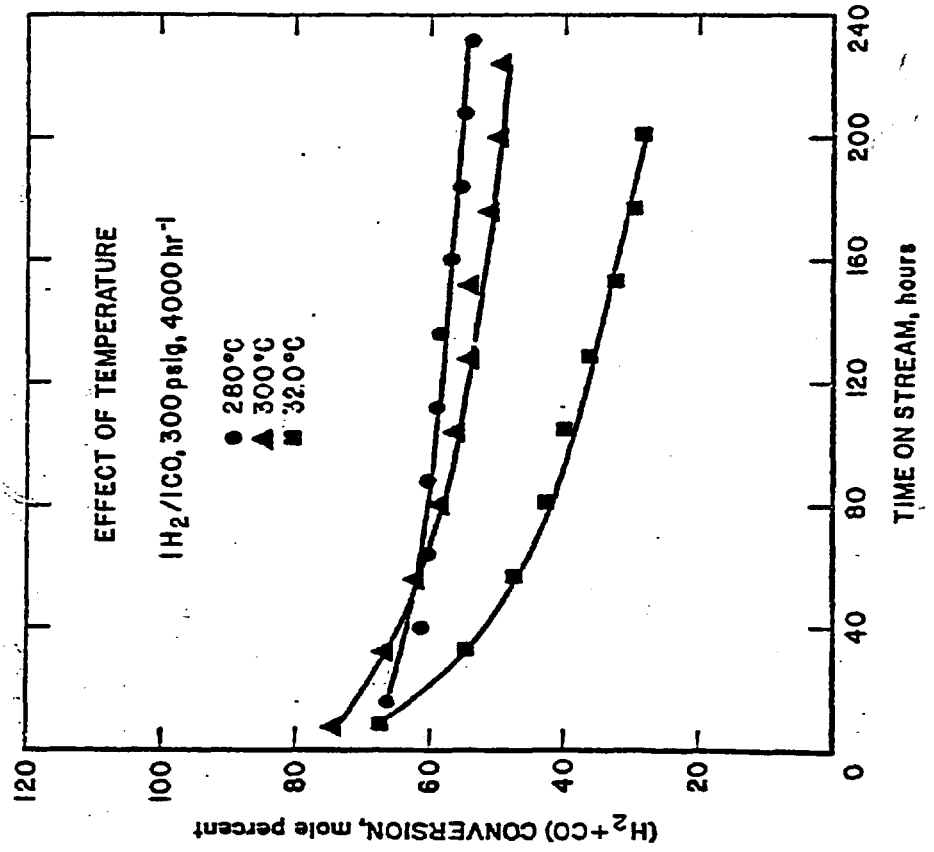
BSI/973

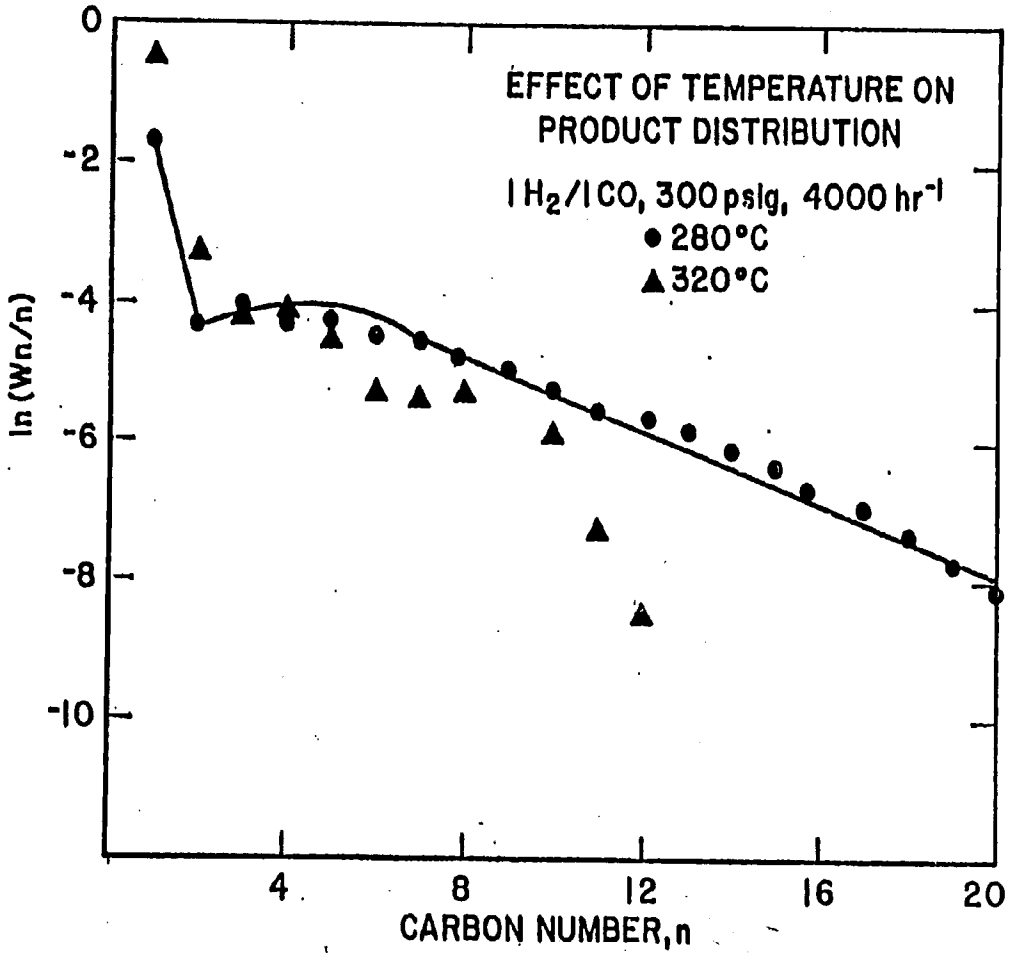
EFFECT OF TEMPERATURE

PROCESS CONDITIONS: 1 H_2/1 CO, 300 psig, 4000 hr^{-1}

TEMPERATURE, °C	280	300	320
HOURS ON STREAM	40	32	33
(H_2 + CO) CONVERSION	61.2	66.7	54.8
H_2 CONVERSION	77.8	82.3	68.8
HYDROCARBON DISTRIBUTION, wt%			
CH_4	18.4	38.8	65.5
$C_2H_6 + C_2H_4$	3.2	5.7	9.7
$C_3H_8 + C_3H_6$	5.3	5.2	5.1
$C_4H_{10} + C_4H_8$	6.1	6.9	3.4
C_5^+	63.1	43.3	14.5
Wax	3.9	0	0
LIQUID PRODUCT COMPOSITION, wt%			
AROMATICS	2	4	46
OLEFINS	82	74	25
SATURATES	16	22	29
WEIGHT FRACTION IN GASOLINE RANGE (BP<204°C)	70	91	95
LIQUID YIELD, gm oil/gm cat·hr	0.39	0.27	0.07

DS1/976


EFFECT OF TEMPERATURE
H_2/CO, 300 psig, 4000 hr^{-1}
● 280°C
▲ 300°C
■ 320°C
(H_2+CO) CONVERSION, mole percent
TIME ON STREAM, hours
120
100
80
60
40
20
0
40
80
120
160
200
240


EFFECT OF TEMPERATURE ON
PRODUCT DISTRIBUTION
1 H2/1 CO, 300 psig, 4000 hr-1
● 280°C
▲ 320°C
ln (Wn/n)
0
-2
-4
-6
-8
-10
4
8
12
16
20
CARBON NUMBER, n

