US008742144B2

(12) United States Patent
Lilga et al.

(10) Patent No.: US 8,742,144 B2
(45) Date of Patent: Jun. 3, 2014

(54) **HYDROXYMETHYLFURFURAL REDUCTION METHODS AND METHODS OF PRODUCING FURANDIMETHANOL**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **13/174,181**

(22) Filed: **Jun. 30, 2011**

(65) **Prior Publication Data**

US 2011/0257419 A1 Oct. 20, 2011

Related U.S. Application Data

(62) Division of application No. 11/760,634, filed on Jun. 8, 2007, now Pat. No. 7,994,347.

(60) Provisional application No. 60/804,409, filed on Jun. 9, 2006.

(51) **Int. Cl.**
C07D 307/02 (2006.01)

(52) **U.S. Cl.**
USPC **549/503**

(58) **Field of Classification Search**
USPC 549/503
See application file for complete search history.

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Primary Examiner — Nizal Chandrakumar
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(57) **ABSTRACT**

A method of reducing hydroxymethylfurfural (HMF) where a starting material containing HMF in a solvent comprising water is provided. H_2 is provided into the reactor and the starting material is contacted with a catalyst containing at least one metal selected from Ni, Co, Cu, Pd, Pt, Ru, Ir, Re and Rh, at a temperature of less than or equal to 250° C. A method of hydrogenating HMF includes providing an aqueous solution containing HMF and fructose. H_2 and a hydrogenation catalyst are provided. The HMF is selectively hydrogenated relative to the fructose at a temperature at or above 30° C. A method of producing tetrahydrofuran dimethanol (THFDM) includes providing a continuous flow reactor having first and second catalysts and providing a feed comprising HMF into the reactor. The feed is contacted with the first catalyst to produce furan dimethanol (FDM) which is contacted with the second catalyst to produce THFDM.

8 Claims, 80 Drawing Sheets

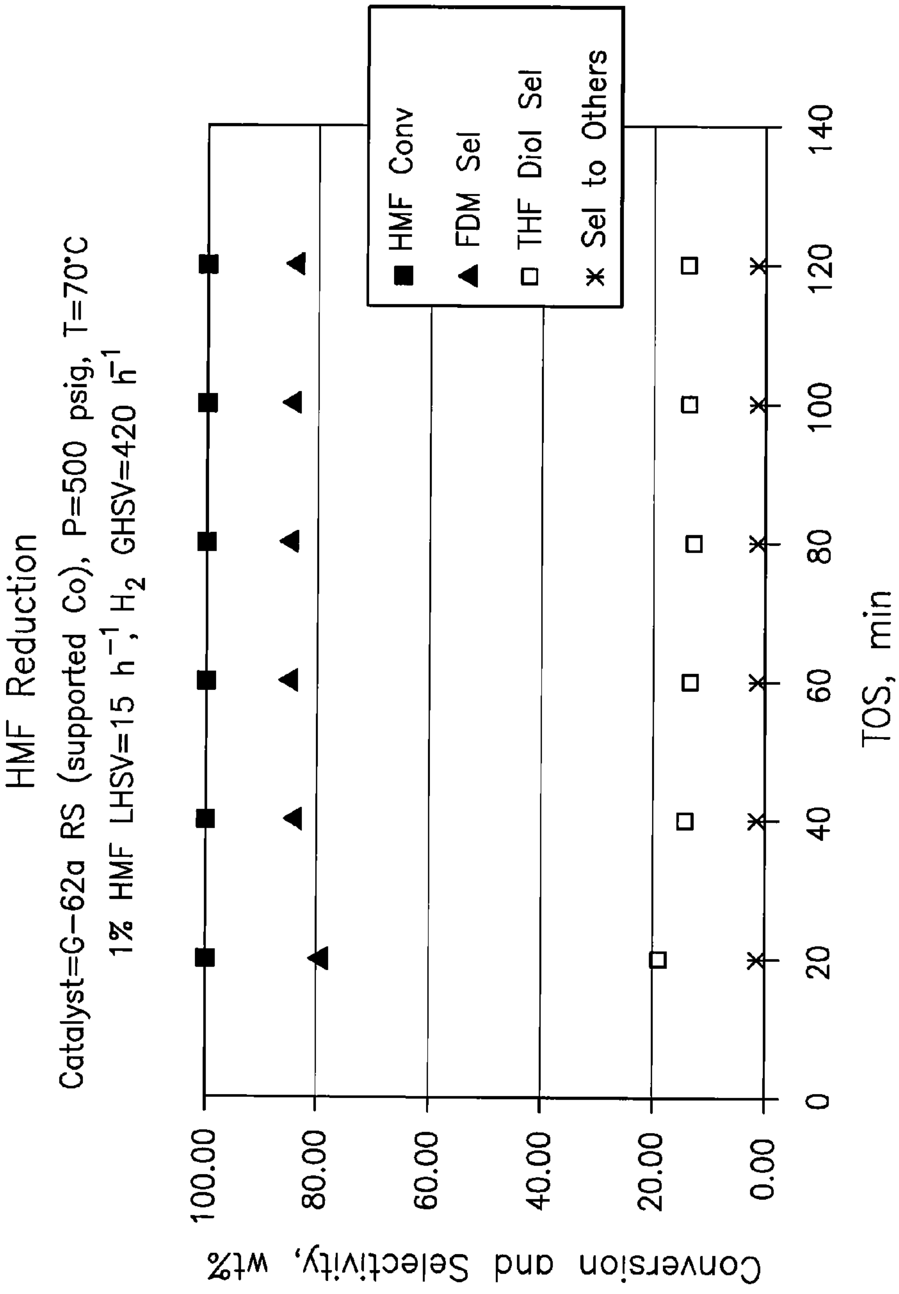

HMF Reduction
Catalyst=G-62a RS (supported Co), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others

FIG. 1

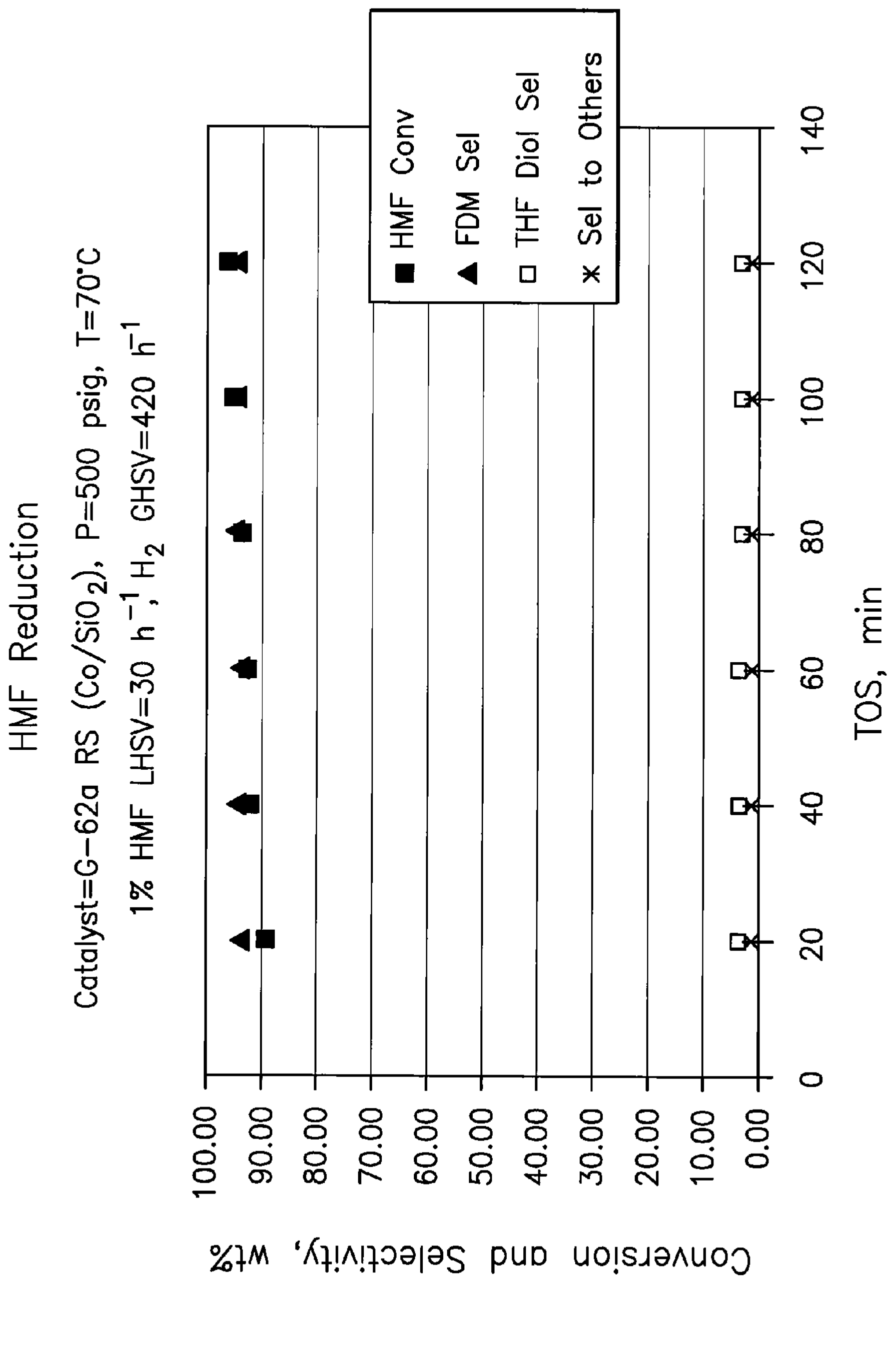

HMF Reduction
Catalyst=G-62a RS (Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=30 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others

Fig. 2

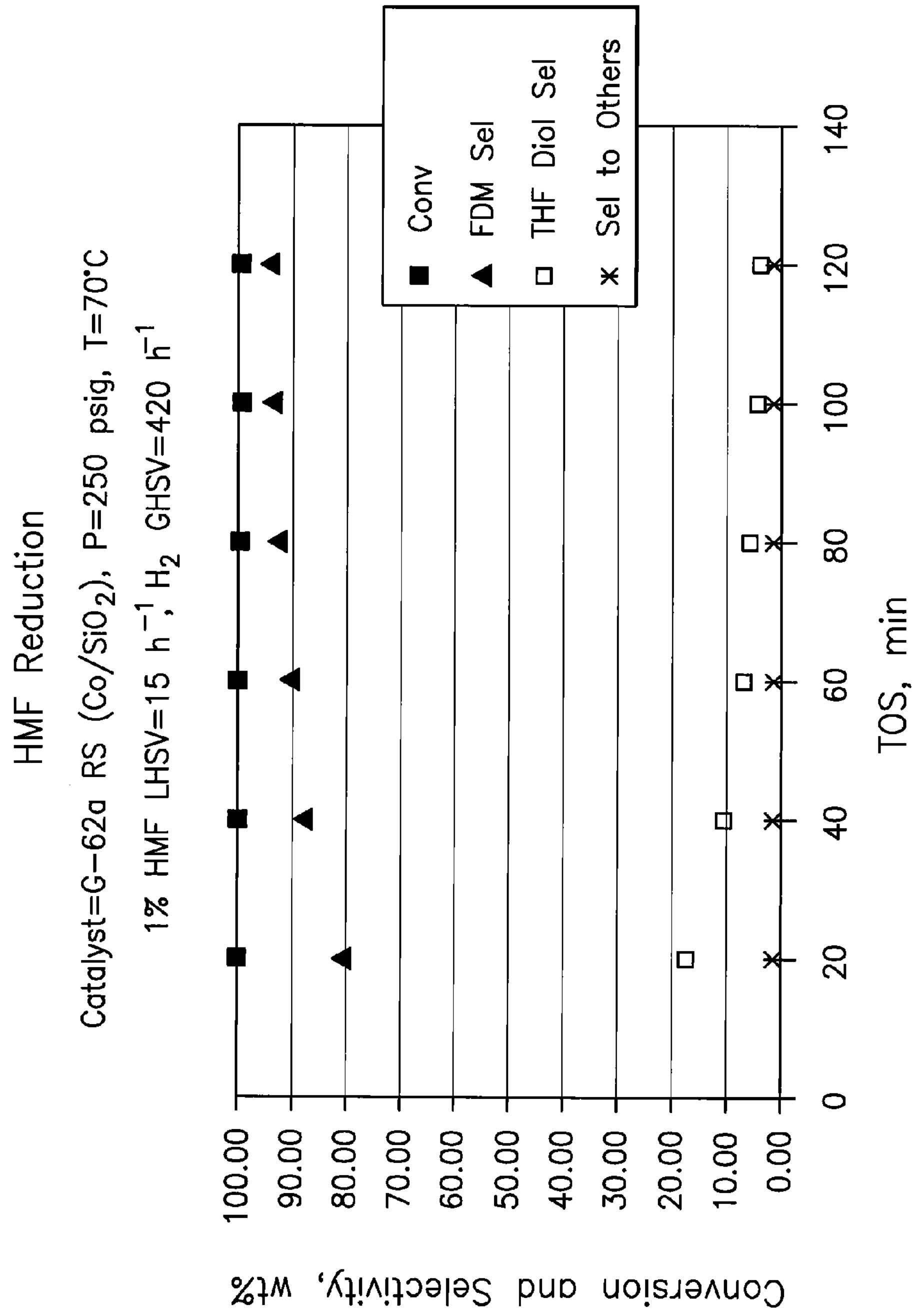

HMF Reduction
Catalyst=G-62a RS (Co/SiO2), P=250 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
Conv
FDM Sel
THF Diol Sel
Sel to Others

FIG. 3

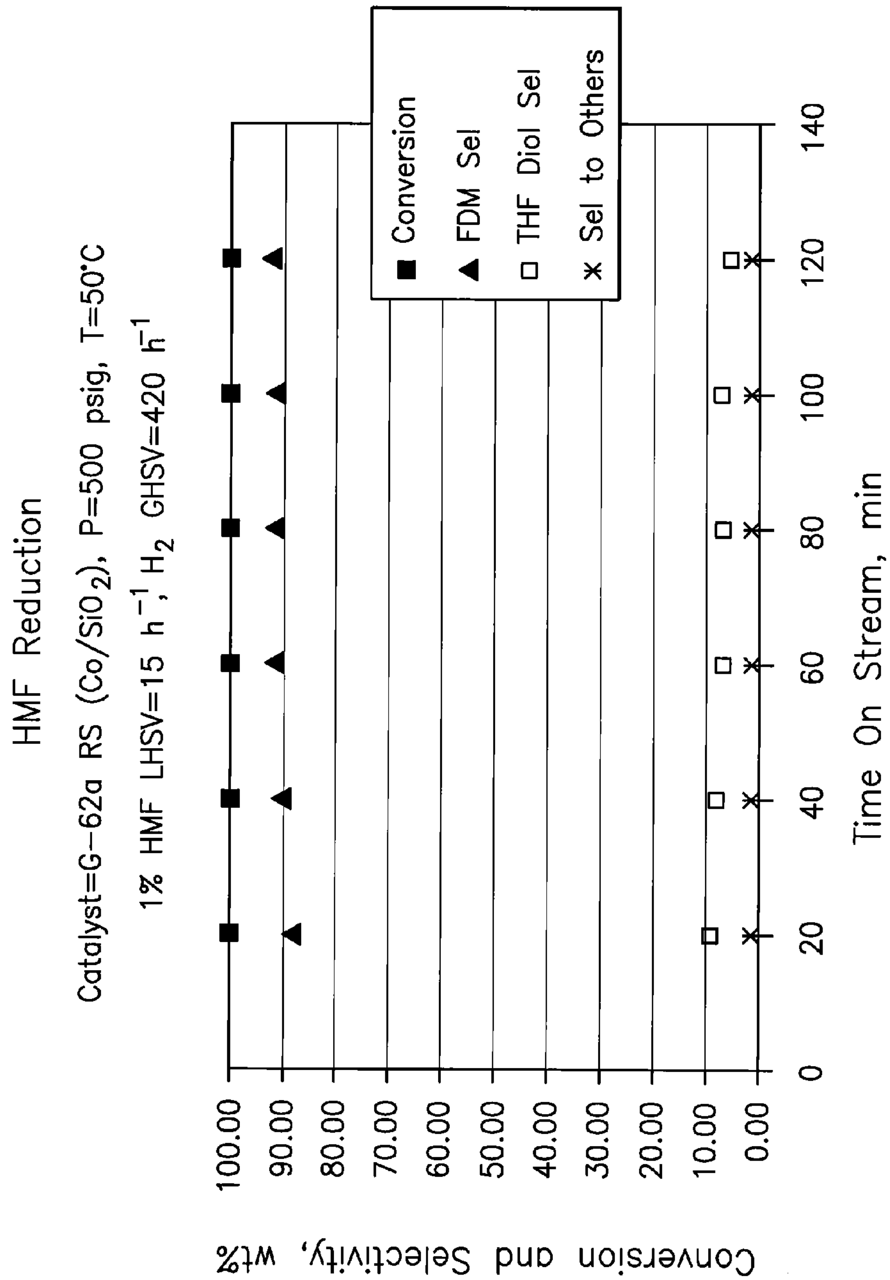

HMF Reduction
Catalyst=G-62a RS (Co/SiO2), P=500 psig, T=50°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
Time On Stream, min
Conversion
FDM Sel
THF Diol Sel
Sel to Others

