Report 4

FISCHER-TROPSCH SLURRY CATALYST DEVELOPMENT

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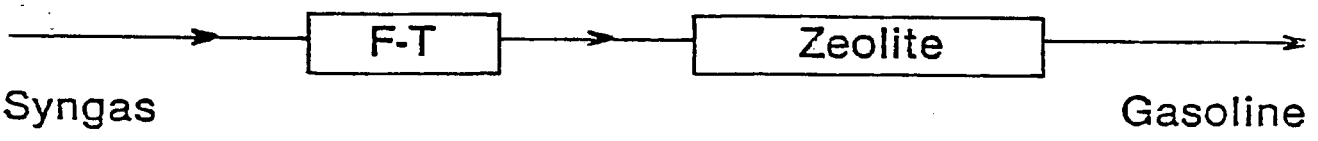
FISCHER-TROPSCH SLURRY CATALYST DEVELOPMENT

Objective: A microreactor study to develop iron-based F-T catalysts for use in a slurry reactor, assuming the slurry reactor is the first stage of a two-stage or dual reactor unit.

1.) Mo-promoted nitrided fused iron
2.) Precipitated iron catalysts
3.) Fe-Mn catalysts
4.) Dual reactor unit



CATALYST PREPARATION

Precipitated Fe

A.) Na_2CO_3 → pH 7-8 (80-90°C) ← $Fe(NO_3)_3 + Cu(NO_3)_2$

Prep #	Fe	Cu	Na
6	95.4	2.7	1.9
7	100	—	0.1
8	98.8	1.2	0.7
9	99.5	0.5	1.4

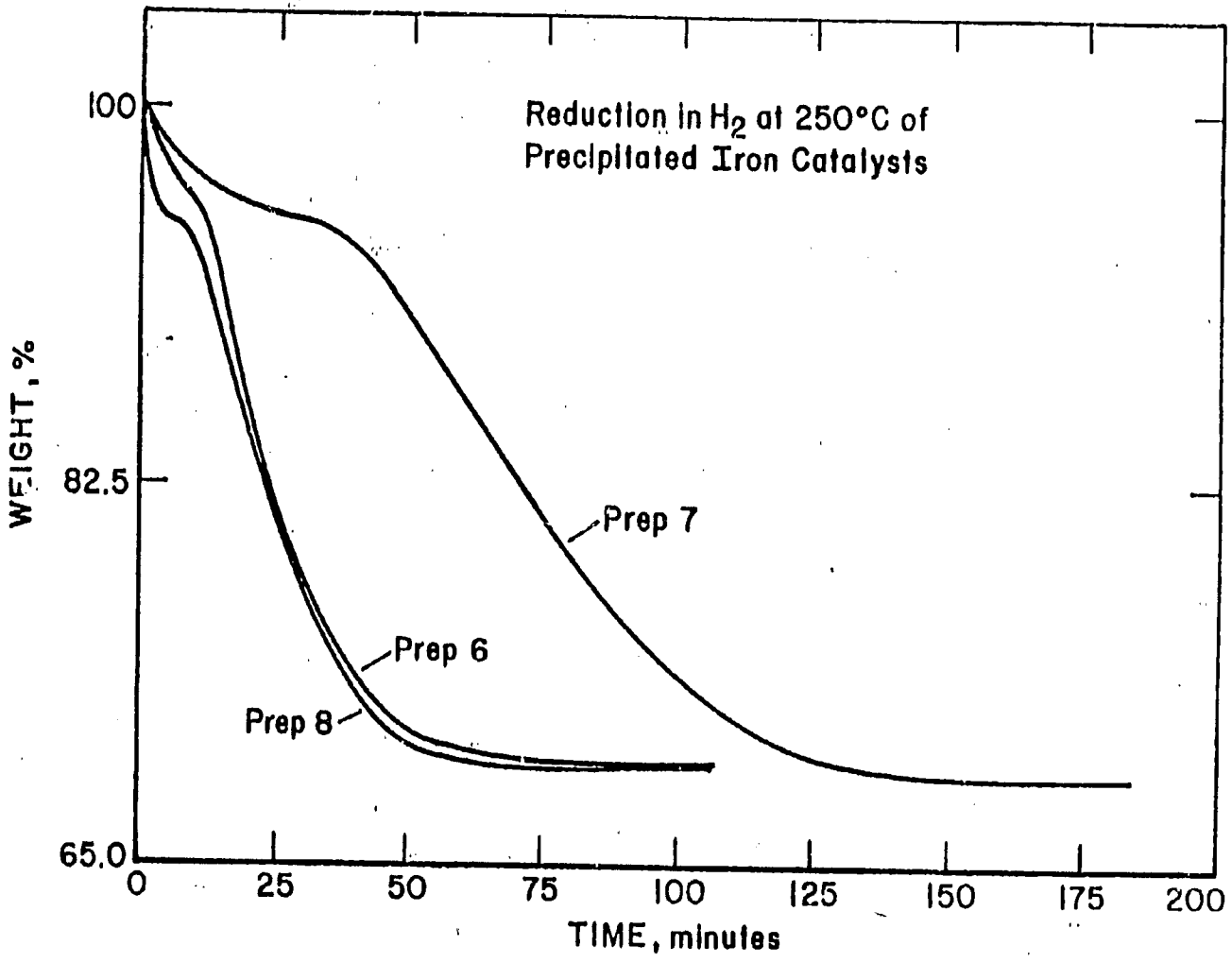
B.) NH_4OH → pH 7-8 (80-90°C) ← $Fe(NO_3)_3 + Cu(NO_3)_2$