BSI-982

PROCESS CONDITIONS: 280°C, 300 psig, 4000 hr^{-1}, 1 H_2/1 CO

CALCINATION TEMPERATURE	0	450°C
HOURS ON STREAM	40	36
(H_2 + CO) CONVERSION	61.2	66.7
H_2 CONVERSION	77.8	84.8
HYDROCARBON DISTRIBUTION, wt%		
CH_4	18.4	18.5
$C_2H_6 + C_2H_4$	3.2	3.2
$C_3H_8 + C_3H_6$	5.3	4.0
$C_4H_{10} + C_4H_8$	6.1	3.5
C_5^+	63.1	70.0
Wax	3.9	0.8
LIQUID PRODUCT COMPOSITION, wt%		
AROMATICS	2	12
OLEFINS	82	70
SATURATES	16	18
WEIGHT FRACTION IN GASOLINE RANGE (BP < 204°C)	70	75
LIQUID YIELD, gm oil/gm cat·hr	.39	.42

DSI/972

Cobalt-thoria-ZSM-5 synthesizes a highly branched olefinic product

A lighter hydrocarbon fraction is produced at lower pressures or lower space velocities.

Temperature increase results in a high fraction of aromatics in the liquid product.

Low feed ratios increase C_5^+ formation.

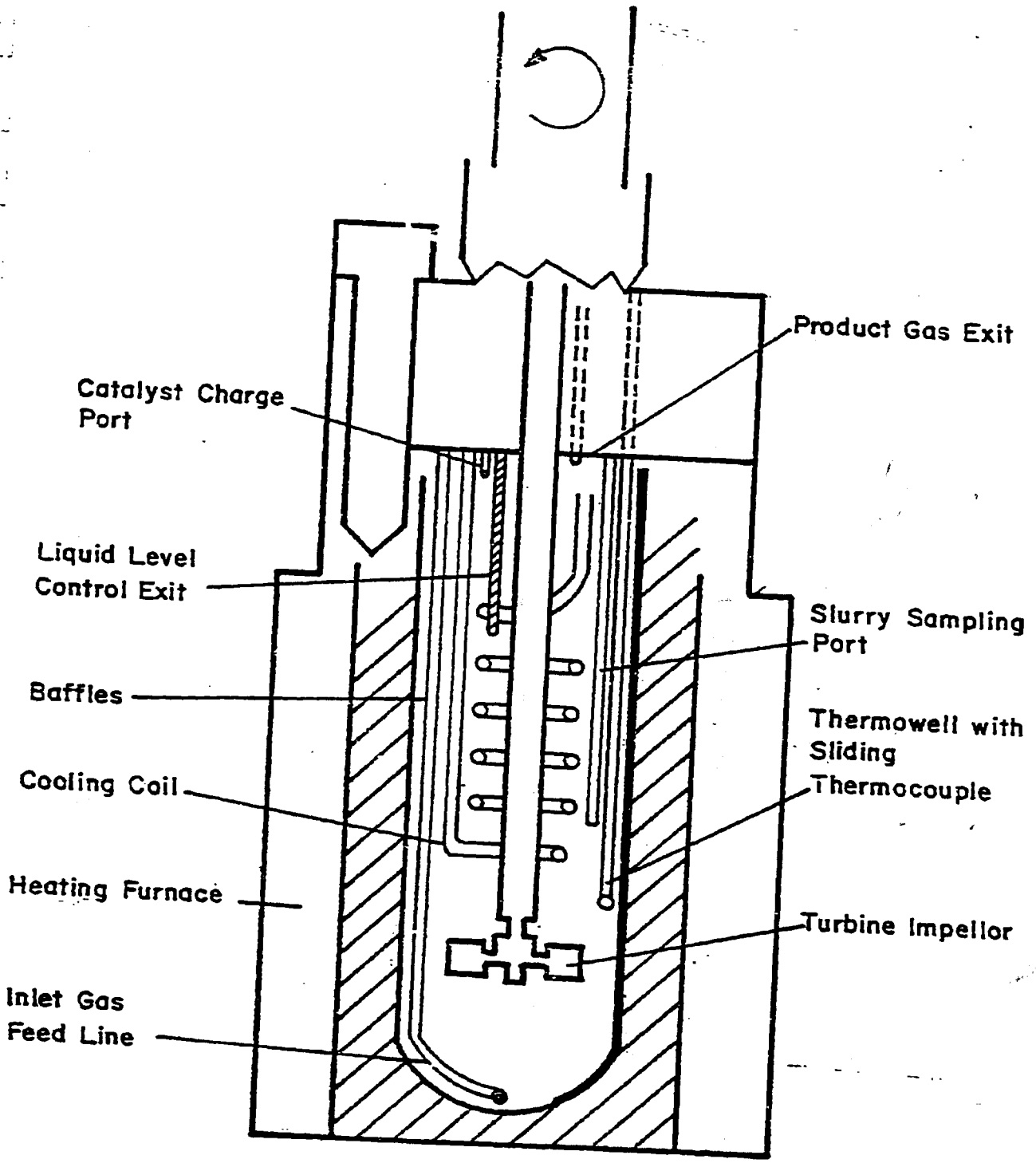
Calcination of the catalyst increases aromatic formation.