Fig. 4

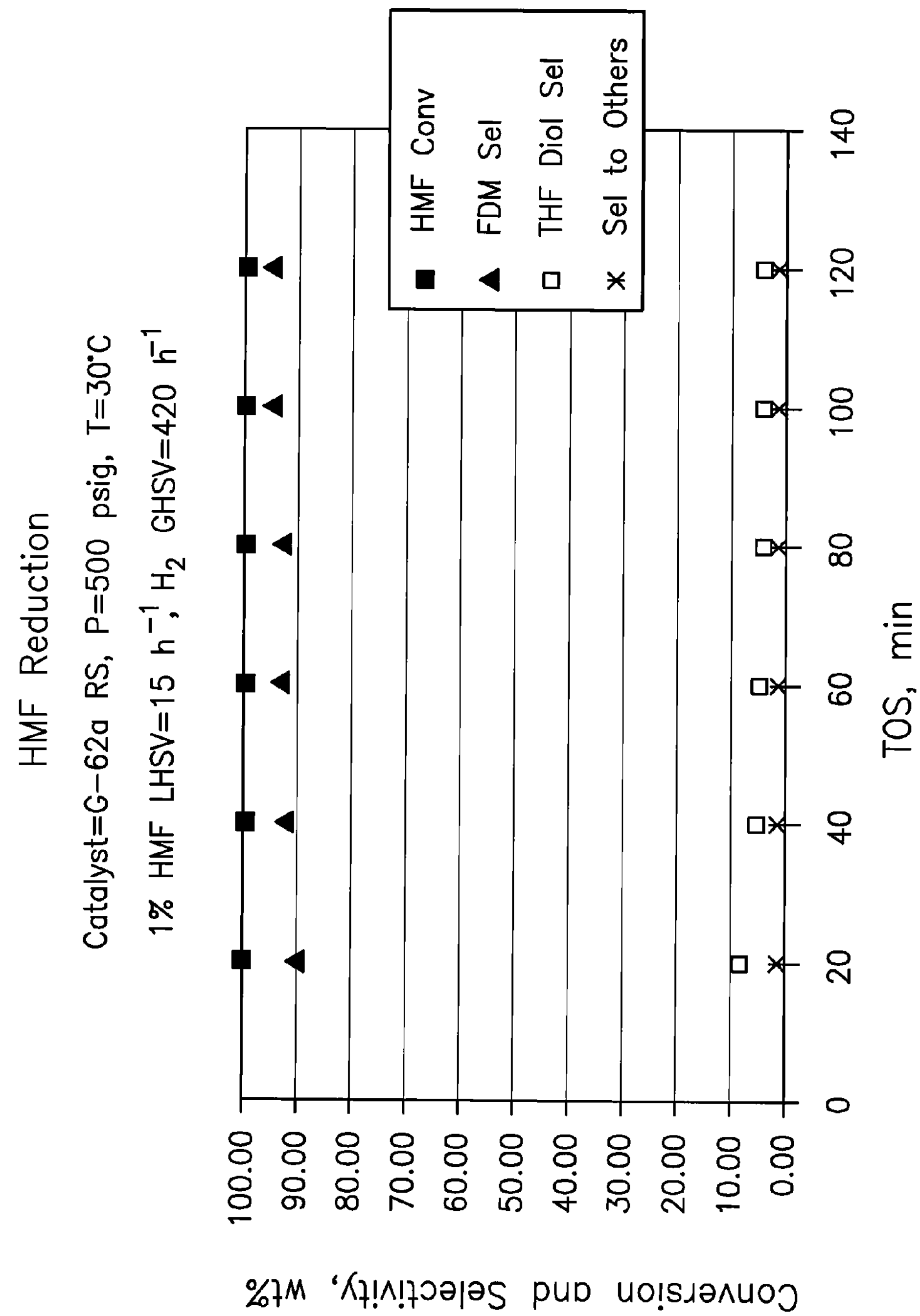

HMF Reduction
Catalyst=G-62a RS, P=500 psig, T=30°C
1% HMF LHSV=15 h^{-1}, H_2 GHSV=420 h^{-1}
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others

FIG. 5

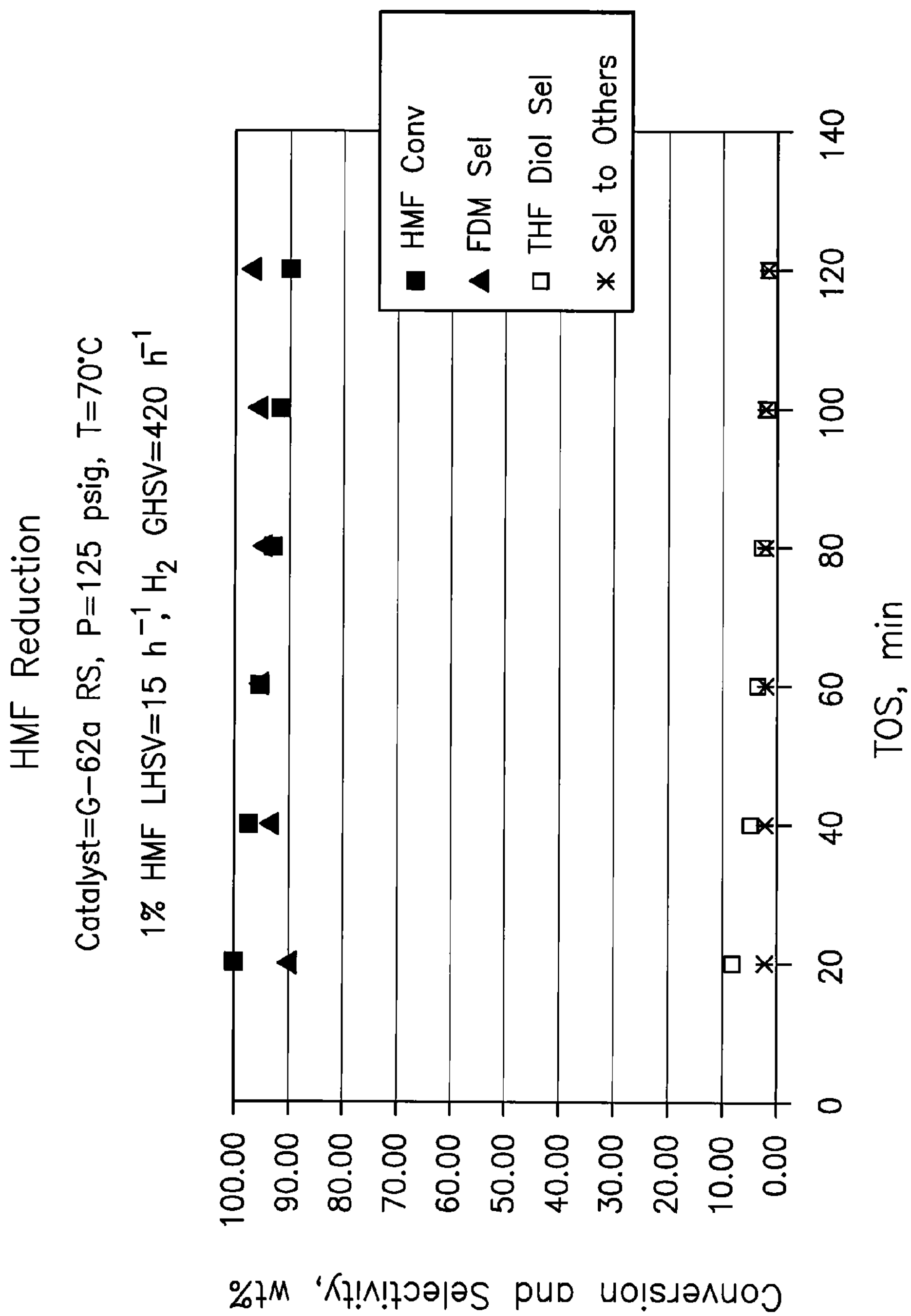

HMF Reduction
Catalyst=G-62a RS, P=125 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 6

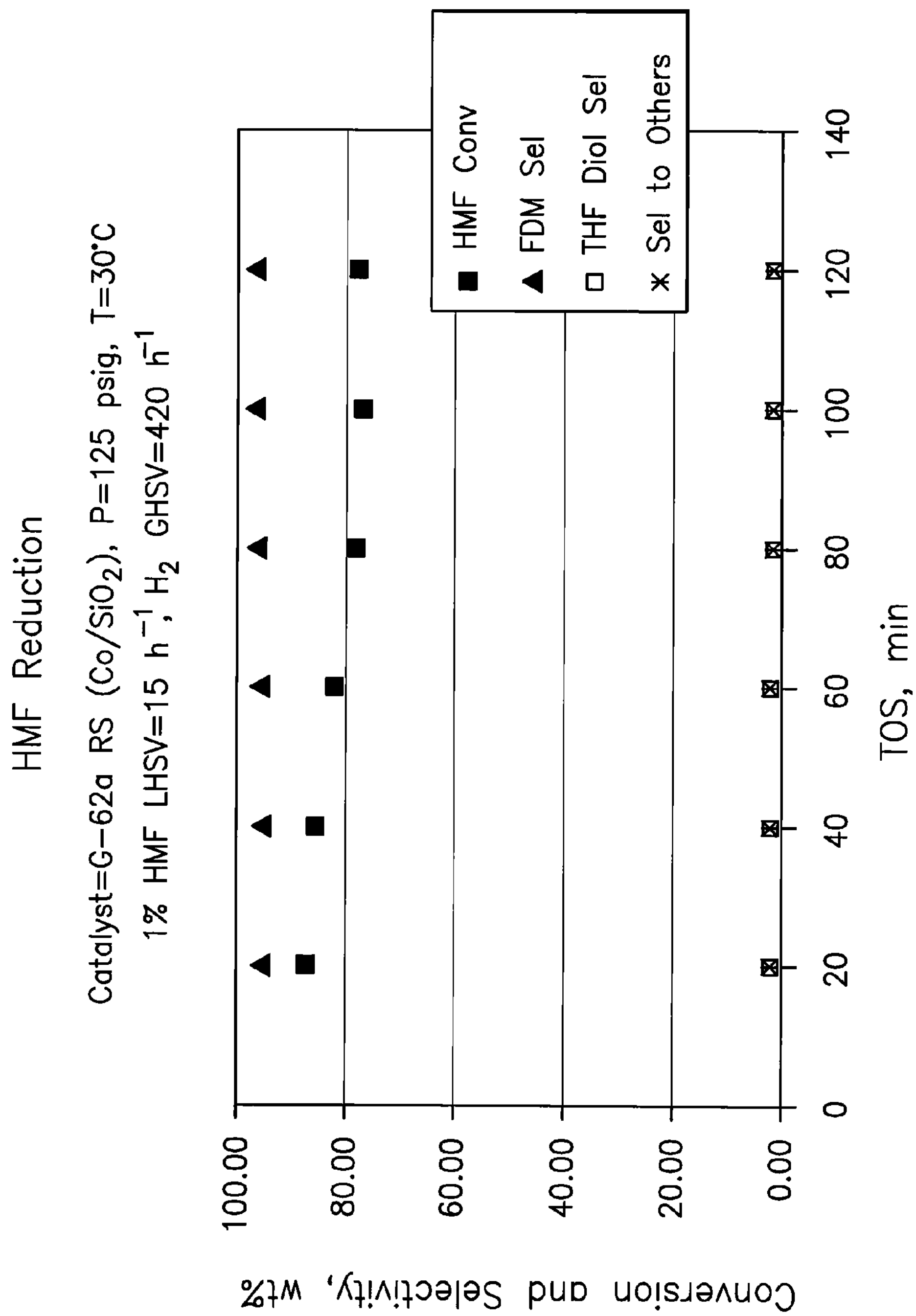

HMF Reduction
Catalyst=G-62a RS (Co/SiO2), P=125 psig, T=30°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min

Fig. 7

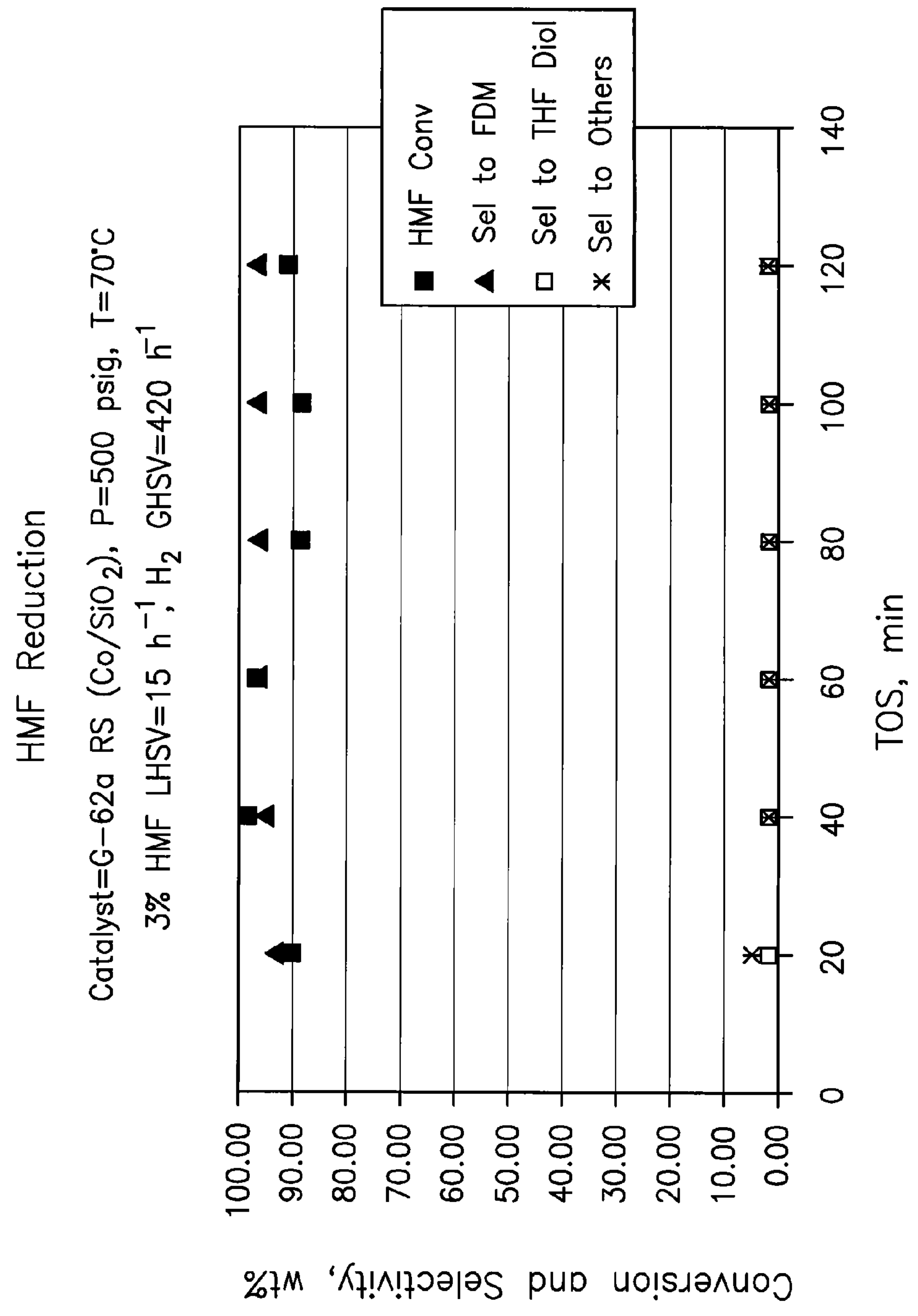

HMF Reduction
Catalyst=G-62a RS (Co/SiO2), P=500 psig, T=70°C
3% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others