Prep #	Fe	Cu
11	98.7	1.3

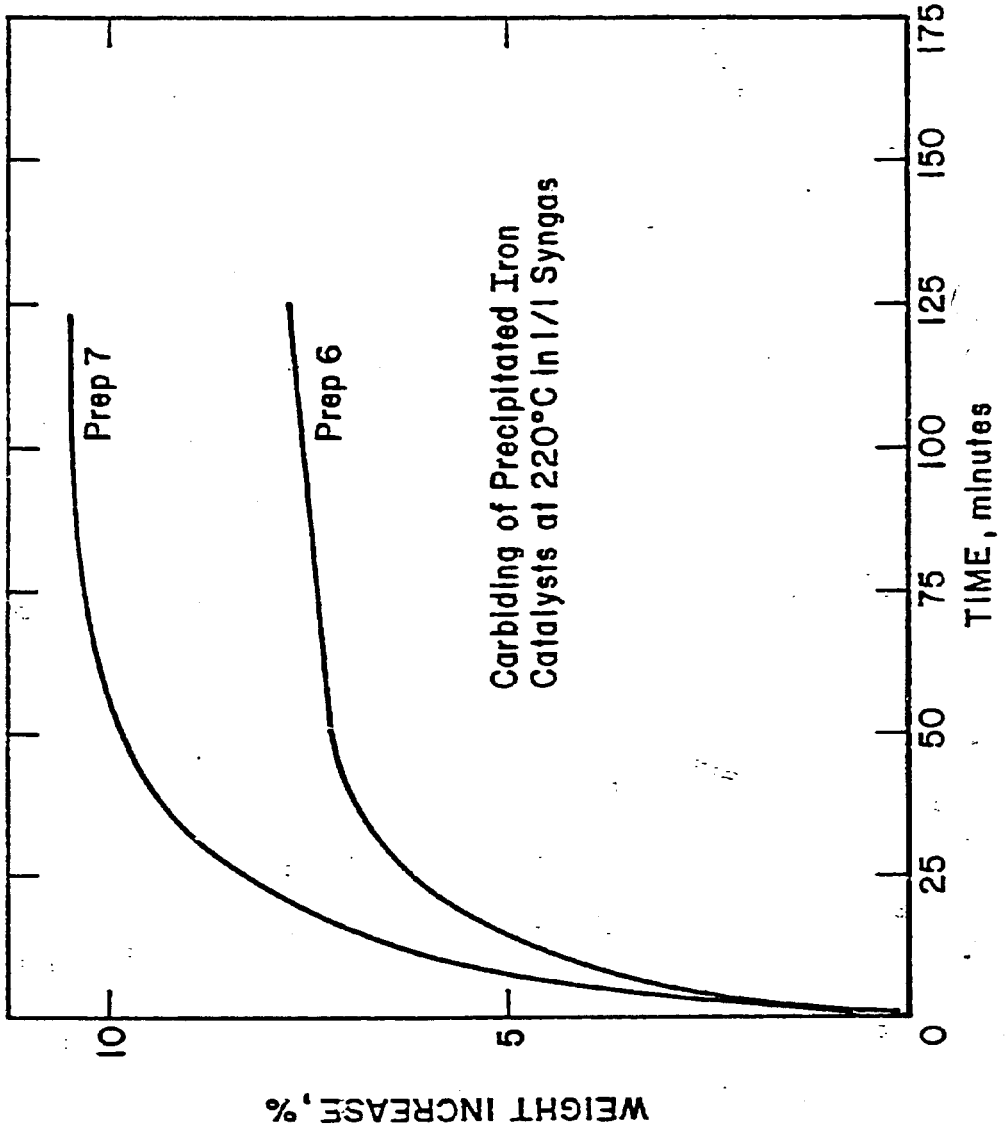
Fe-Mn

NH_4OH → pH 8.5 (80-90°C) ← $Fe(NO_3)_3 + Mn(NO_3)_2$

12 Fe-88 Mn, 25 Fe-75 Mn, 31 Fe-69 Mn


Reduction in H_2 at 250°C of
Precipitated Iron Catalysts
100
82.5
65.0
WEIGHT, %
Prep 7
Prep 6
Prep 8
0
25
50
75
100
125
150
175
200
TIME, minutes

DSI/1540


Carbiding of Precipitated Iron
Catalysts at 220°C in 1/1 Syngas
Prep 7
Prep 6
WEIGHT INCREASE, %
TIME, minutes
0
5
10
25
50
75
100
125
150
175