Activity 1: Bifunctional Zeolite Catalyst Investigation

→ Activity 2: Three-Phase Catalyst Study

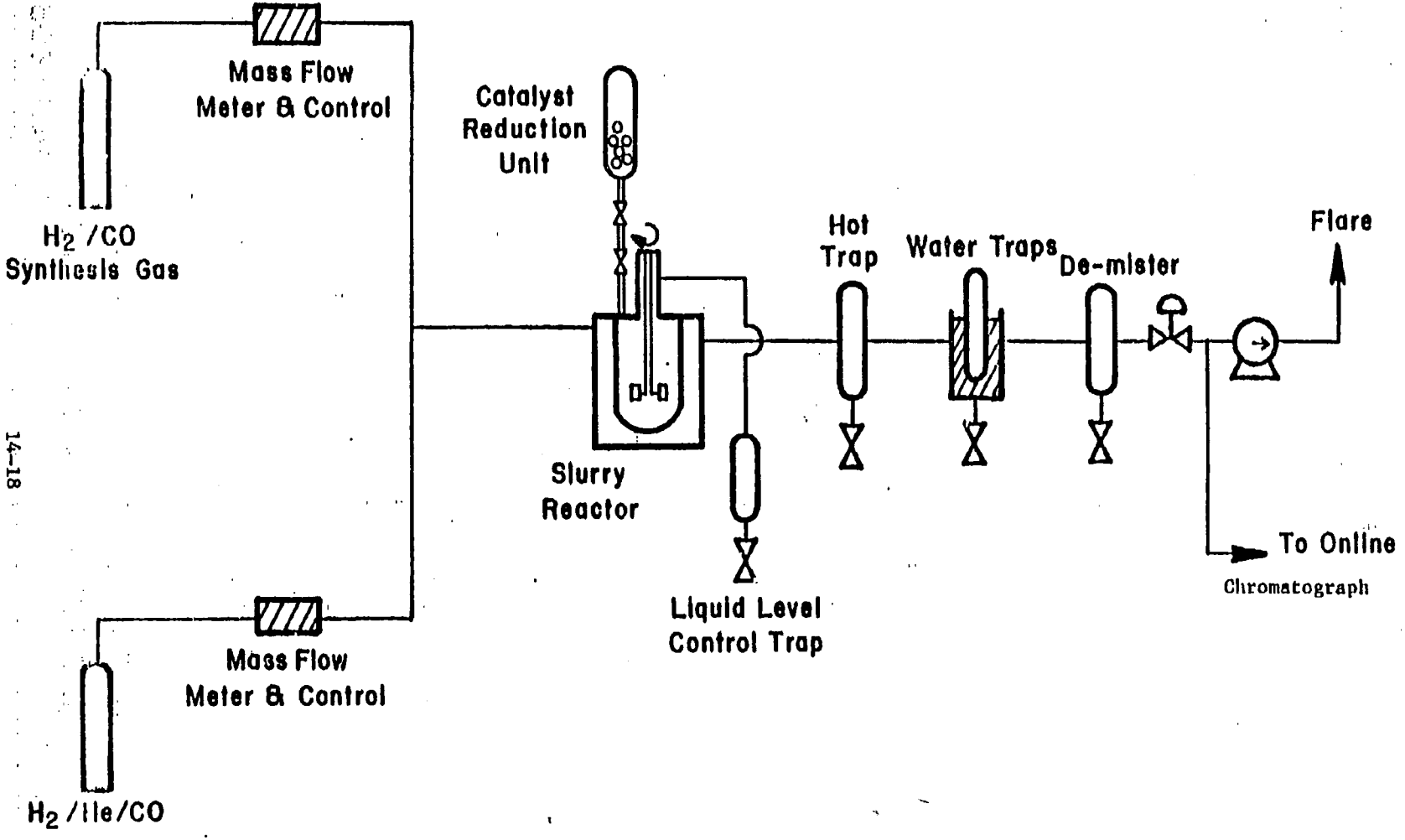
Activity 3: PETC-UOP Cooperative Effort

Activity 4: Automation of Bench Reactor Units



SLURRY REACTOR FOR INDIRECT LIQUEFACTION CATALYSTS

BSI-255

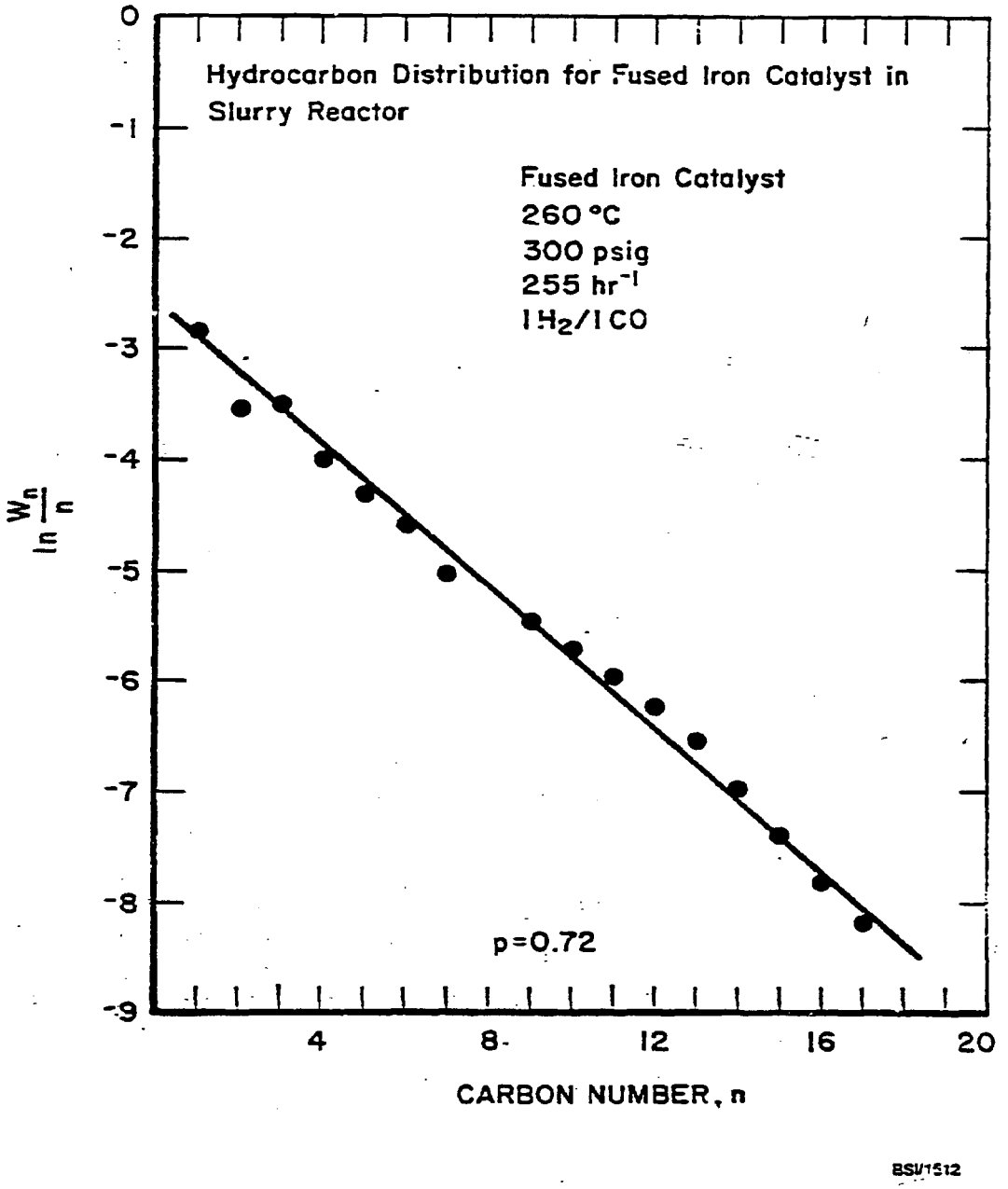


SCHEMATIC SLURRY REACTOR

BSI-257

BASELINE DATA TESTS

Catalyst:	Fused Iron
Particle Size:	<63 micron
Liquid Medium:	n-paraffin wax