FIG. 8

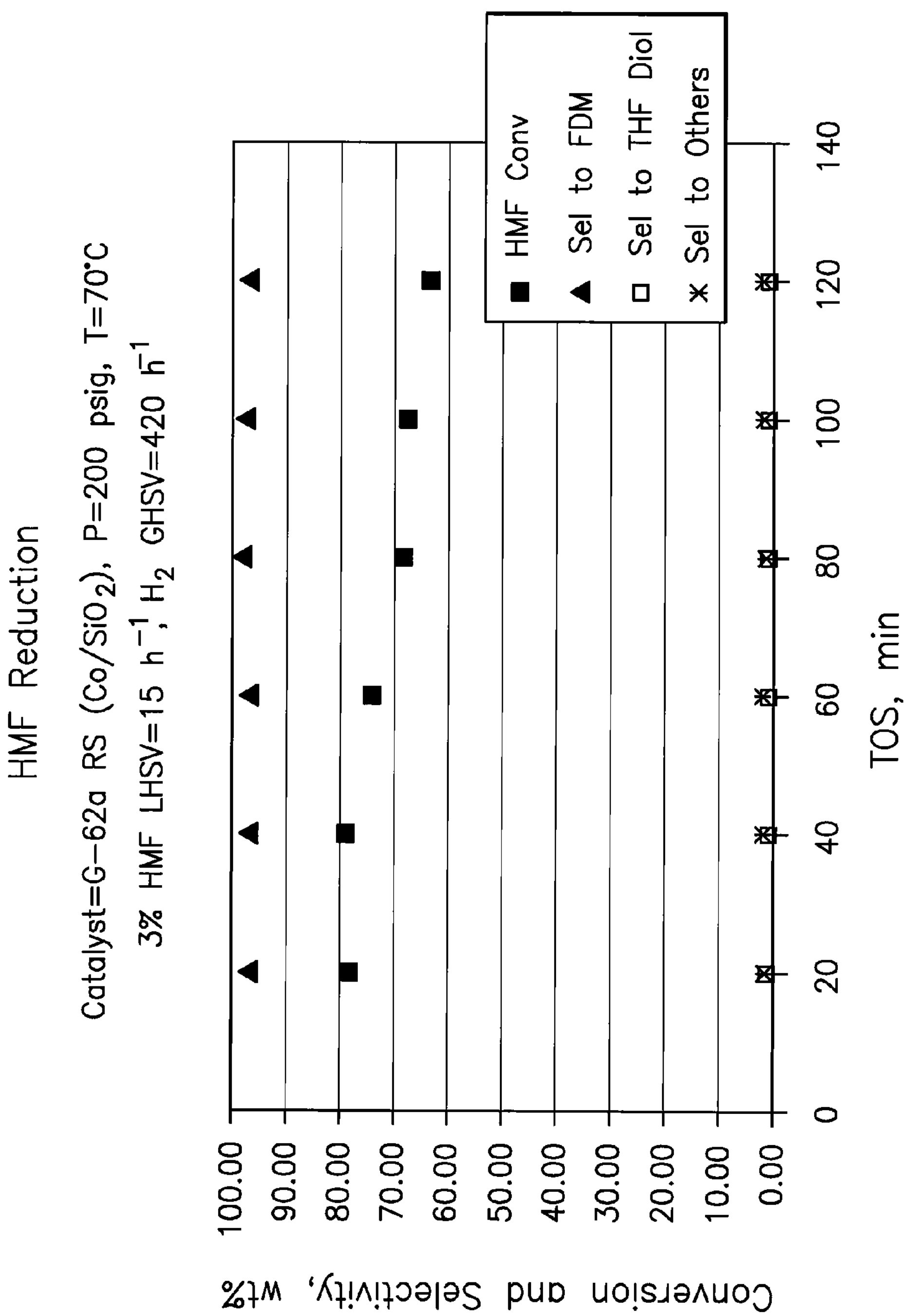

HMF Reduction
Catalyst=G-62a RS (Co/SiO2), P=200 psig, T=70°C
3% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 9

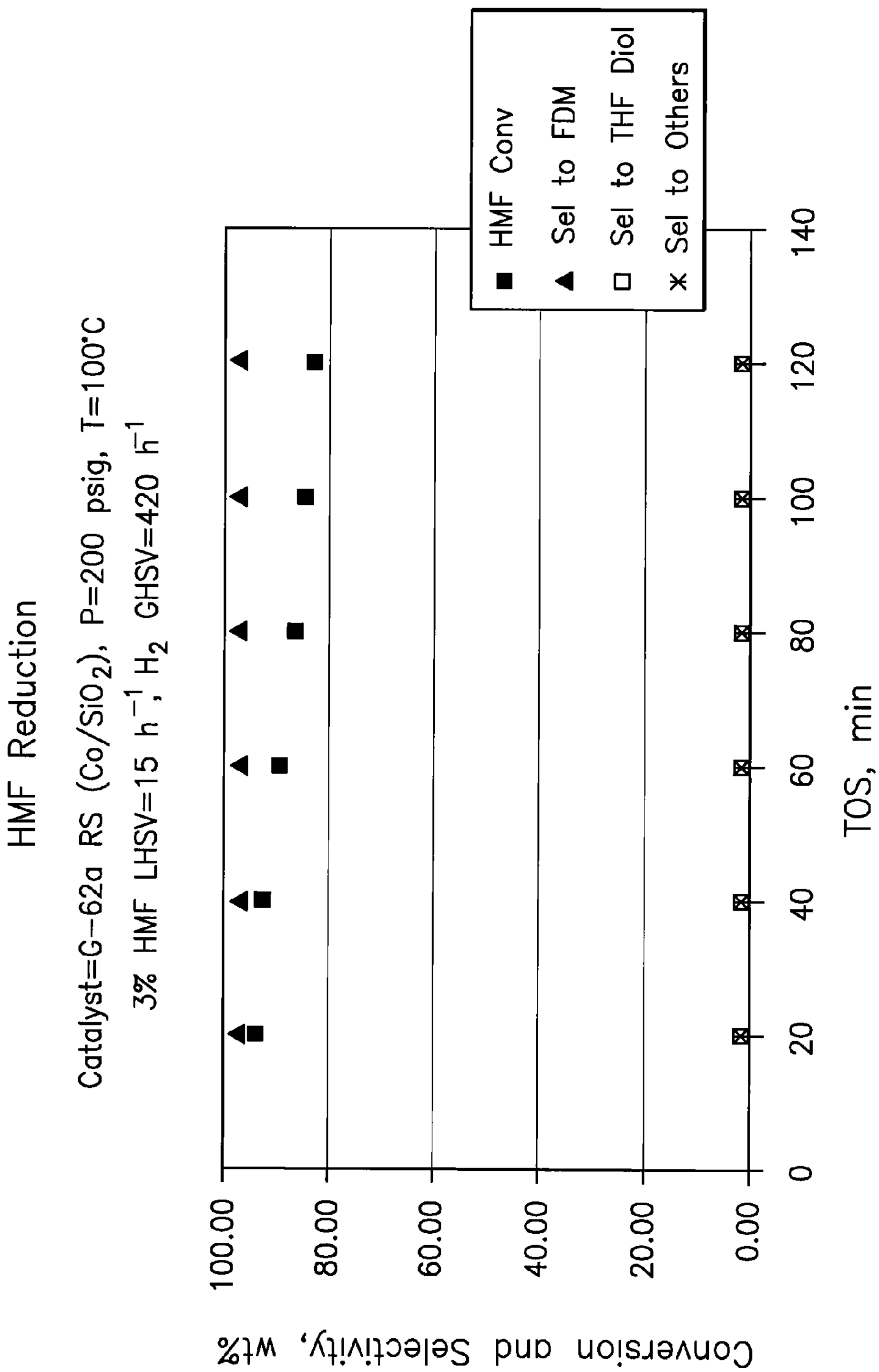

HMF Reduction
Catalyst=G−62a RS (Co/SiO2), P=200 psig, T=100°C
3% HMF LHSV=15 h−1, H2 GHSV=420 h−1
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others

FIG. 10

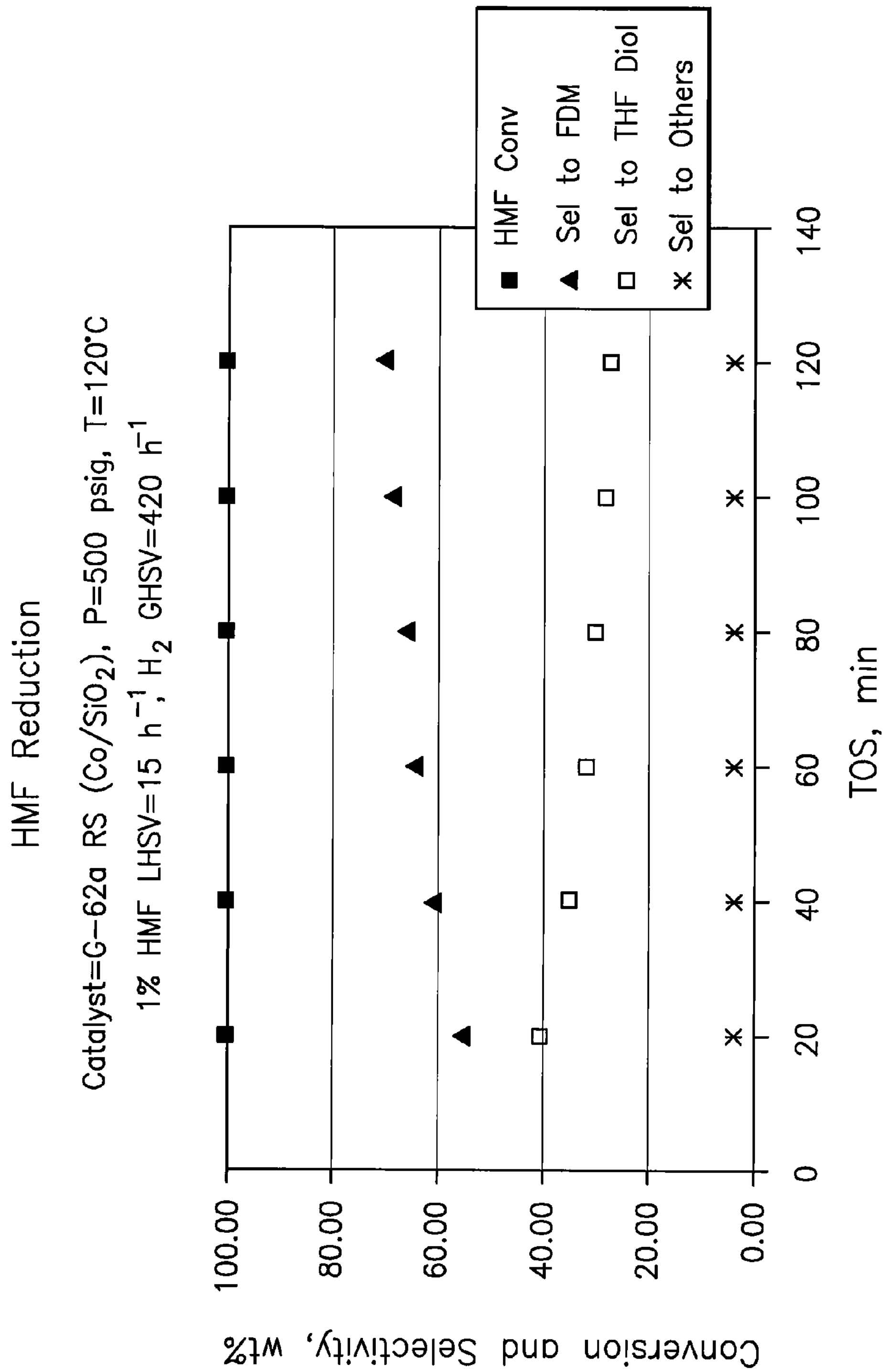

HMF Reduction
Catalyst=G-62a RS (Co/SiO2), P=500 psig, T=120°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 11

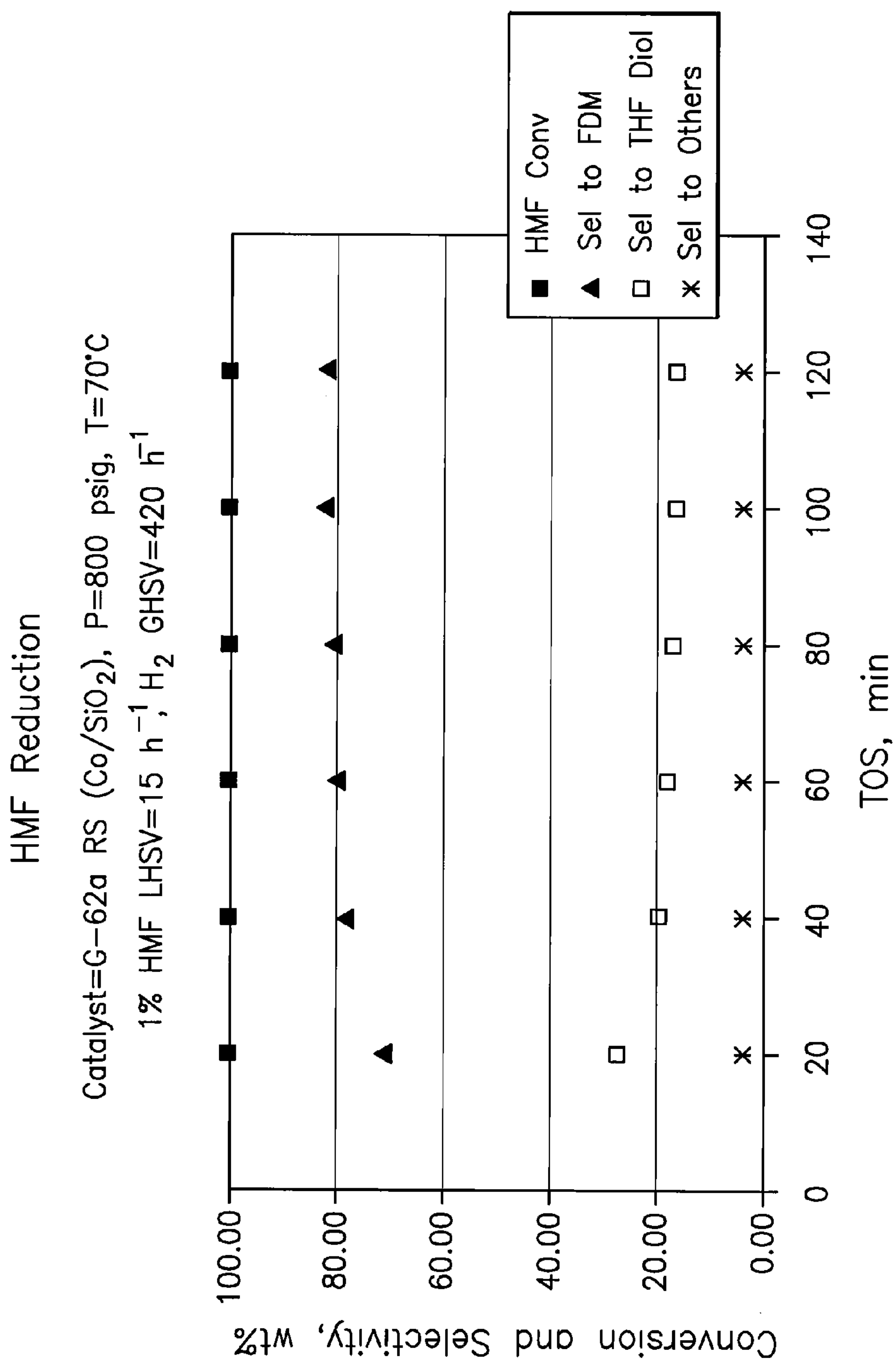
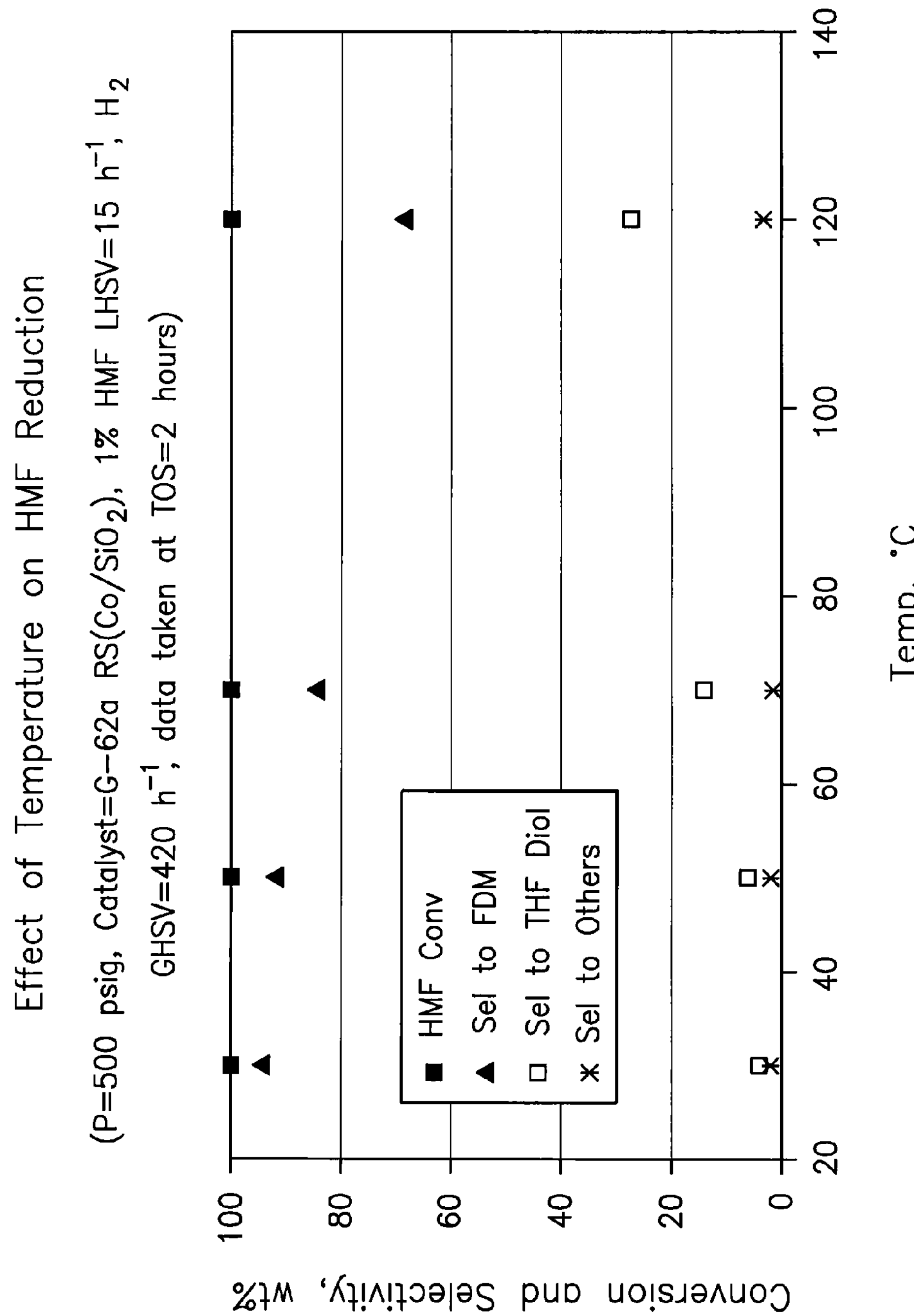