IISM1639

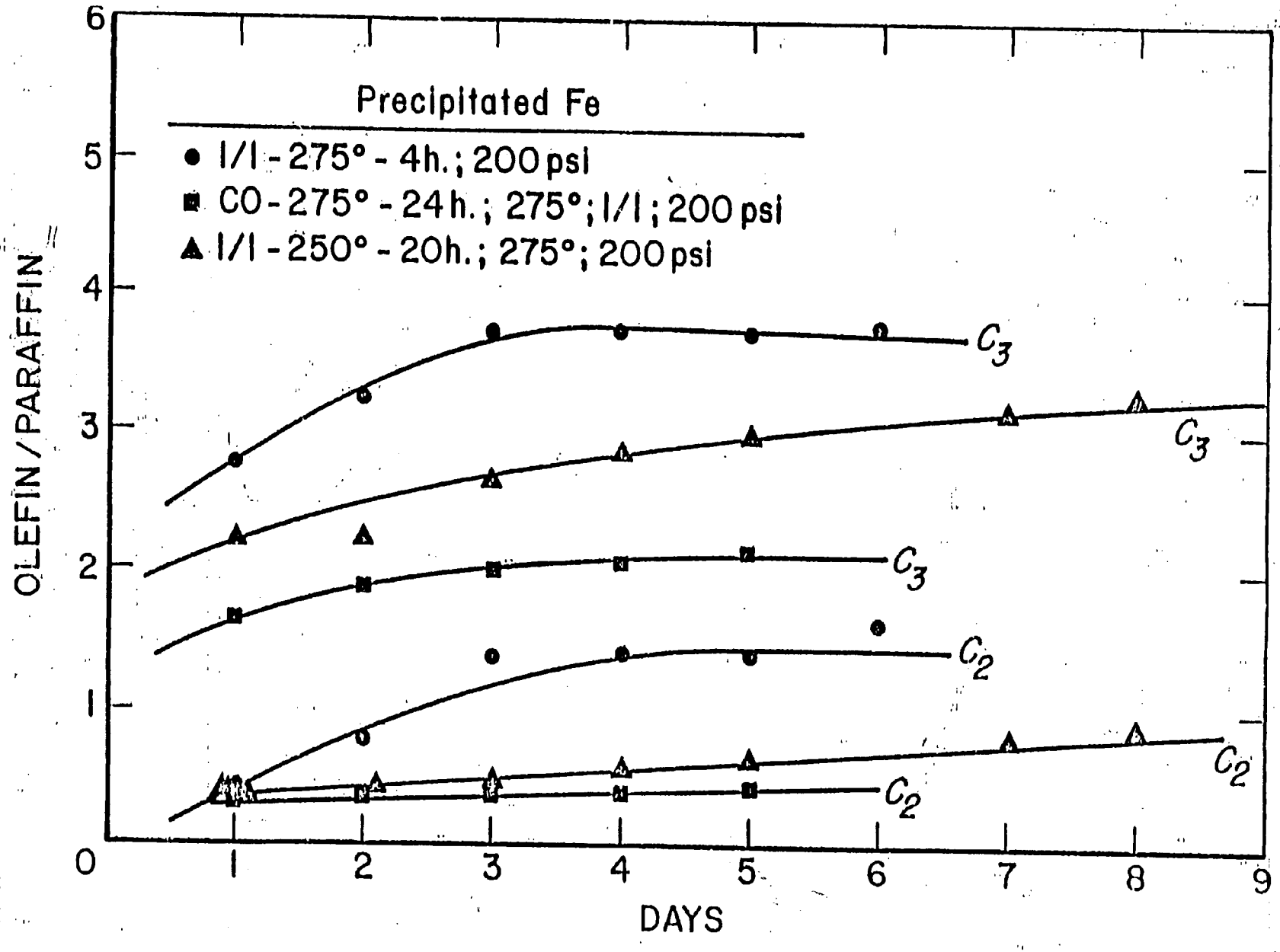
MICROREACTOR CONDITIONS

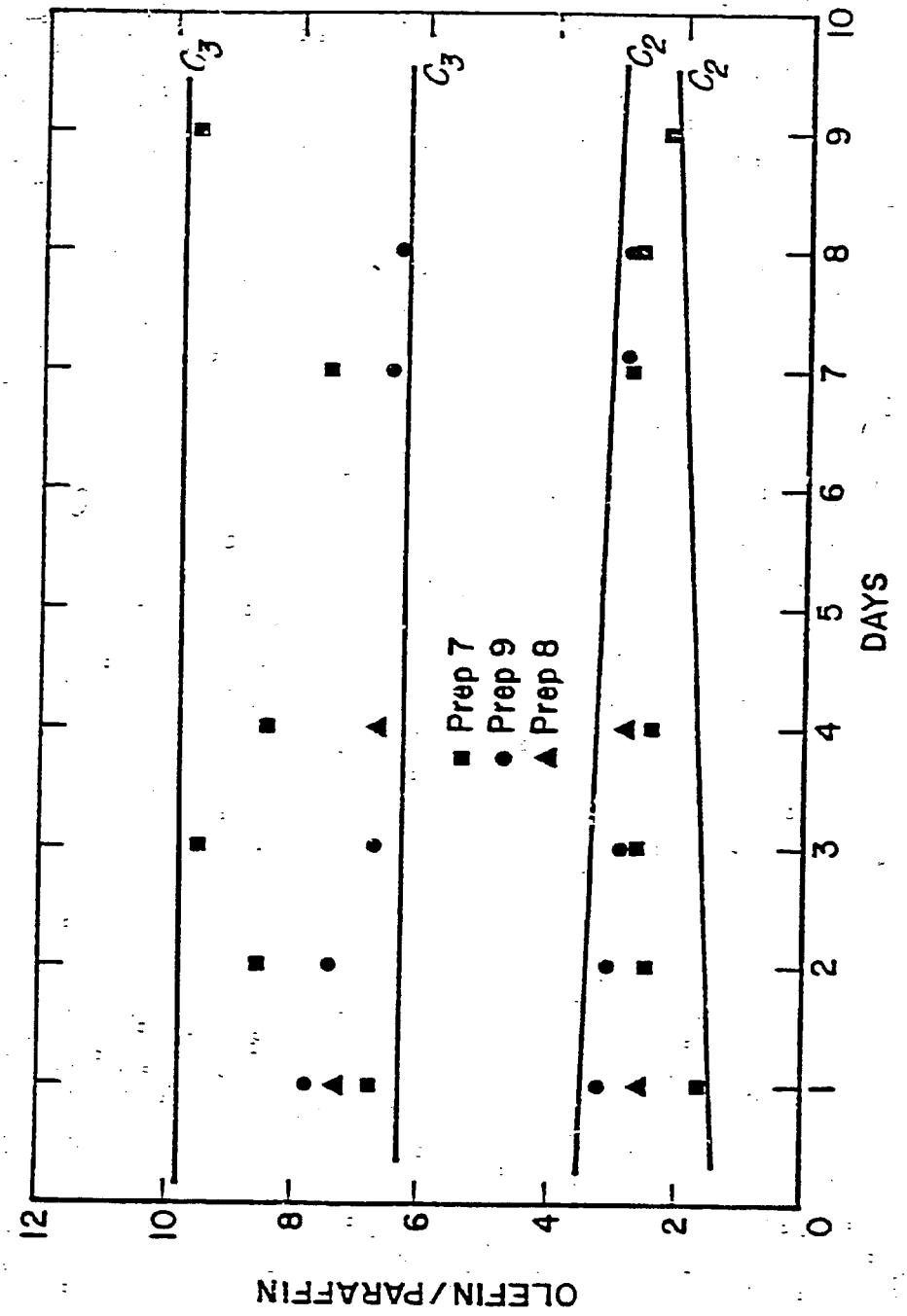
275°C

200 psig

$H_2/CO = 1$

-200 + 325


Precipitated Fe
● 1/1 - 275° - 4h.; 200 psi
■ CO - 275° - 24 h.; 275°; 1/1; 200 psi
▲ 1/1 - 250° - 20h.; 275°; 200 psi
OLEFIN / PARAFFIN
DAYS
0
1
2
3
4
5
6
7
8
9
C_3
C_3
C_3
C_2
C_2
C_2


OLEFIN / PARAFFIN
DAYS
Prep 7
Prep 9
Prep 8
C_3
C_3
C_2
C_2
0
2
4
6
8
10
12
1
2
3
4
5
6
7
8
9
10