Loading:	100 gm unreduced catalyst/liter of slurry
Gas Space Velocity:	255 hr^{-1}
Temperature:	245-280°C
Pressure:	100-300 psig
Impellor Speed:	250-1000 rpm
Feed Gas Ratio:	$1H_2/1CO$


Hydrocarbon Distribution for Fused Iron Catalyst in Slurry Reactor
Fused Iron Catalyst
260 °C
300 psig
255 hr⁻¹
1 H2/1 CO
p=0.72
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
4
8
12
16
20
CARBON NUMBER, n
BSU1512

Catalyst:	Iron-Manganese
Particle Size:	<63 micron
Liquid Medium:	n-paraffin wax
Catalyst Loading:	50 grams/liter of slurry
Gas Space Velocity:	44-90 hr^{-1}
Temperature:	275-300°C
Pressure:	200 psig
Impellor Speed:	1000 rpm
Feed Gas Ratio:	$1H_2/1CO$

IRON-MANGANESE RESULTS

PROCESS CONDITIONS: $1H_2/1CO$, 275°C, 200 psig, 90 hr^{-1}

(H_2+CO) CONVERSION	38.3
CO CONVERSION	41.6
HYDROCARBON DISTRIBUTION, wt%	
CH_4	6.7
C_2-C_4	35.2
C_5^+	58.1
OLEFIN/PARAFFIN RATIO	
C_2	2.3
C_3	8.4
LIQUID PRODUCT COMPOSITION, wt%	
AROMATICS	12
OLEFINS	76
SATURATES	12