HMF Reduction
Catalyst=G-62a RS (Co/SiO2), P=800 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 12



Effect of Temperature on HMF Reduction
(P=500 psig, Catalyst=G-62a RS(Co/SiO2), 1% HMF LHSV=15 h-1, H2
GHSV=420 h-1, data taken at TOS=2 hours)
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
Temp, °C
100
80
60
40
20
0
20
40
60
80
100
120
140

FIG 13

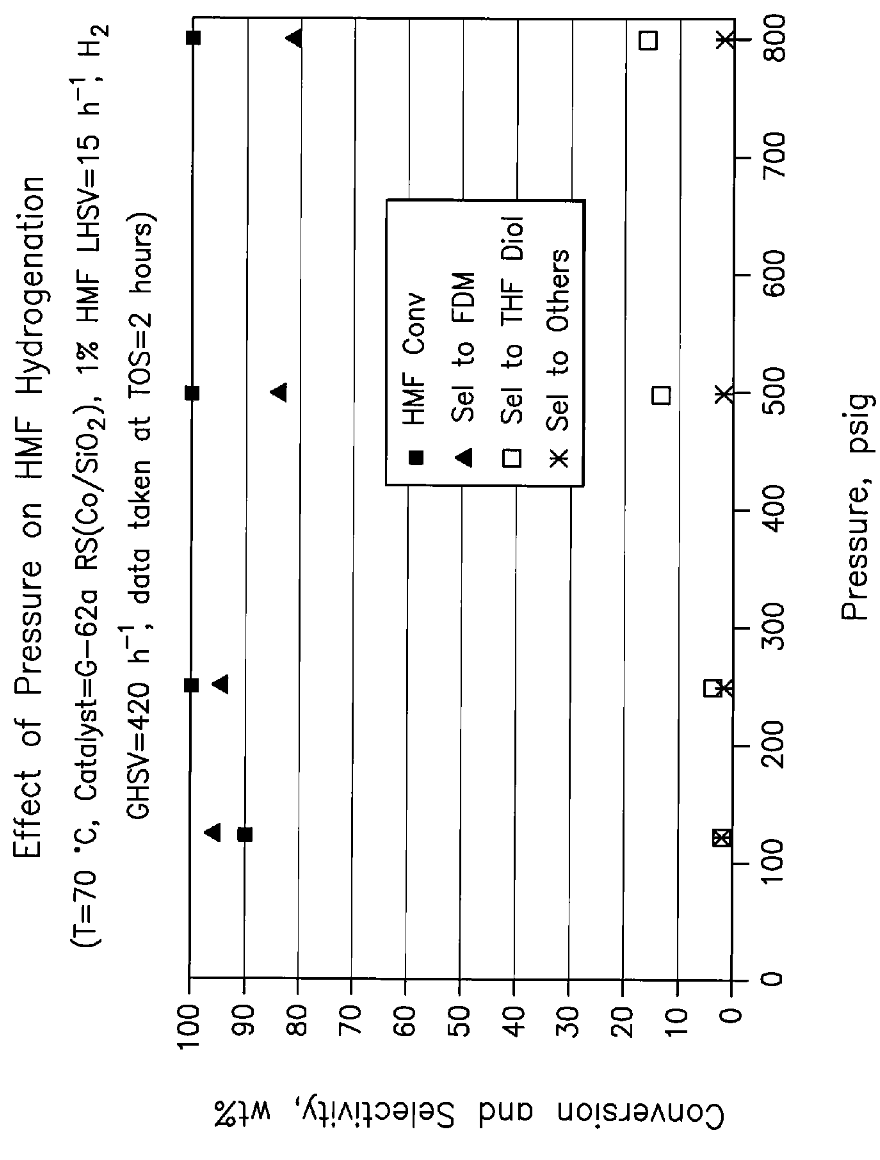

Effect of Pressure on HMF Hydrogenation
(T=70 °C, Catalyst=G-62a RS(Co/SiO2), 1% HMF LHSV=15 h-1; H2
GHSV=420 h-1, data taken at TOS=2 hours)
Conversion and Selectivity, wt%
100
90
80
70
60
50
40
30
20
10
0
Pressure, psig
0
100
200
300
400
500
600
700
800
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others

FIG. 14

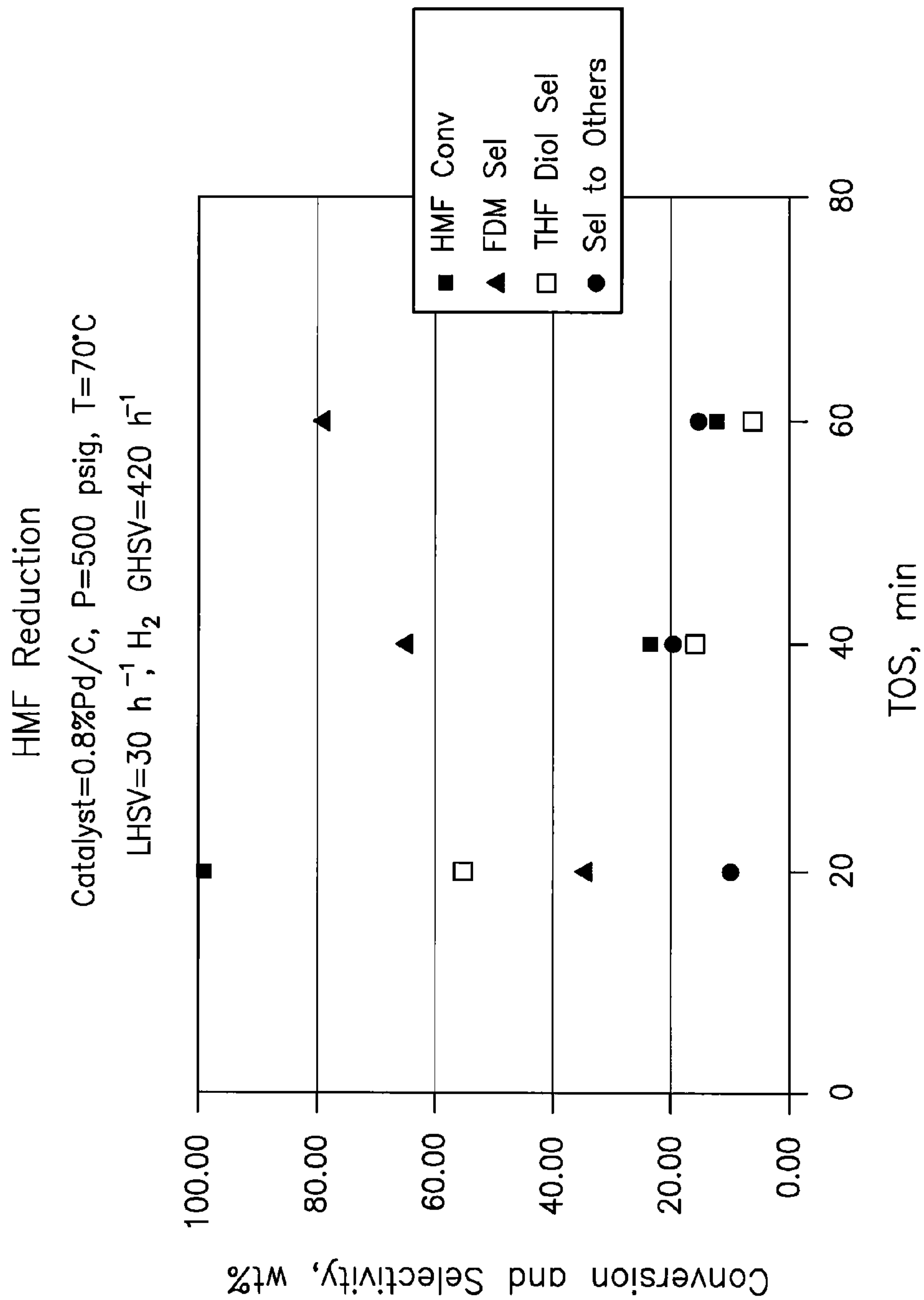

HMF Reduction
Catalyst=0.8%Pd/C, P=500 psig, T=70°C
LHSV=30 h⁻¹, H2 GHSV=420 h⁻¹
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
TOS, min

Fig. 15

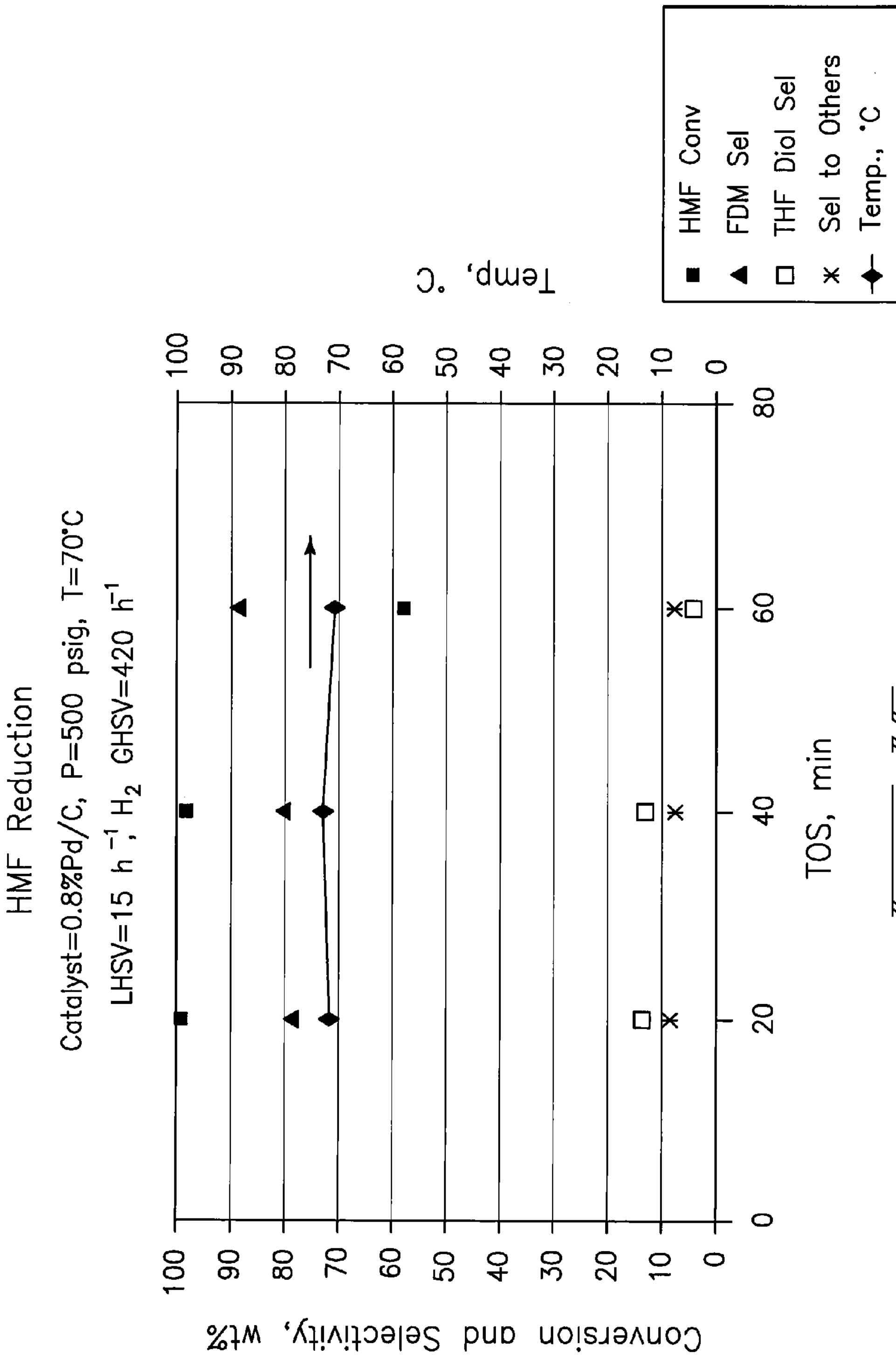

HMF Reduction
Catalyst=0.8%Pd/C, P=500 psig, T=70°C
LHSV=15 h^-1, H2 GHSV=420 h^-1
Conversion and Selectivity, wt%
TOS, min
Temp., °C
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Temp., °C
0
10
20
30
40
50
60
70
80
90
100

FIG. 16

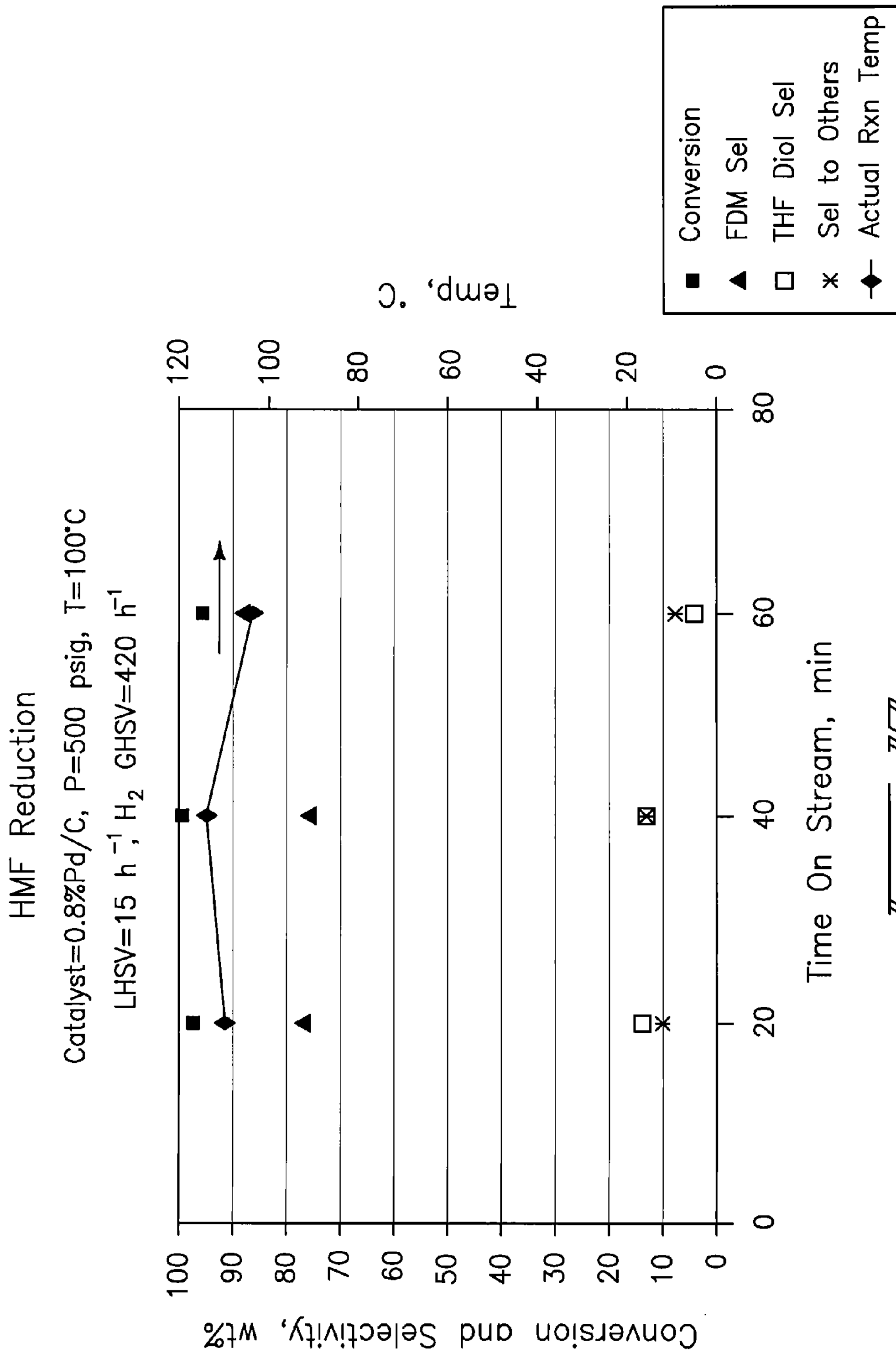

HMF Reduction
Catalyst=0.8%Pd/C, P=500 psig, T=100°C
LHSV=15 h^{-1}, H_2 GHSV=420 h^{-1}
Conversion and Selectivity, wt%
Temp, °C
Time On Stream, min
0
20
40
60
80
10
30
50
70
90
100
120
Conversion
FDM Sel
THF Diol Sel
Sel to Others
Actual Rxn Temp