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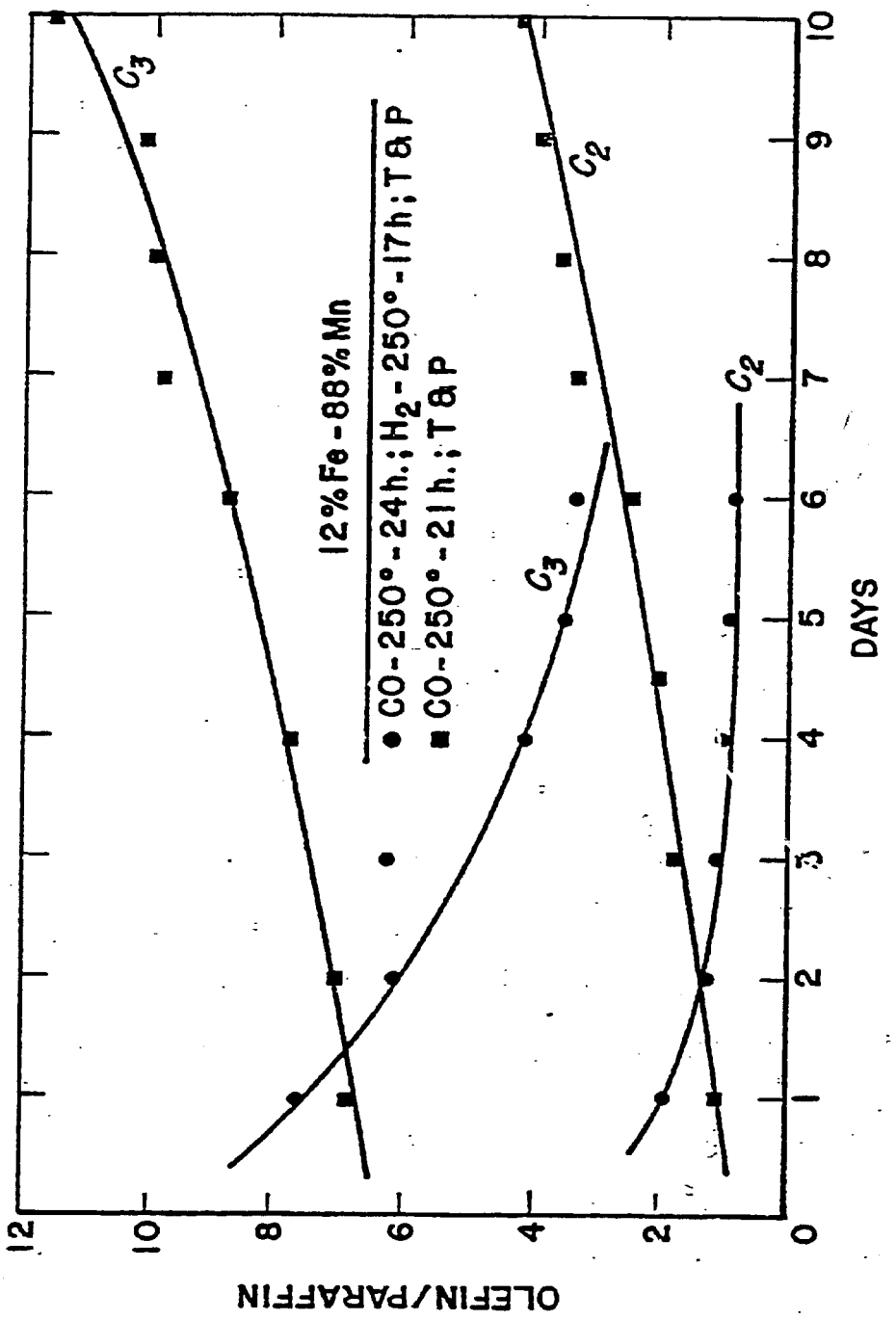
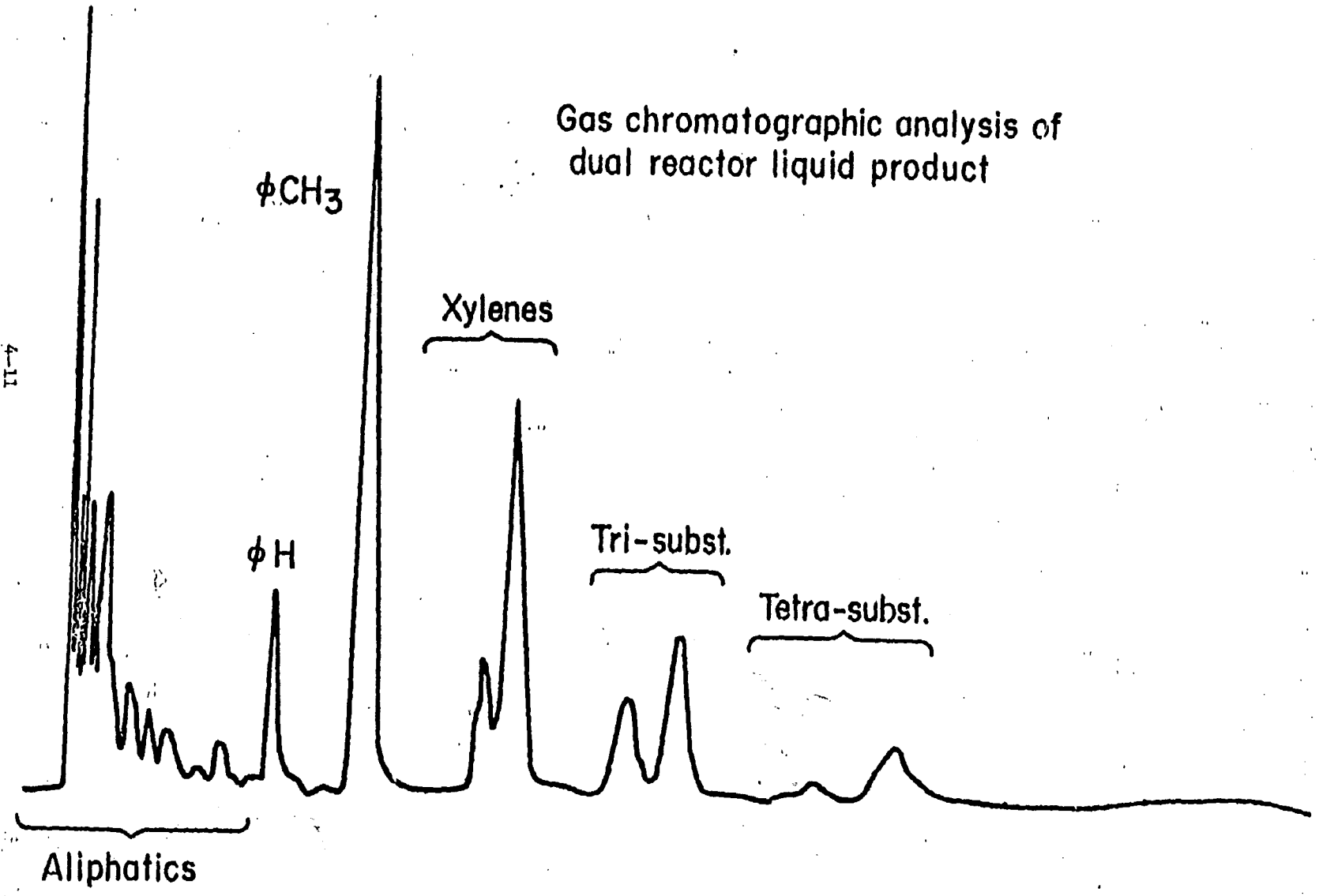