USES

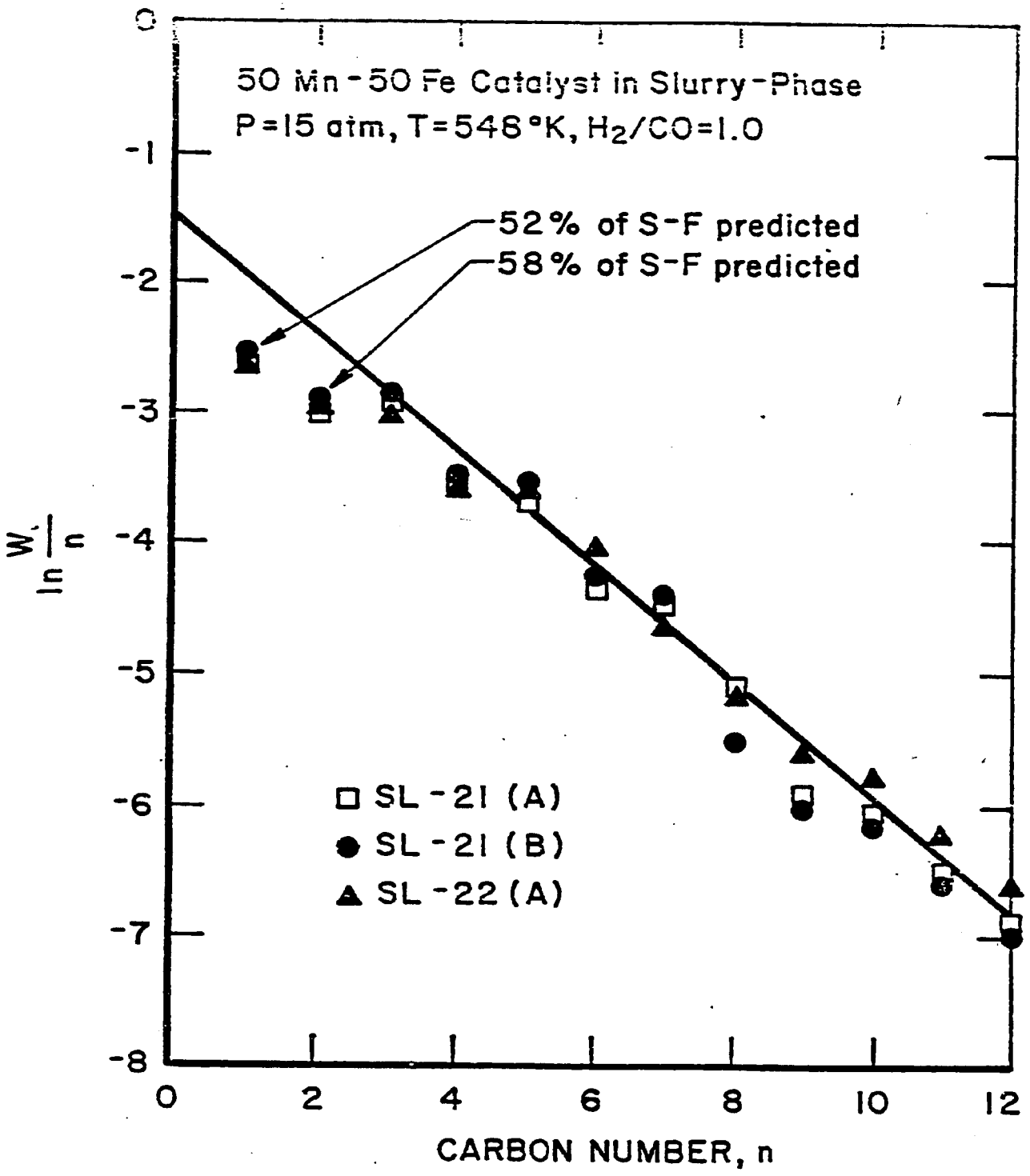
CATALYST DEVELOPMENT

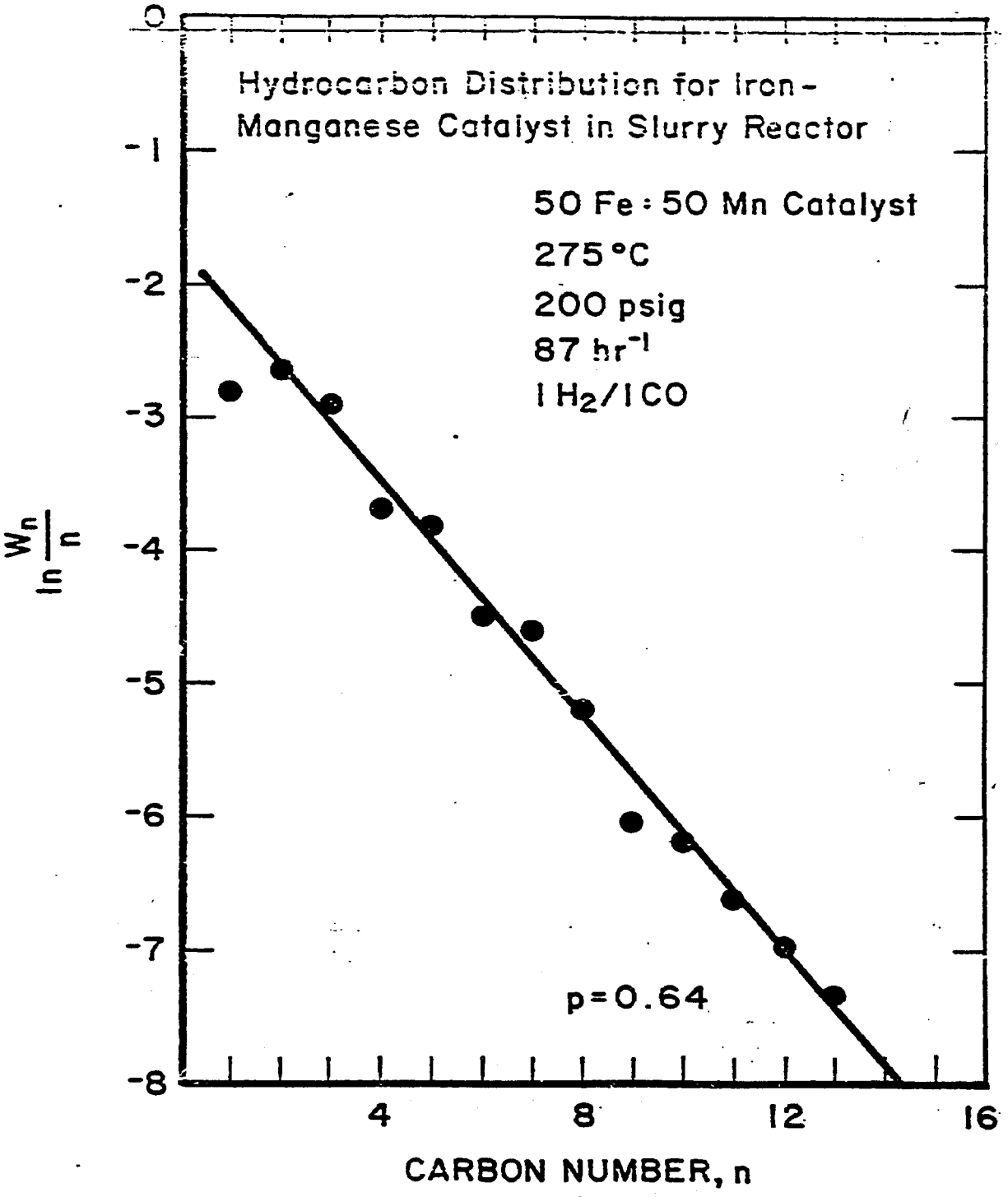
- **EXPERIMENT DESIGN**
- **DATA INTERPRETATION & FORMULA IMPROVEMENT**

PROCESS DEVELOPMENT

- **EXPERIMENT DESIGN**
- **EVALUATION OF REACTOR SYSTEMS**
- **OPTIMIZATION OF OPERATING CONDITIONS**

UOP 831-28


50 Mn - 50 Fe Catalyst in Slurry-Phase
P = 15 atm, T = 548 °K, H2/CO = 1.0
52% of S-F predicted
58% of S-F predicted
SL-21 (A)
SL-21 (B)
SL-22 (A)
0
-1
-2
-3
-4
-5
-6
-7
-8
0
2
4
6
8
10
12
CARBON NUMBER, n
BS1-1217


Hydrocarbon Distribution for Iron-Manganese Catalyst in Slurry Reactor
50 Fe : 50 Mn Catalyst
275 °C
200 psig
87 hr⁻¹
1 H2/1 CO
p=0.64
0
-1
-2
-3
-4
-5
-6
-7
-8
4
8
12
16
CARBON NUMBER, n
Wn/n

BSI/1511