FIG. 17

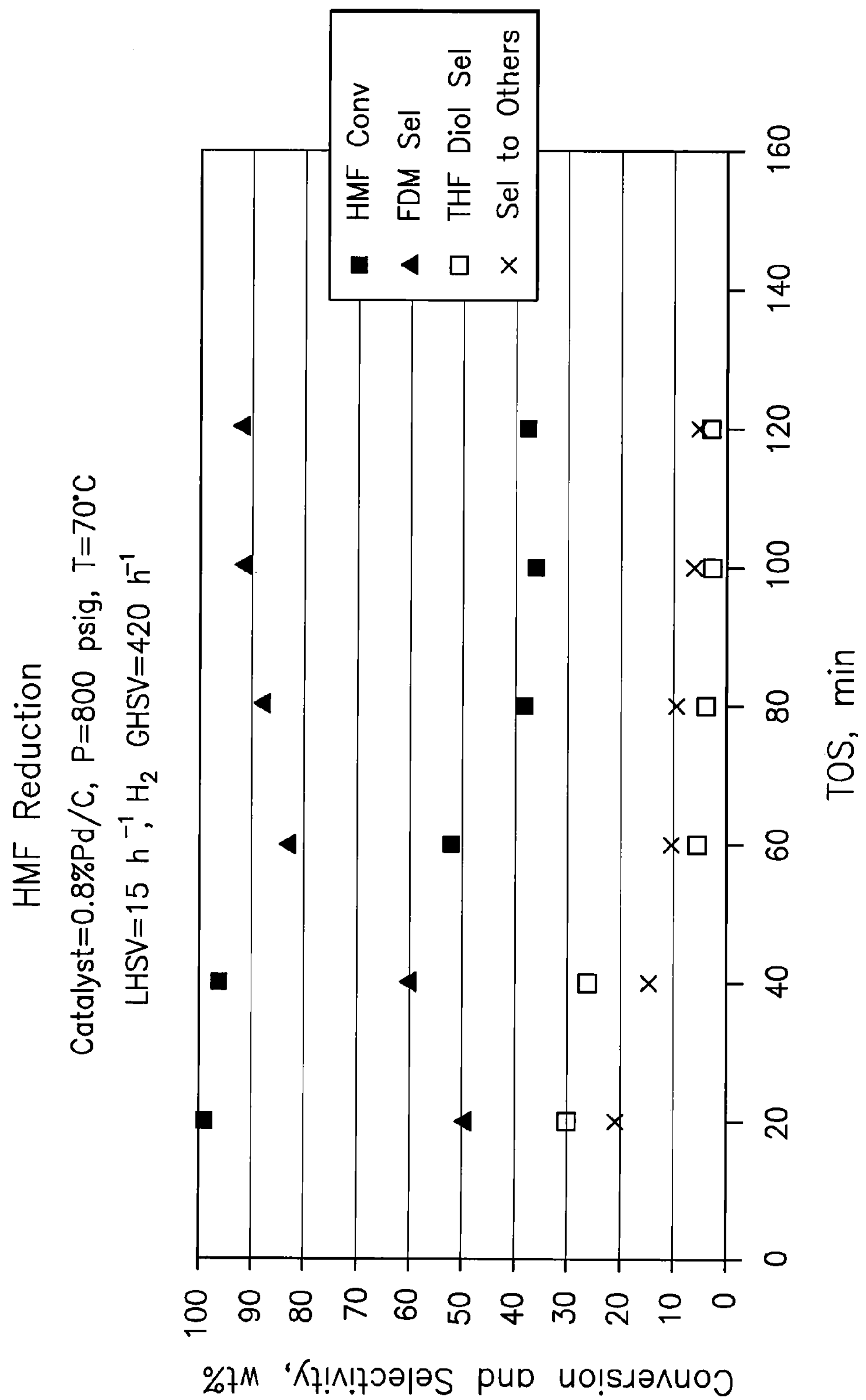

HMF Reduction
Catalyst=0.8%Pd/C, P=800 psig, T=70°C
LHSV=15 h⁻¹, H₂ GHSV=420 h⁻¹
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100
90
80
70
60
50
40
30
20
10
0
TOS, min
0
20
40
60
80
100
120
140
160

FIG. 18

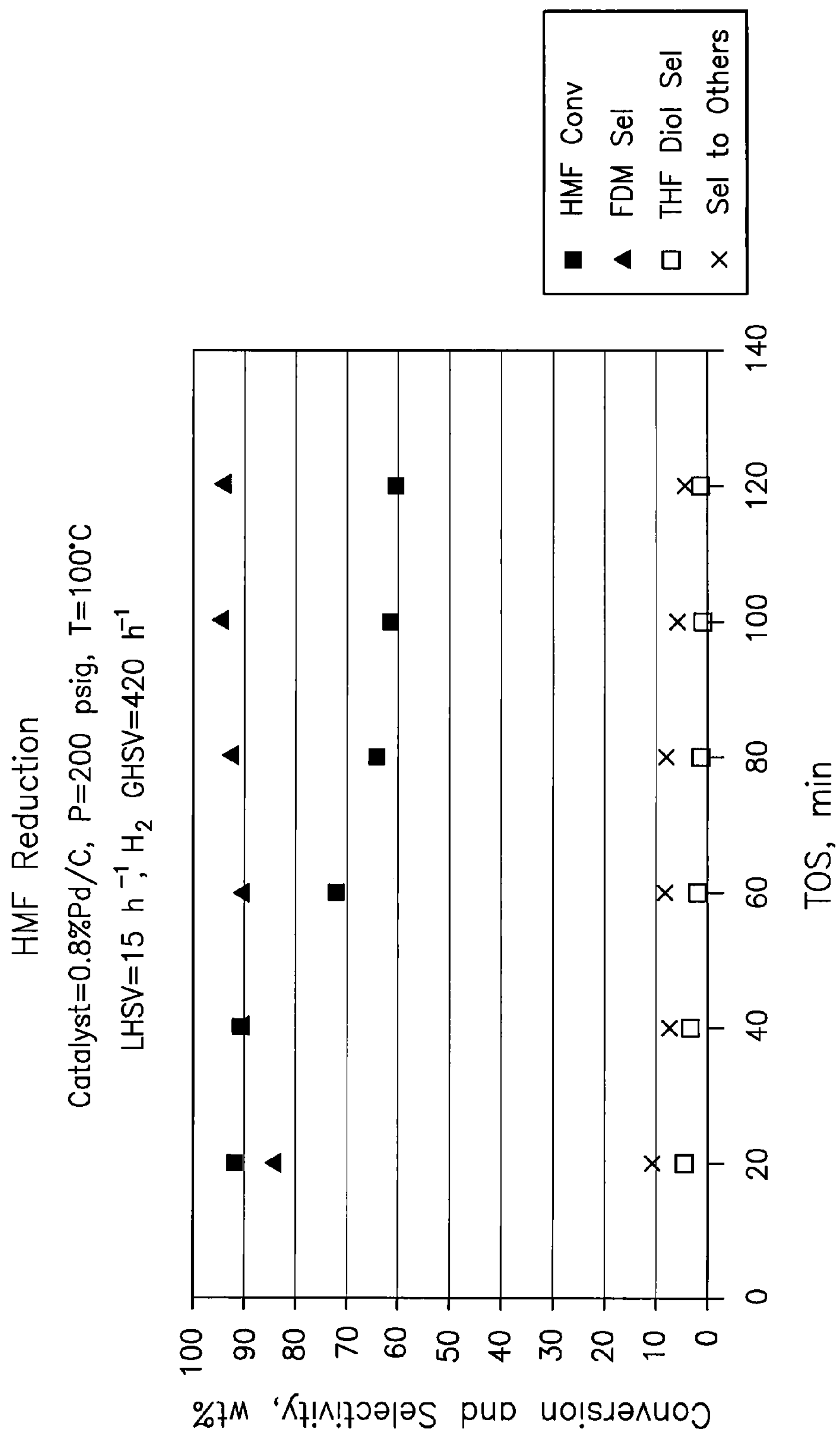

HMF Reduction
Catalyst=0.8%Pd/C, P=200 psig, T=100°C
LHSV=15 h⁻¹, H₂ GHSV=420 h⁻¹
Conversion and Selectivity, wt%
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others

Fig. 19

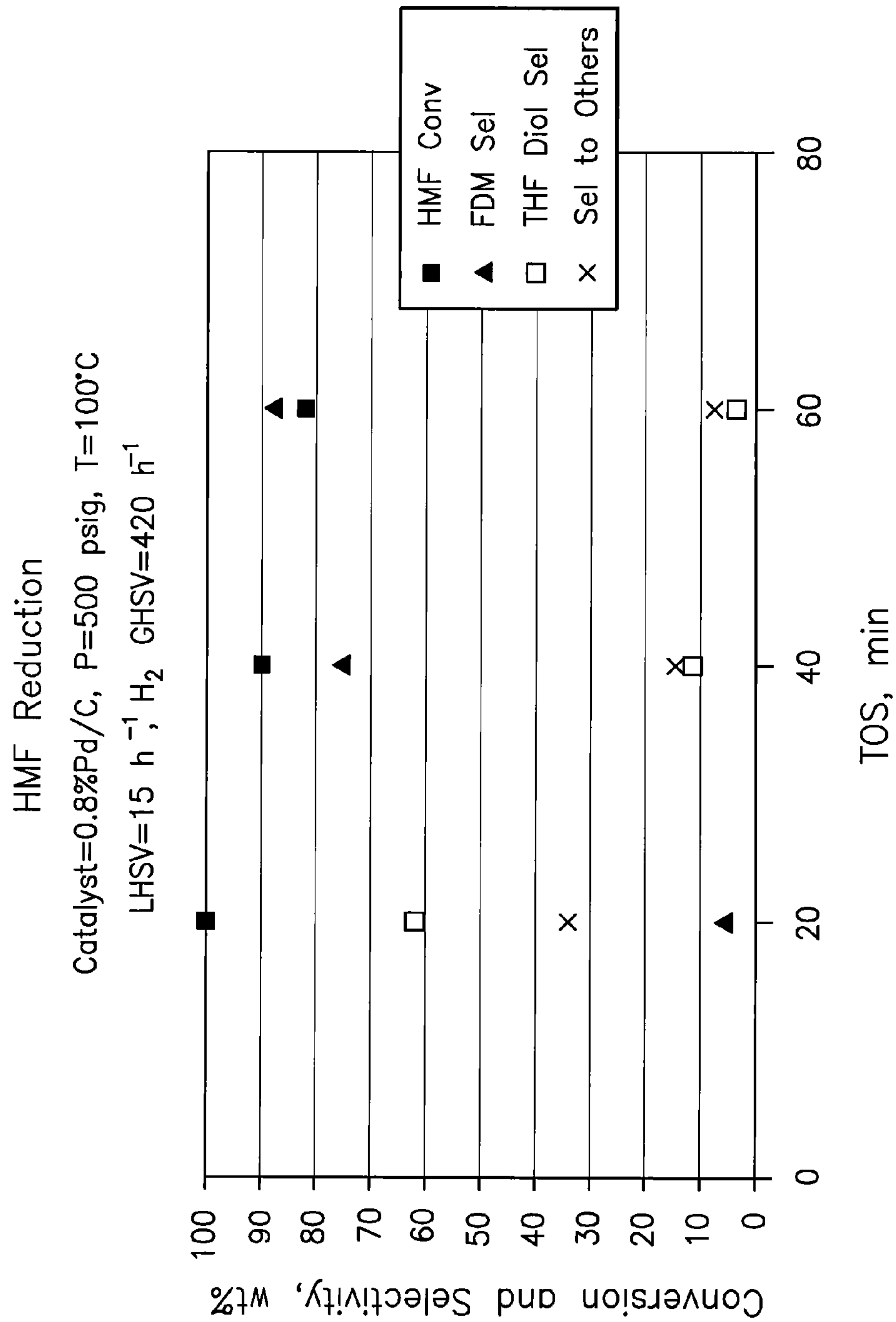

HMF Reduction
Catalyst=0.8%Pd/C, P=500 psig, T=100°C
LHSV=15 h⁻¹, H2 GHSV=420 h⁻¹
Conversion and Selectivity, wt%
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others

FIG. 20

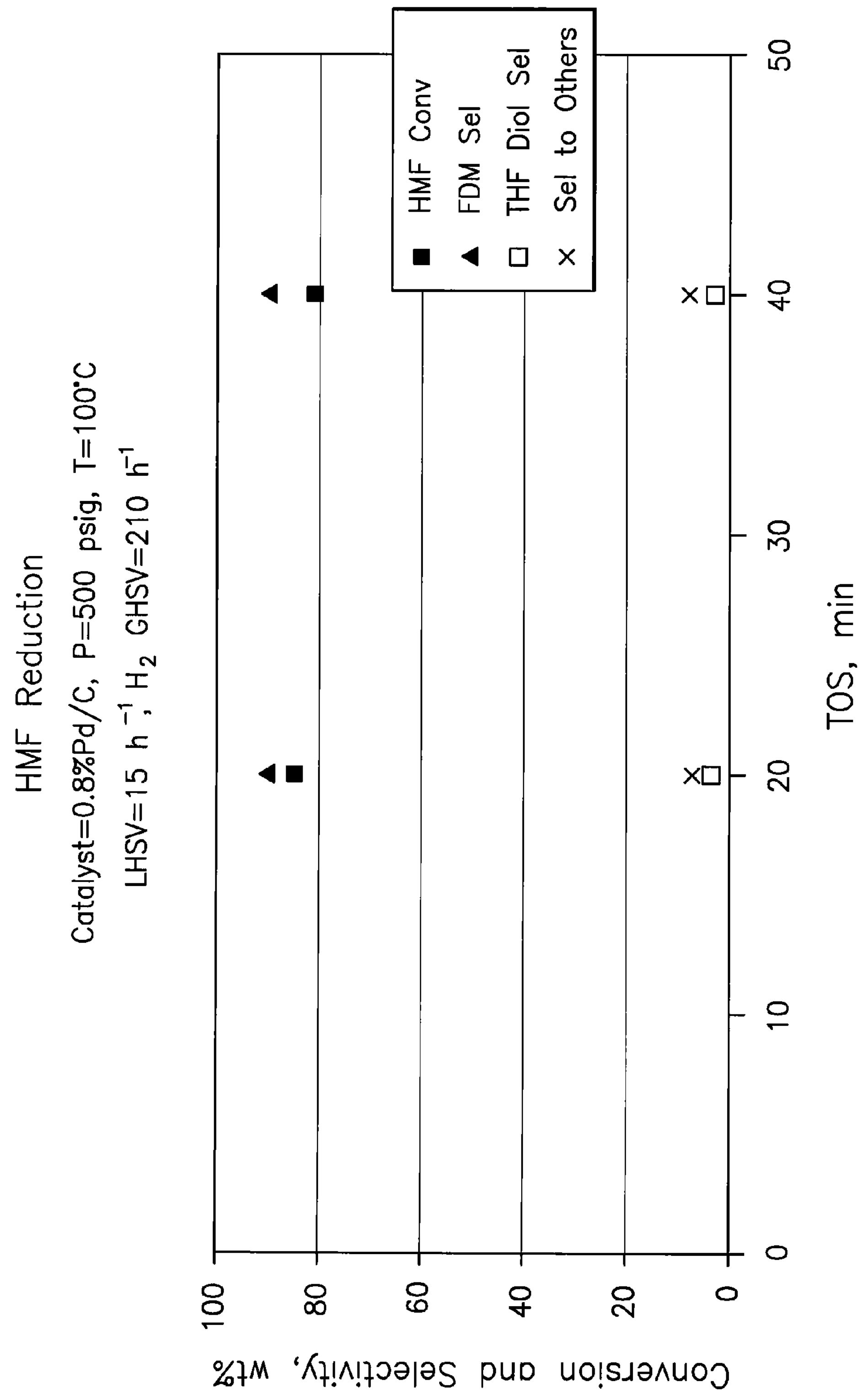

HMF Reduction
Catalyst=0.8%Pd/C, P=500 psig, T=100°C
LHSV=15 h⁻¹, H2 GHSV=210 h⁻¹
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100
80
60
40
20
0
0
10
20
30
40
50
TOS, min