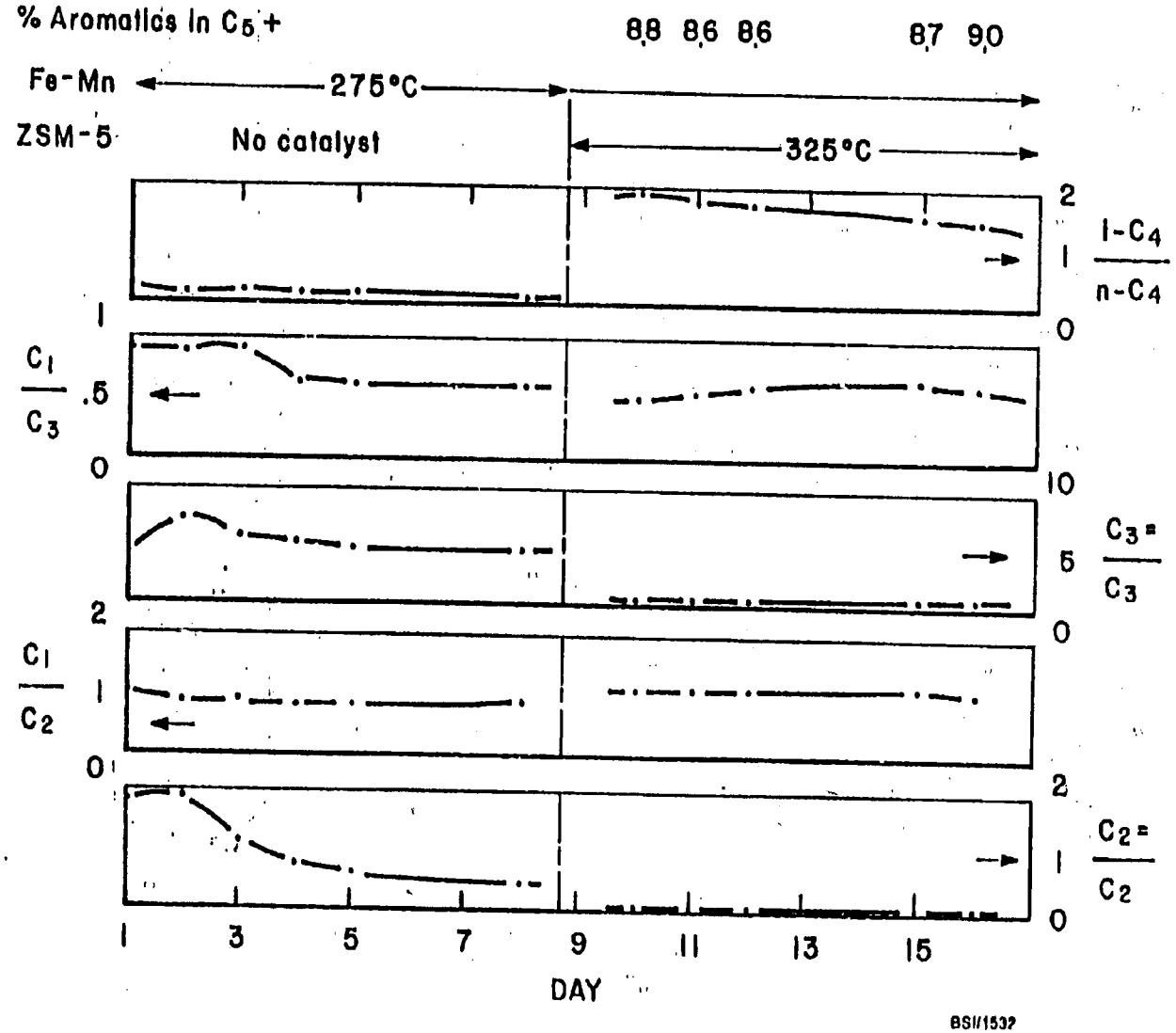
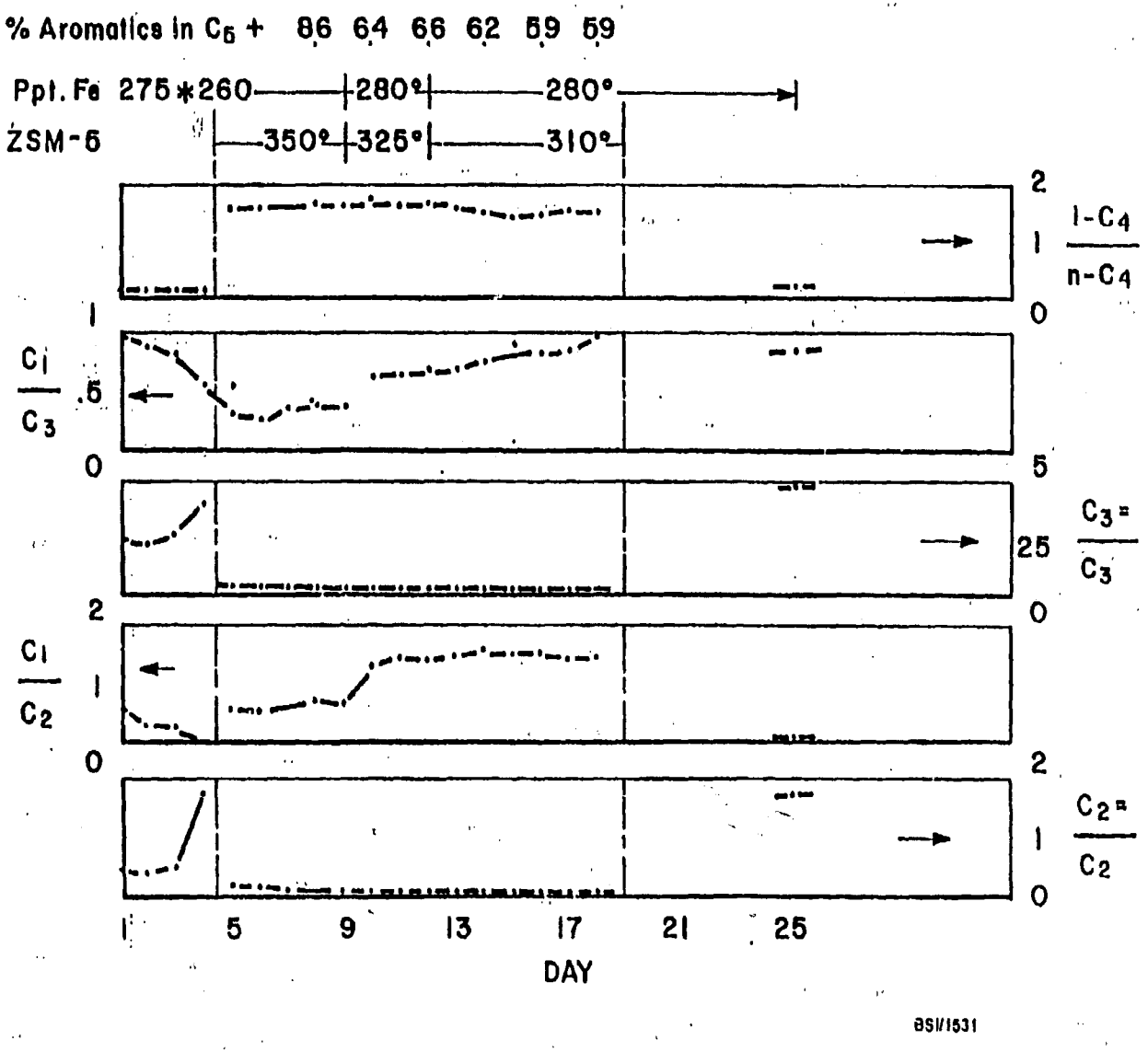