Fig. 21

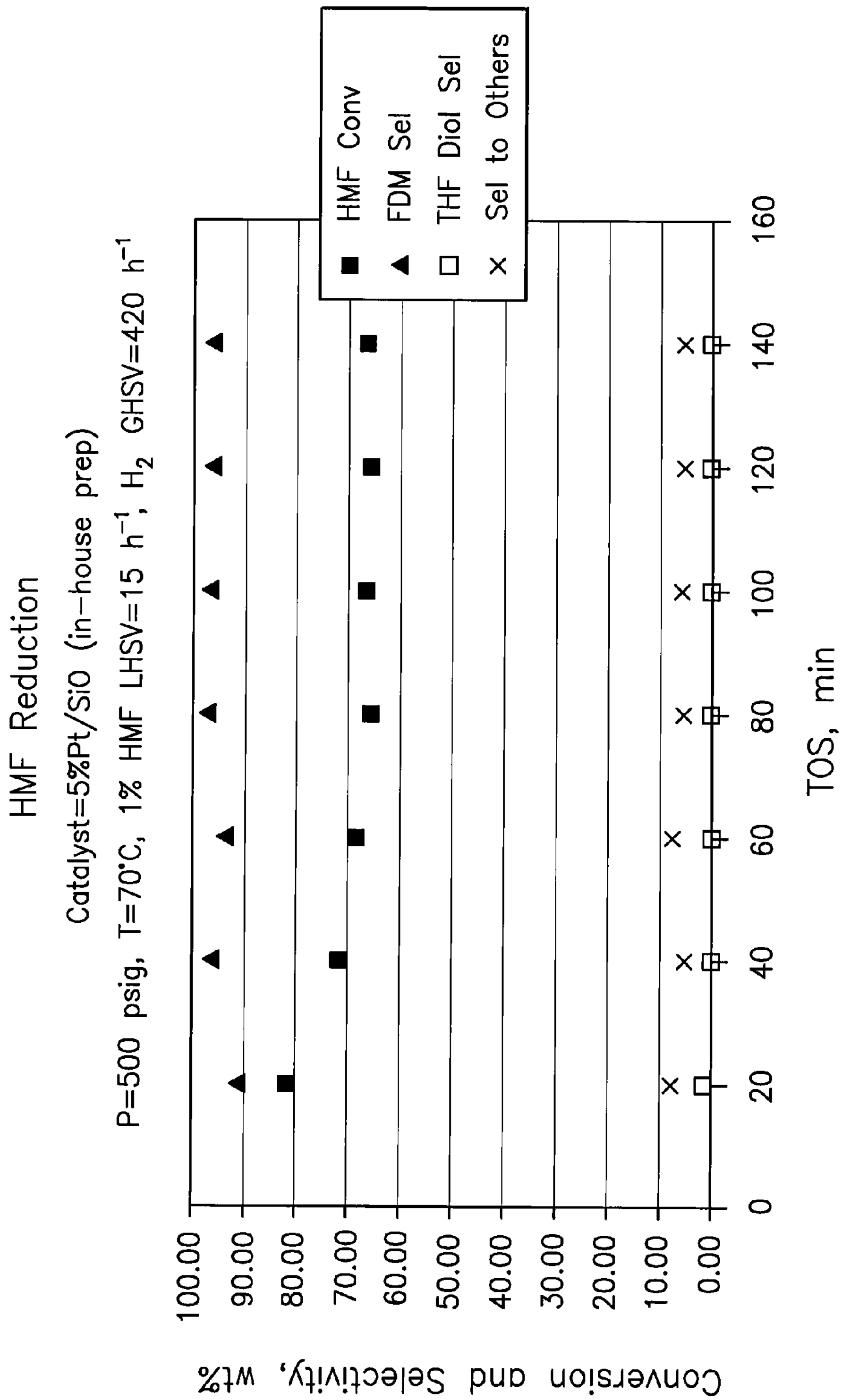

HMF Reduction
Catalyst=5%Pt/SiO (in-house prep)
P=500 psig, T=70°C, 1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
TOS, min

Fig. 22

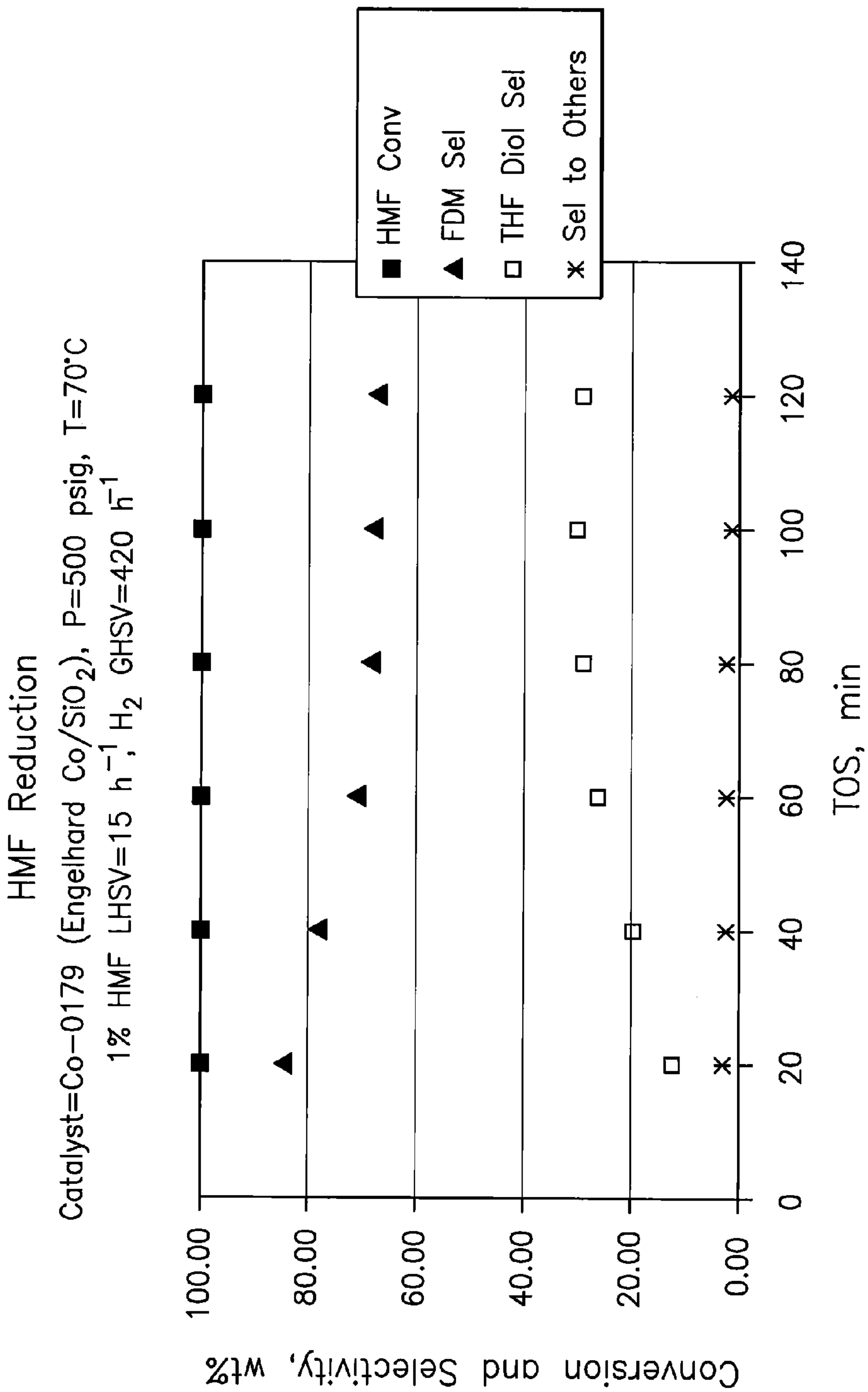

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 23

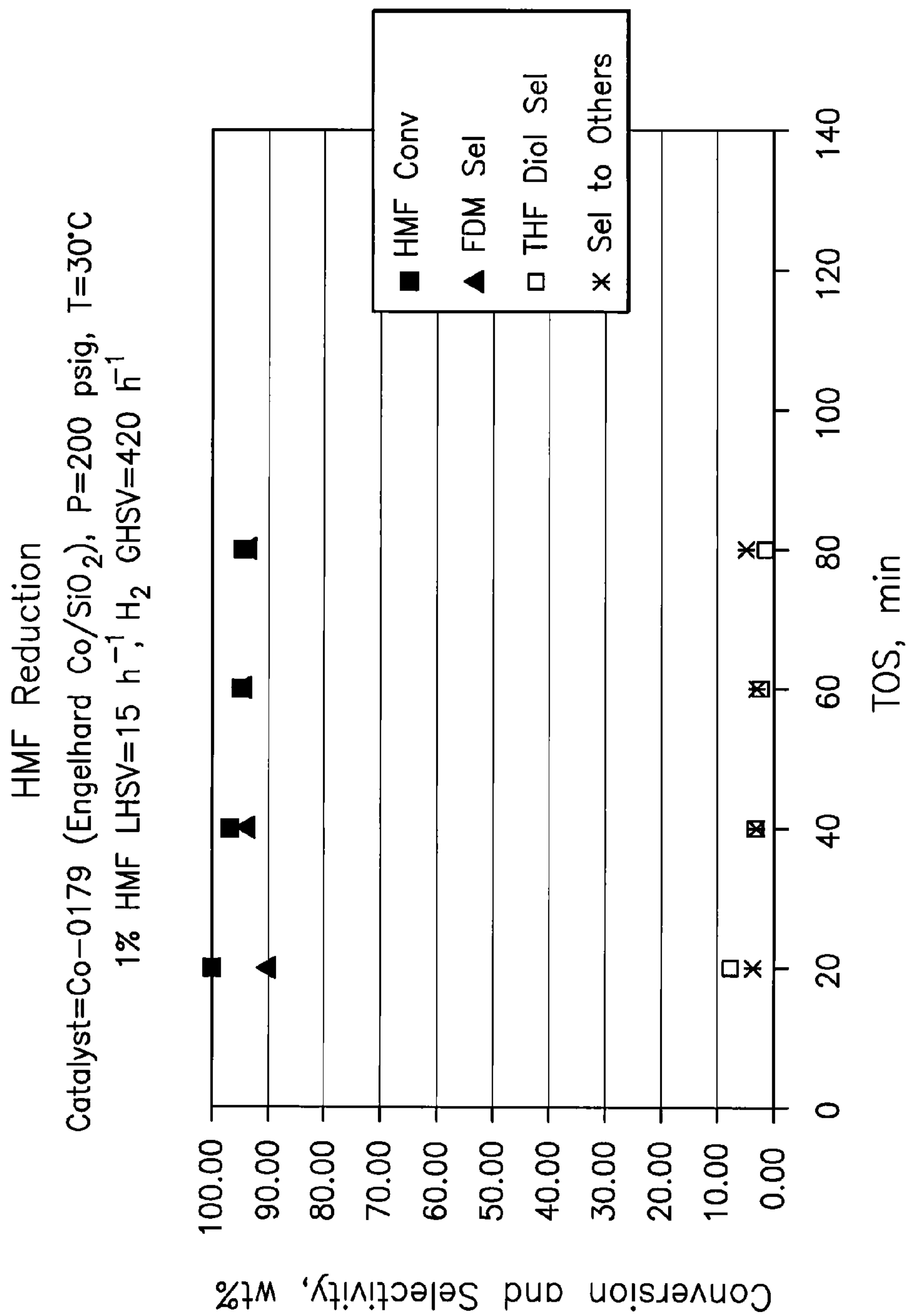

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=200 psig, T=30°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others

FIG. 24

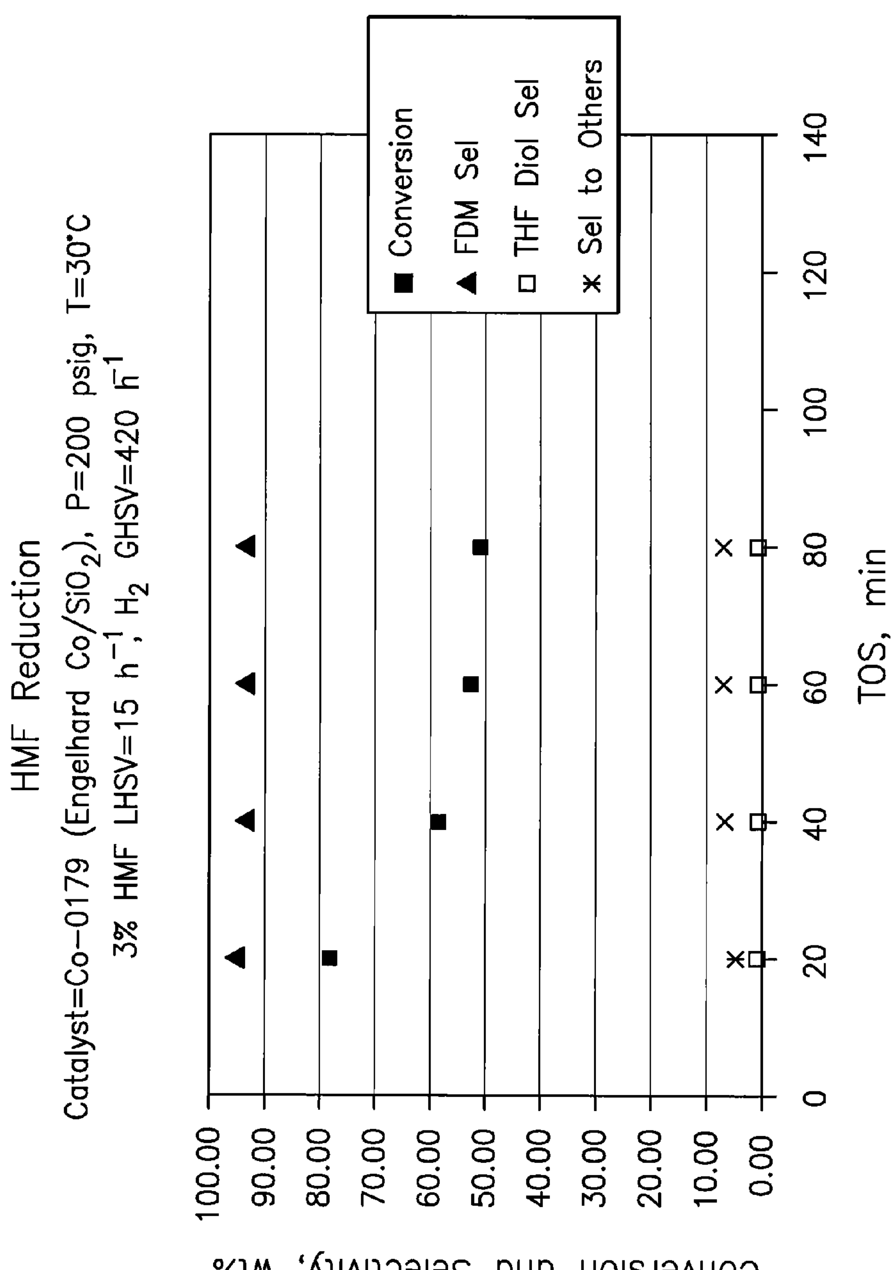

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=200 psig, T=30°C
3% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
Conversion
FDM Sel
THF Diol Sel
Sel to Others

FIG. 25

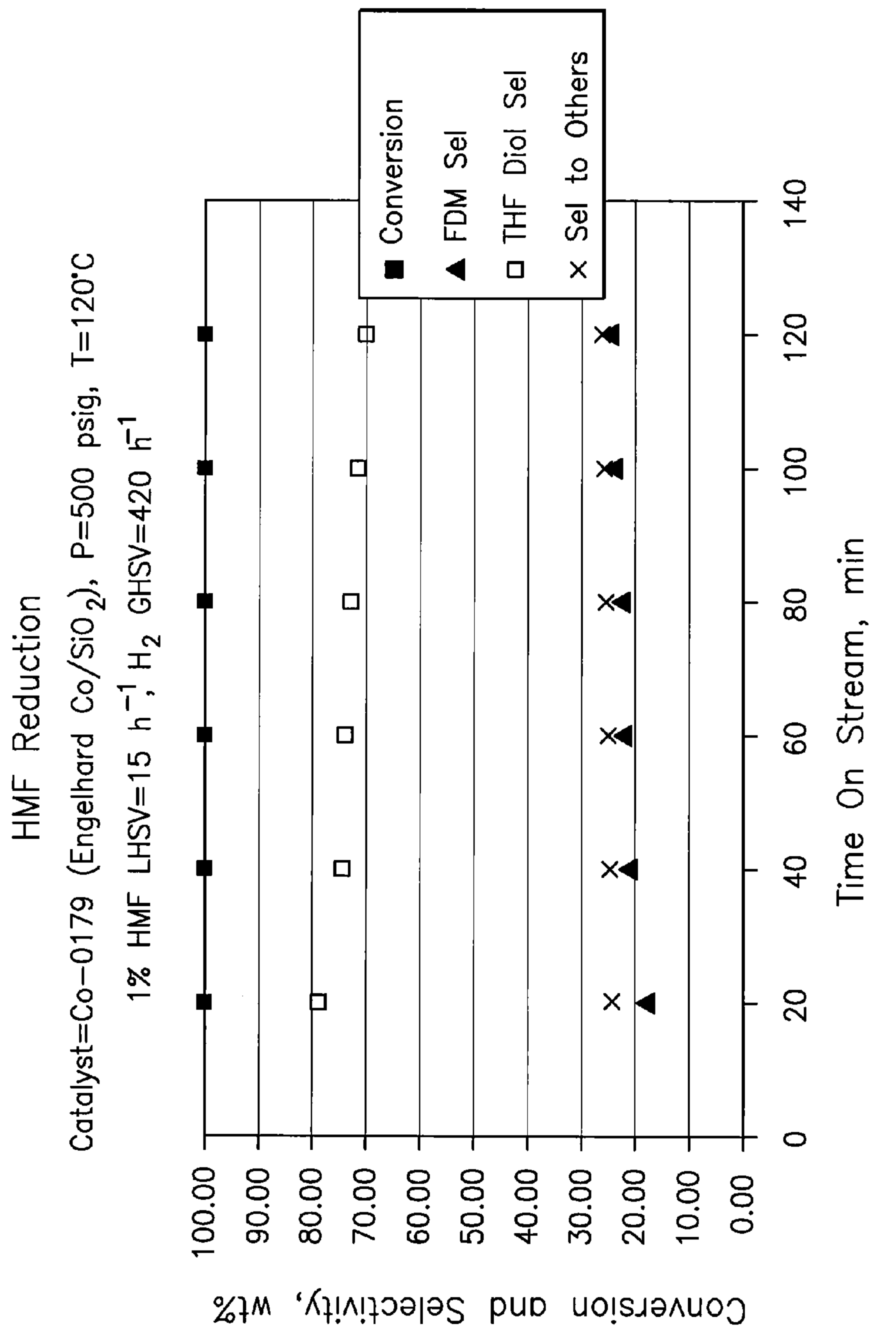

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=120°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
Time On Stream, min

Fig 26

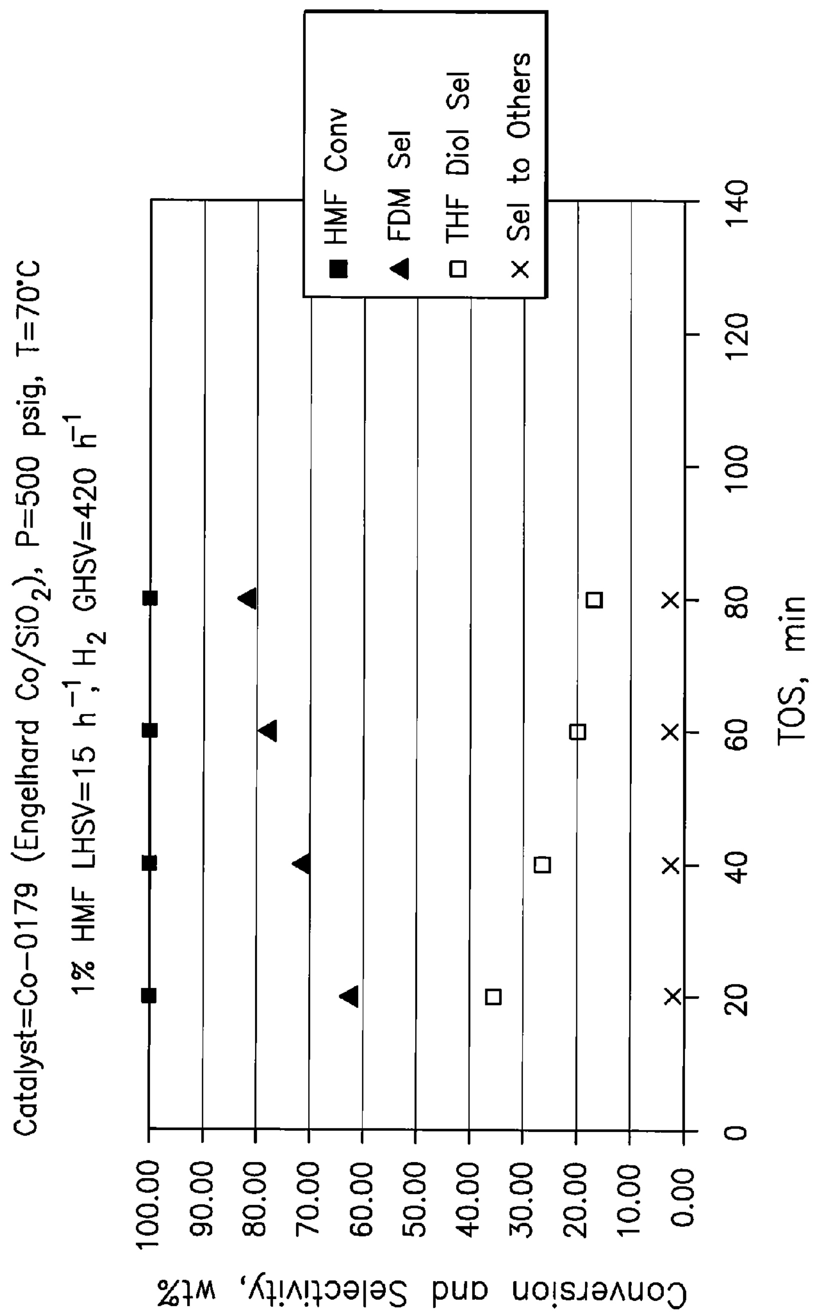

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min

Fig. 27

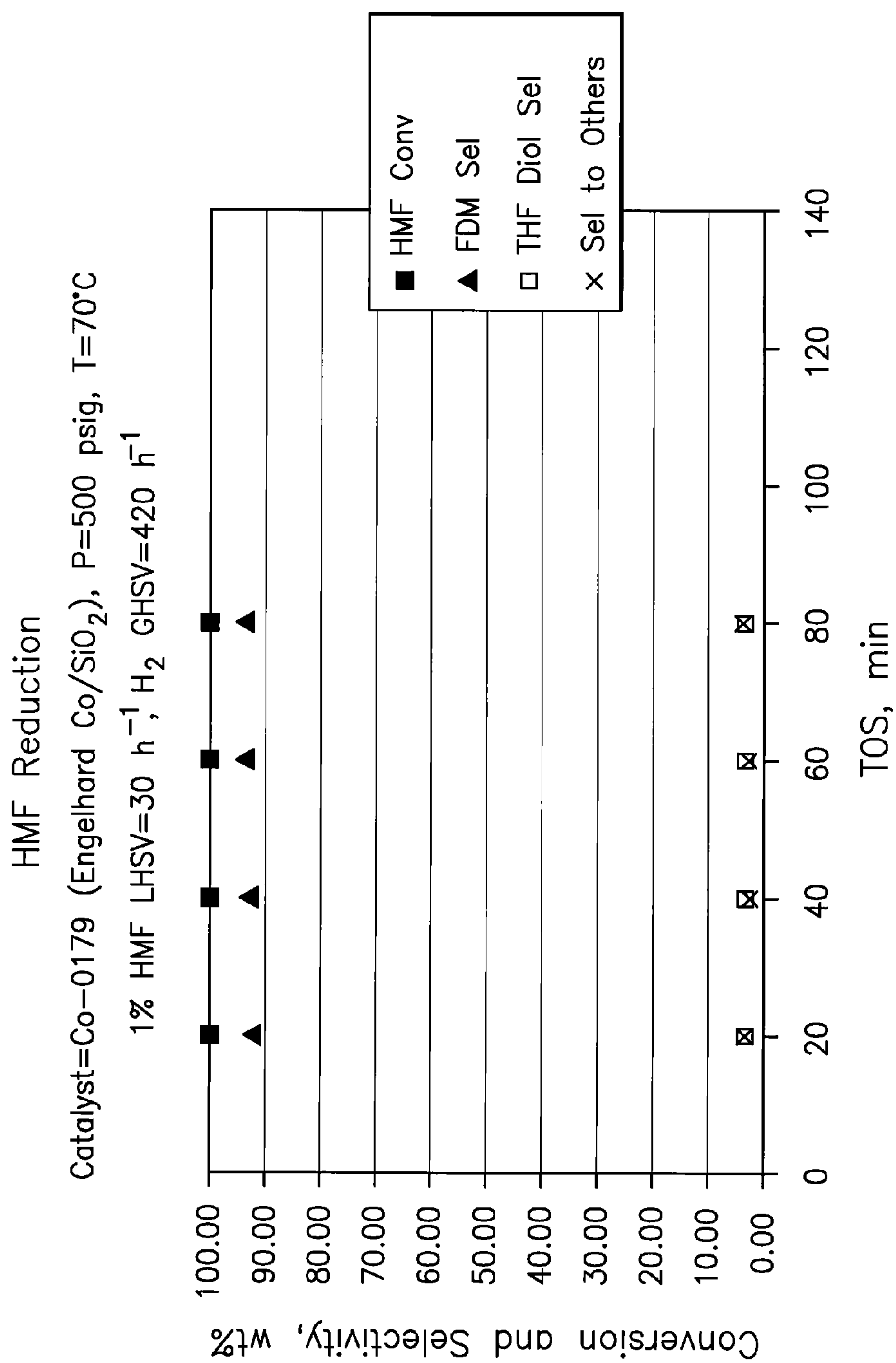

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=30 h-1, H2 GHSV=420 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 28

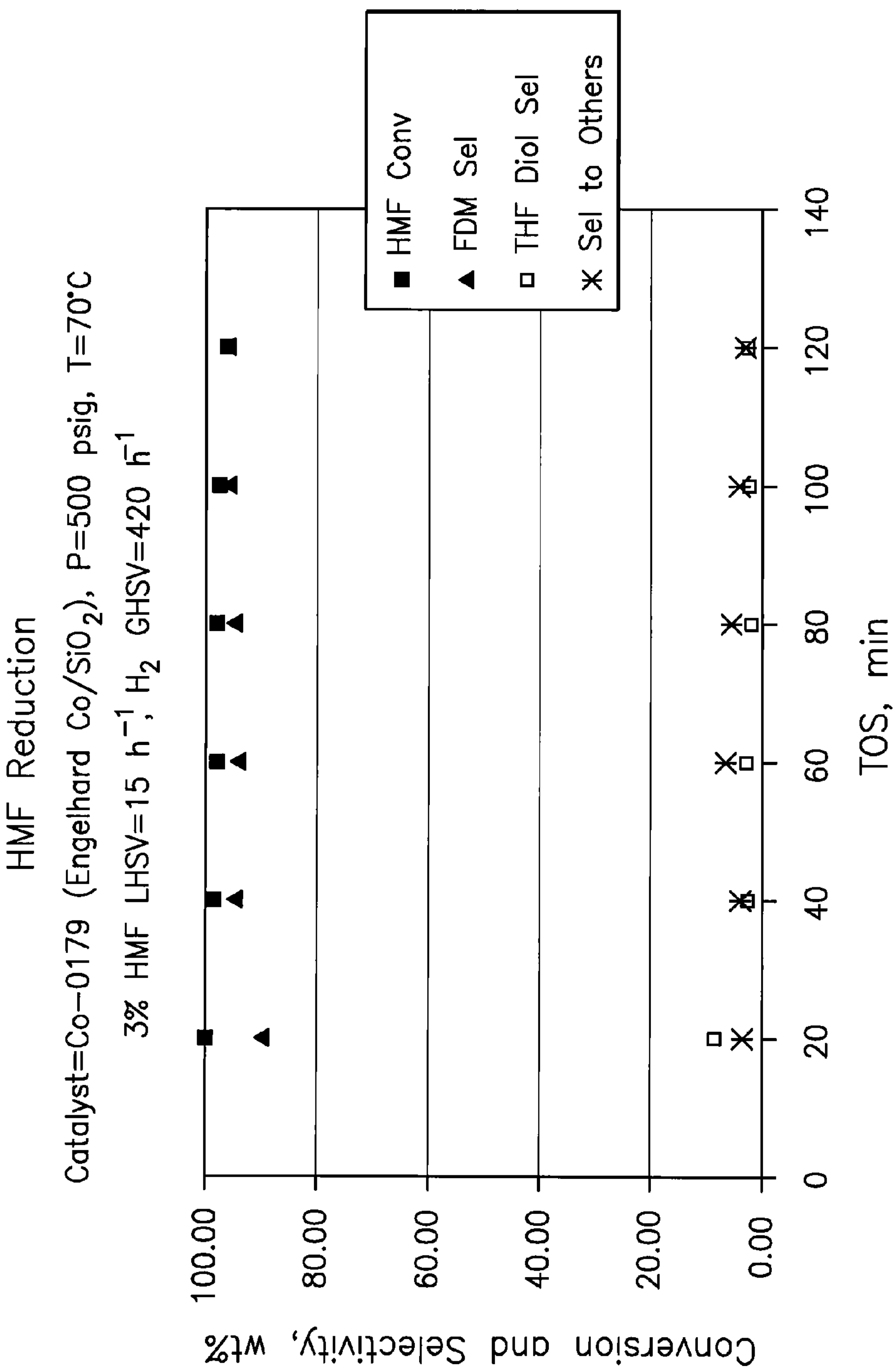

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
3% HMF LHSV=15 h-1, H2 GHSV=420 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 29

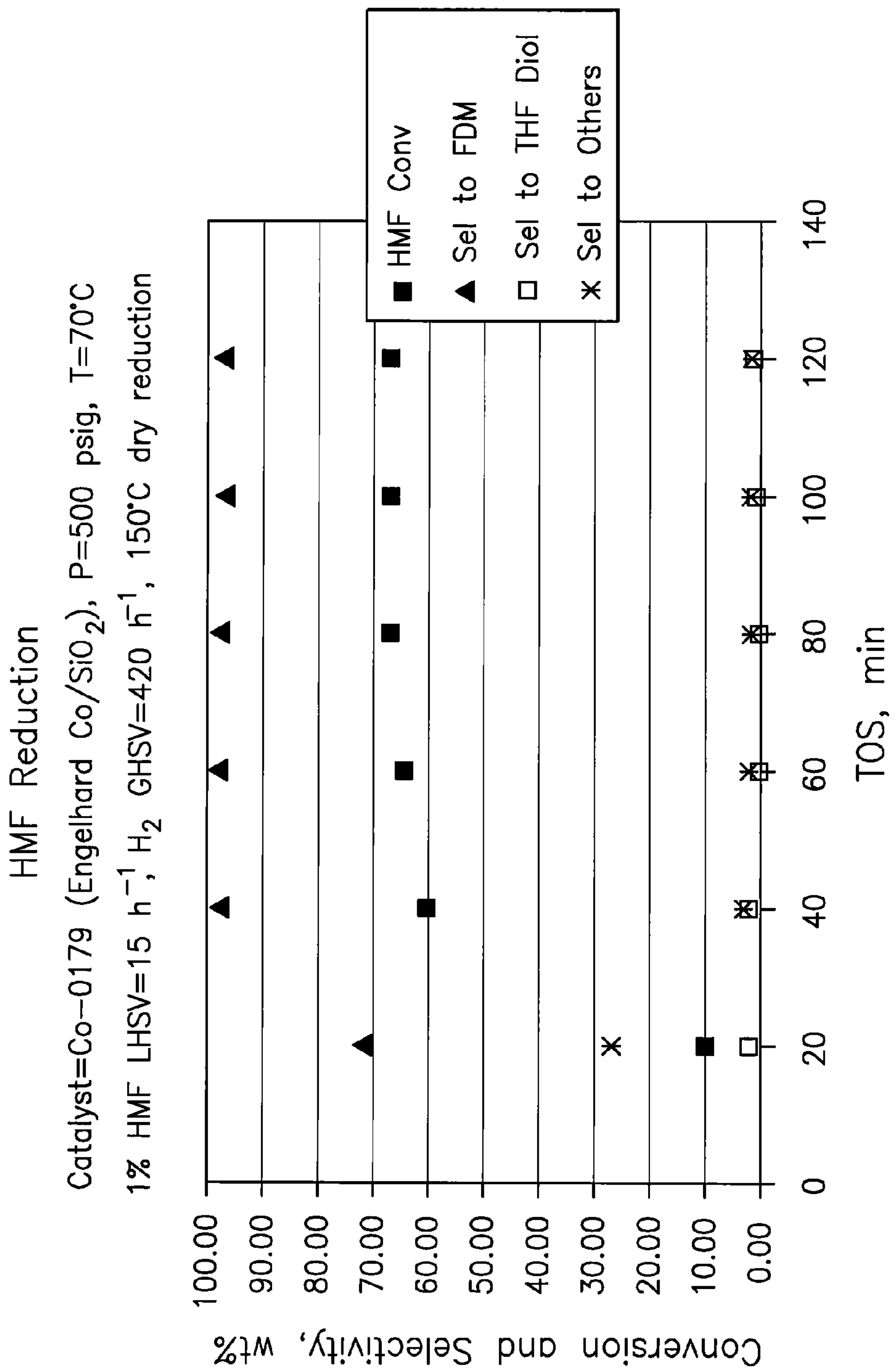

HMF Reduction
Catalyst=Co–0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1, 150°C dry reduction
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 30

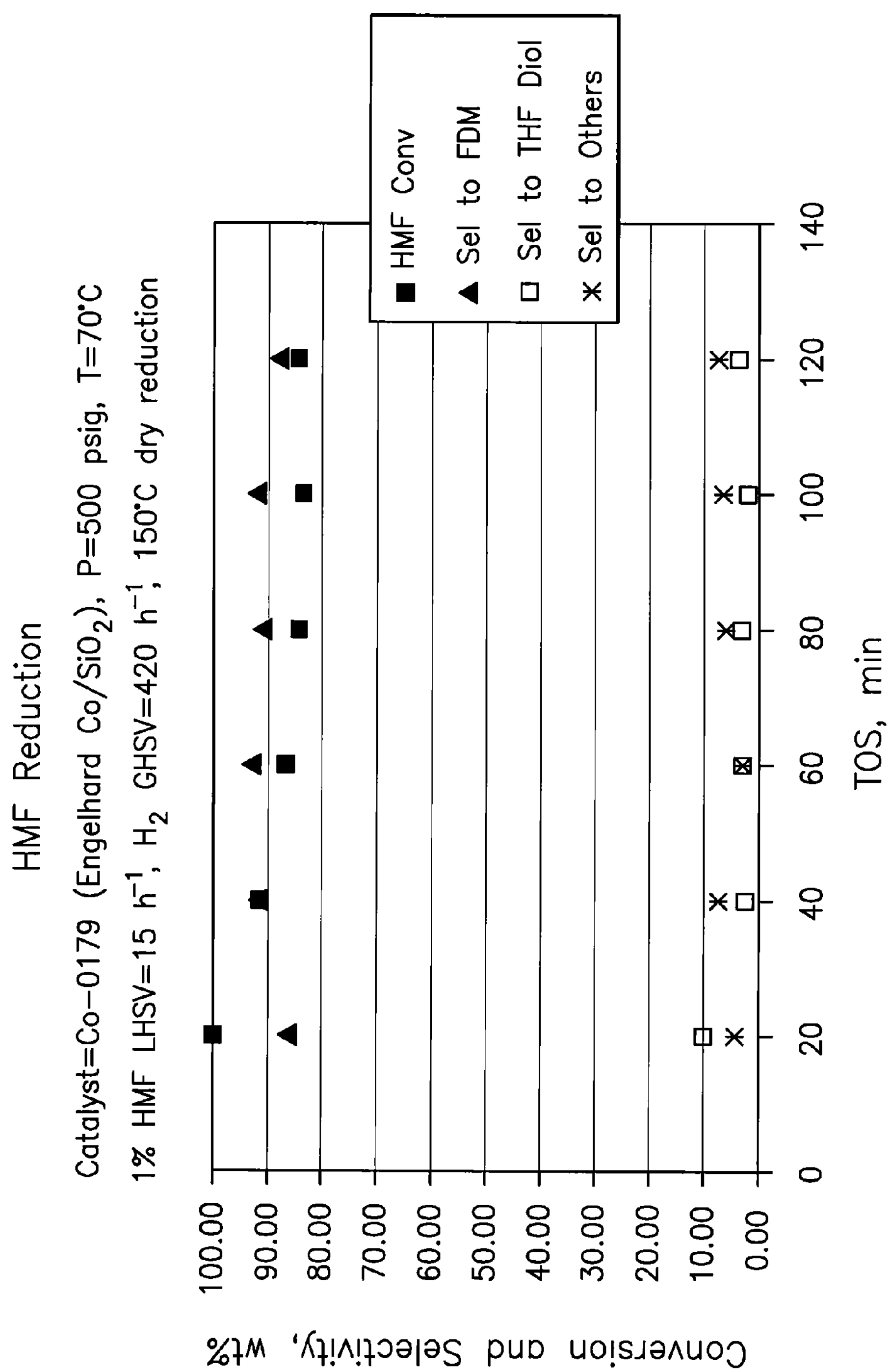

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1, 150°C dry reduction
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Conversion and Selectivity, wt%
0
20
40
60
80
100
120
140
TOS, min