12%Fe-88%Mn
● CO-250°-24h.;H2-250°-17h;T&P
■ CO-250°-21h.;T&P
C3
C2
C3
C2
OLEFIN/PARAFFIN
DAYS
0
2
4
6
8
10
12
1
2
3
4
5
6
7
8
9
10
DSII1536

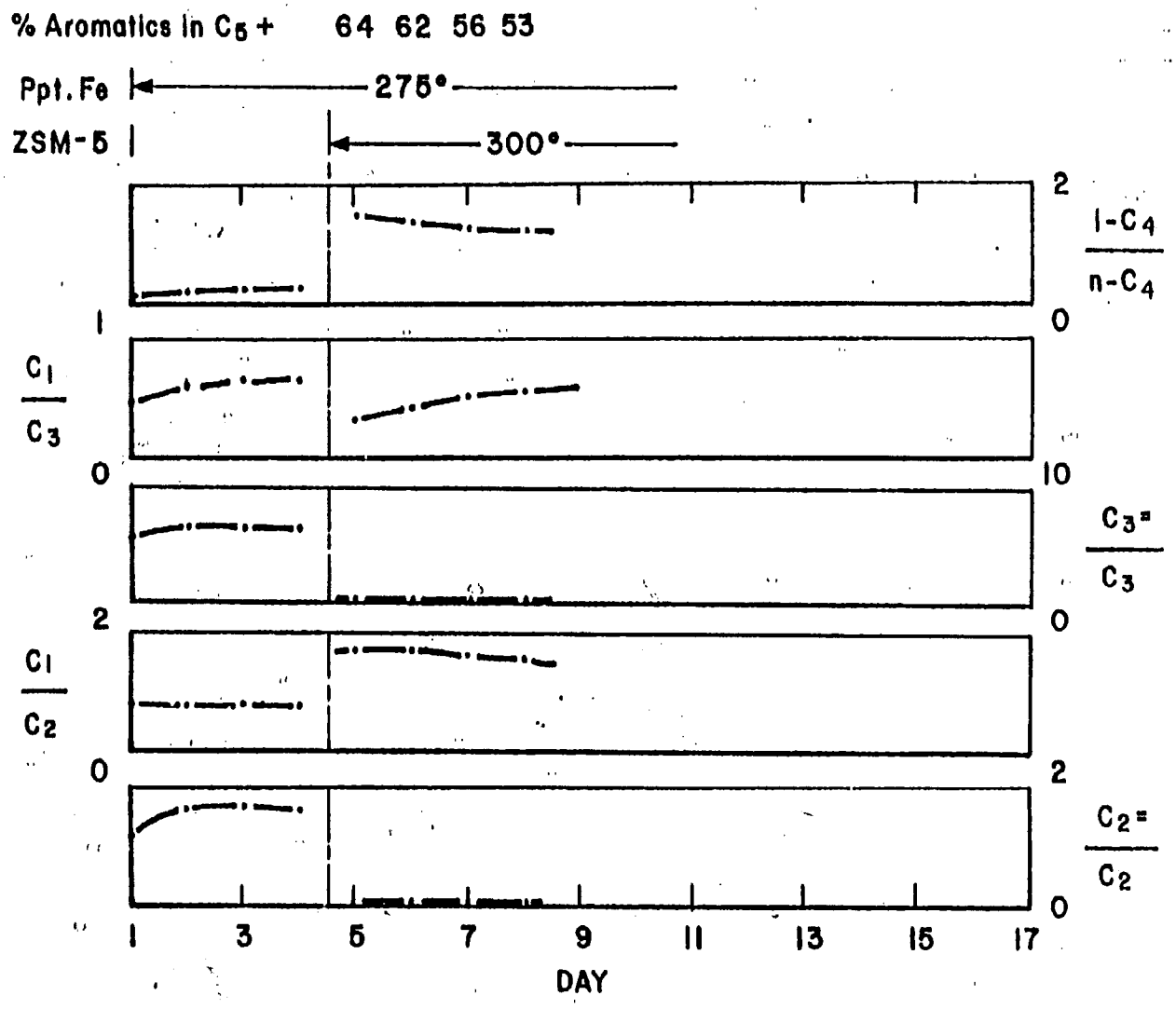
DATA ANALYSIS

- Maximize C_{5+}
- Minimize CH_4, C_2-C_4 saturates
- Upgrade C_2-C_4 olefins to gasoline over ZSM-5
- Heavy hydrocarbons crack over ZSM-5
  $C_n \rightarrow C_3$, C_4, C_5 etc.
  No C_2 or CH_4
- C_1/C_2 Increase expected since C_2H_4 will be upgraded
- C_1/C_3 Increase due to $C_3=$ upgrading
  Decrease due to cracking
  Net result: ?
- isobutane/n-butane
- % Aromatics in C_{5+}


Gas chromatographic analysis of
dual reactor liquid product
φCH3
Xylenes
φH
Tri-subst.
Tetra-subst.
Aliphatics


% Aromatics in C5+
8.8 8.6 8.6
8.7 9.0
Fe-Mn
ZSM-5
275°C
No catalyst
325°C
I-C4 / n-C4
C1 / C3
C3= / C3
C1 / C2
C2= / C2
DAY
BSII/1532


% Aromatics in C6 + 86 64 66 62 59 59
Ppt. Fe 275 * 260 280° 280°
ZSM-5 350° 325° 310°
2
1
0
I-C4 / n-C4
1
.5
0
Ci / C3
5
0
25
0
C3= / C3
2
1
0
Ci / C2
2
1
0
C2= / C2
1
5
9
13
17
21
25
DAY
BSI/1531


% Aromatics in C5 + 64 62 56 53
Ppt. Fe
275°
ZSM-5
300°
2
I-C4 / n-C4
1
0
C1 / C3
0
10
C3= / C3
2
0
C1 / C2
0
2
C2= / C2
0
1 3 5 7 9 11 13 15 17
DAY
BSW1530

DUAL REACTOR UNIT

CATALYST	PRECIPITATED Fe (Na_2CO_3)
Reactor 1	275° C
S.V. 1	3600 hr^{-1} (V/W)
Reactor 2	300° C

	FT	FT + ZSM-5
CO Conversion	30	31
Selectivity, %		
CH_4	7.9	7.7
C_2H_4	5.4	–
C_2H_6	4.2	4.3
C_3H_6	10.0	0.2
C_3H_8	1.6	7.1
C_4H_8	8.3	9.6
C_4H_{10}	1.7	24.0
C_5+	60.0	47.0

CONCLUSION

- THE PRODUCTION OF MIDBARREL (TURBINE AND DIESEL) BOILING RANGE HYDROCARBONS IS POSSIBLE FROM BOTH METHANOL AND PROPYLENE BY THE USE OF NEW UNION CARBIDE MOLECULAR SIEVES.
- THE UNION CARBIDE MOLECULAR SIEVE UCC-104 IS ABLE TO CONVERT PROPYLENE TO C_5^+ LIQUID CONSISTING MAINLY OF GASOLINE IN NEAR QUANTITATIVE YIELD (> 95% SELECTIVITY)
- SEVERAL SUPERIOR SHAPE SELECTIVE CATALYSTS SSC ARE NOW AVAILABLE FOR THE FORMULATION OF CATALYSTS FOR THE DIRECT CONVERSION OF SYNGAS EITHER TO GASOLINE OR TO TURBINE AND DIESEL OIL