Fig. 31

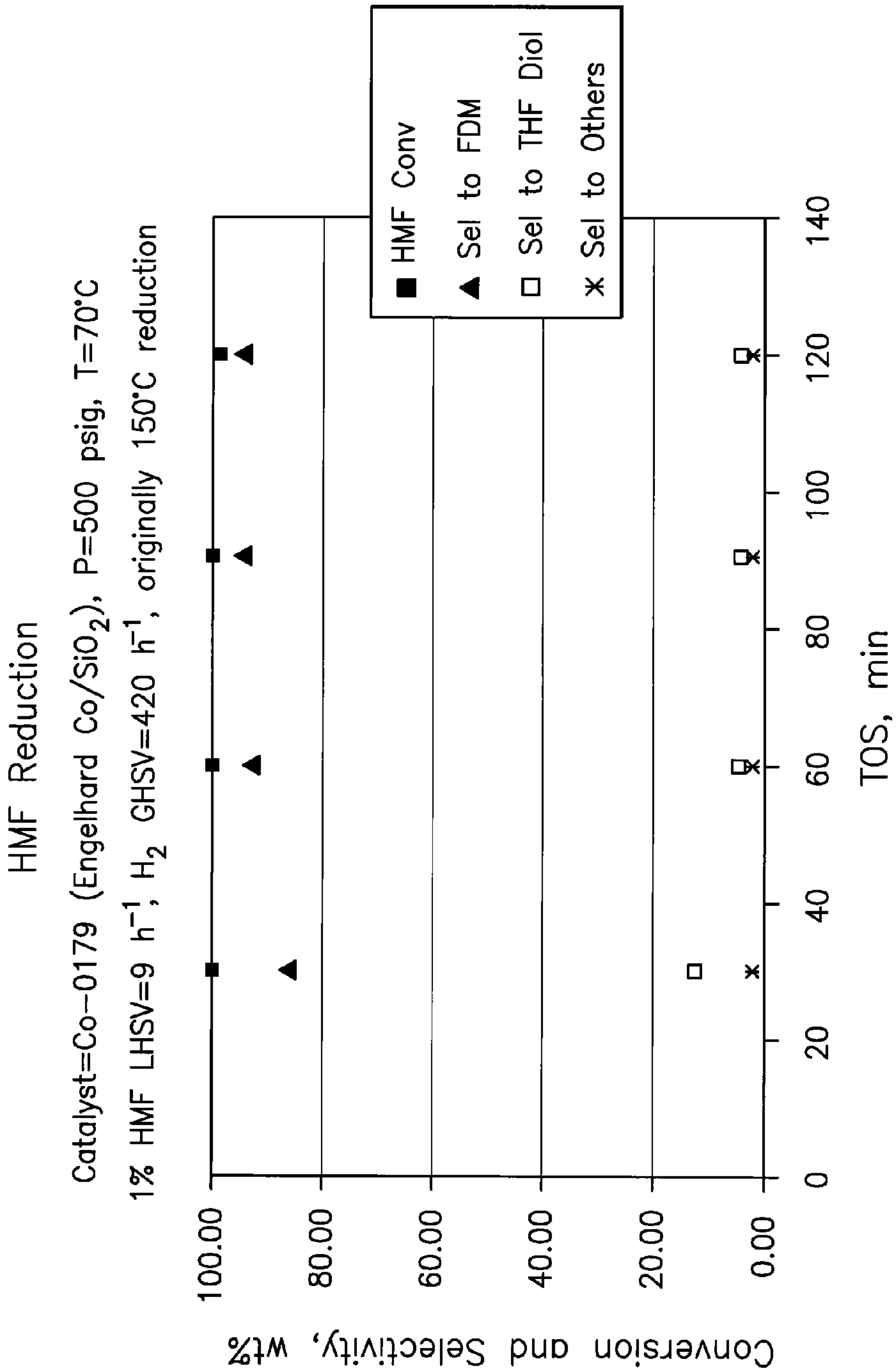

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=9 h-1, H2 GHSV=420 h-1, originally 150°C reduction
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min

Fig. 32

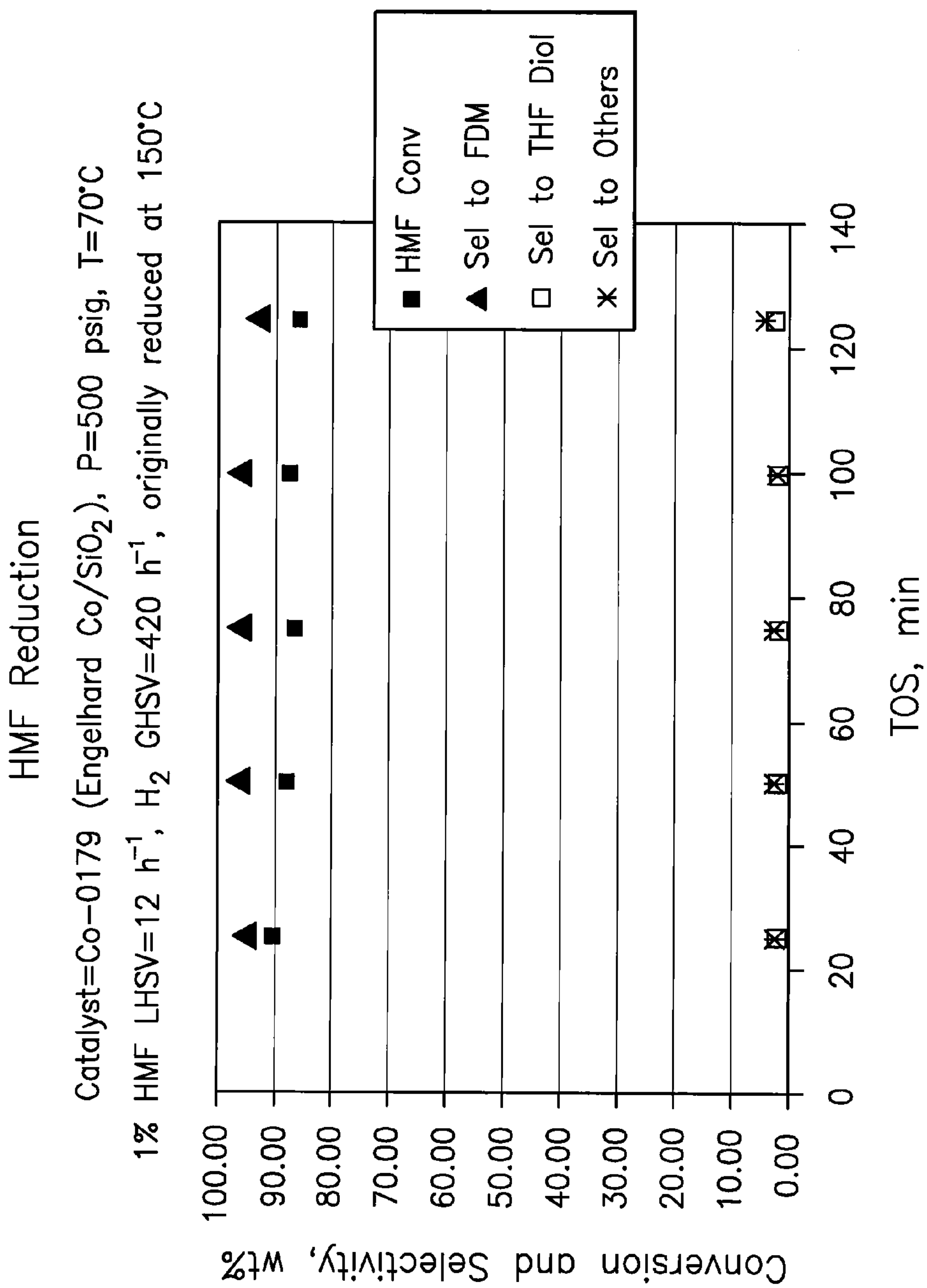

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=12 h-1, H2 GHSV=420 h-1, originally reduced at 150°C
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others

FIG. 33

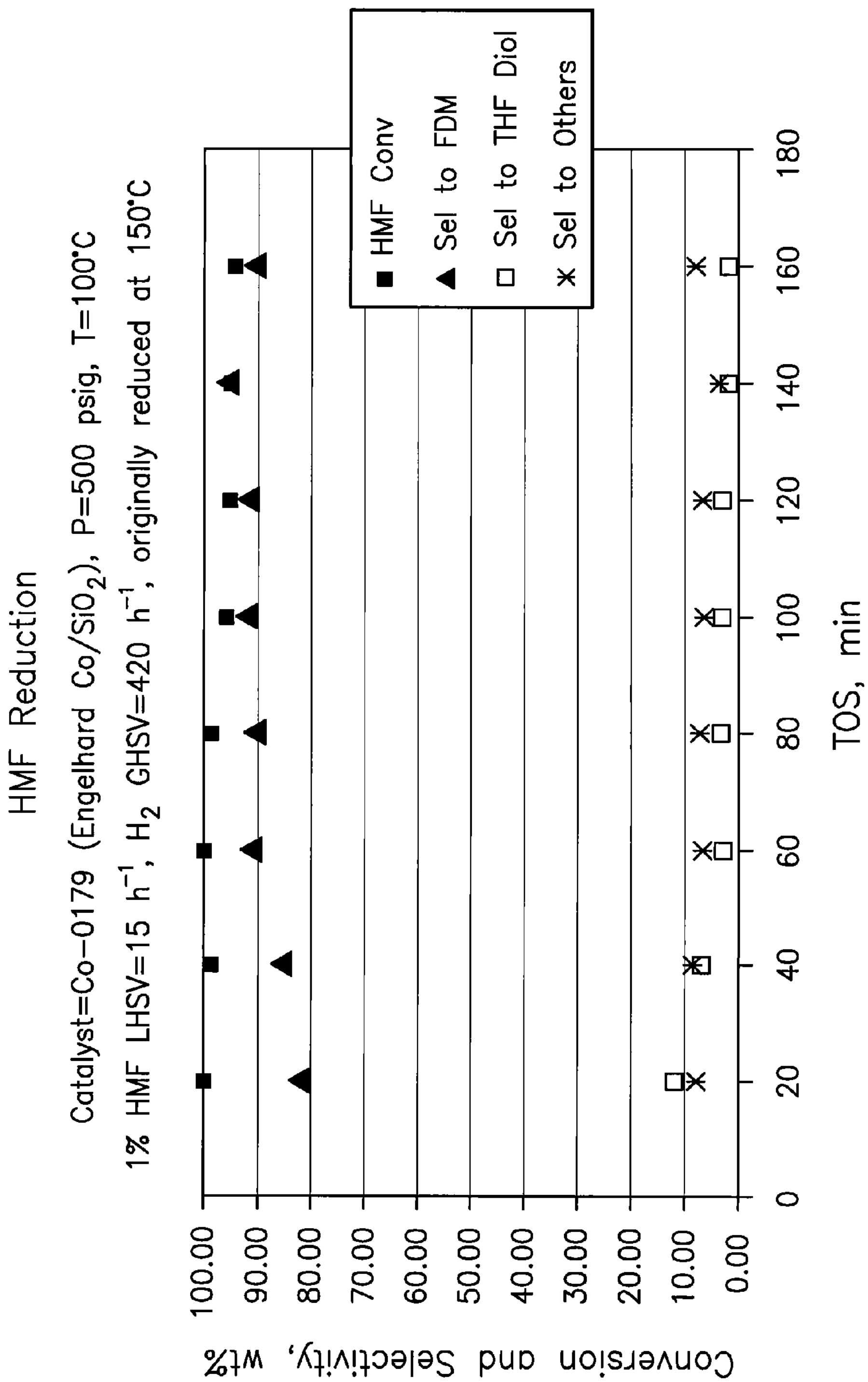

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=100°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1, originally reduced at 150°C
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
TOS, min

FIG. 34

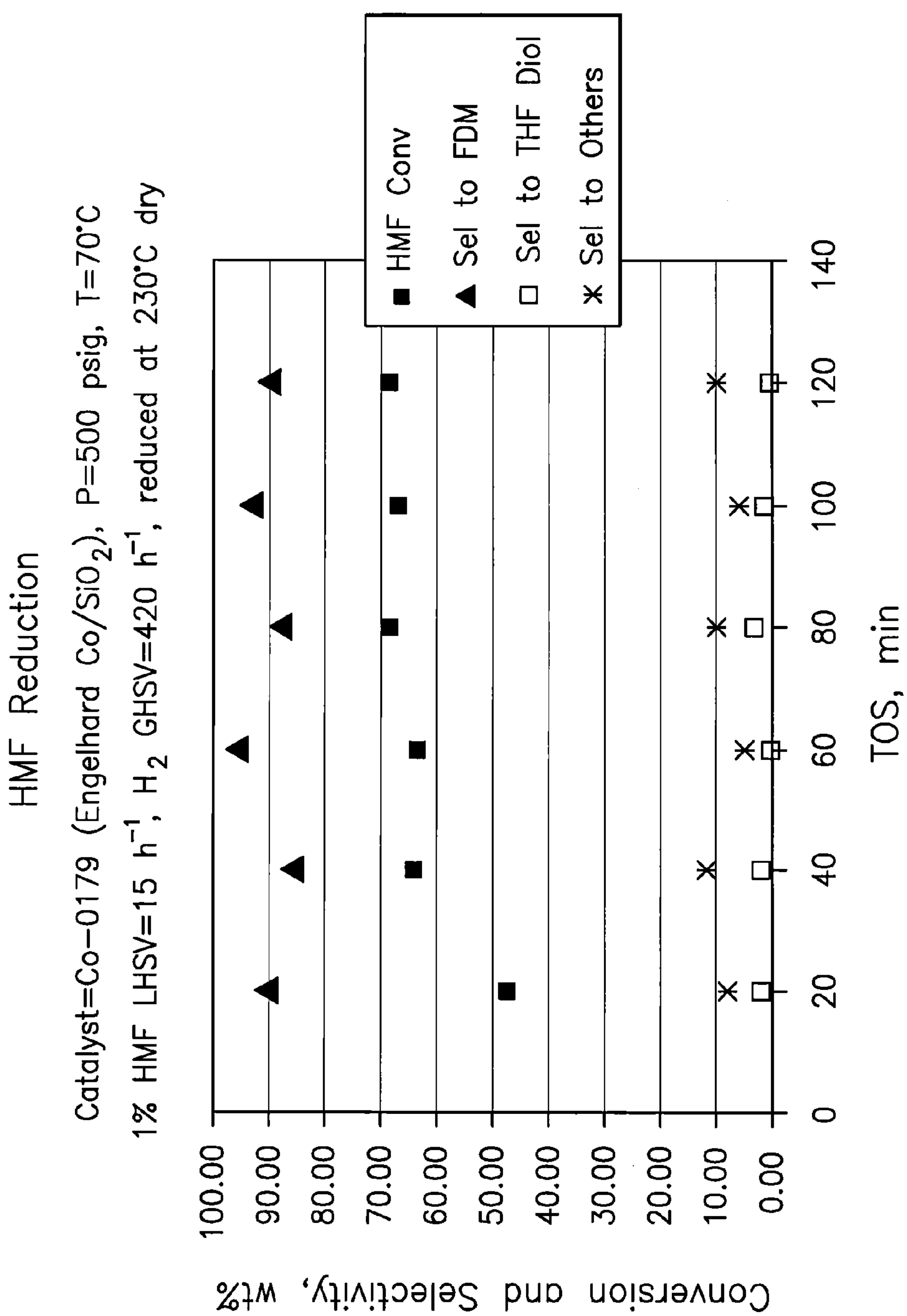

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1, reduced at 230°C dry
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min

FIG. 35

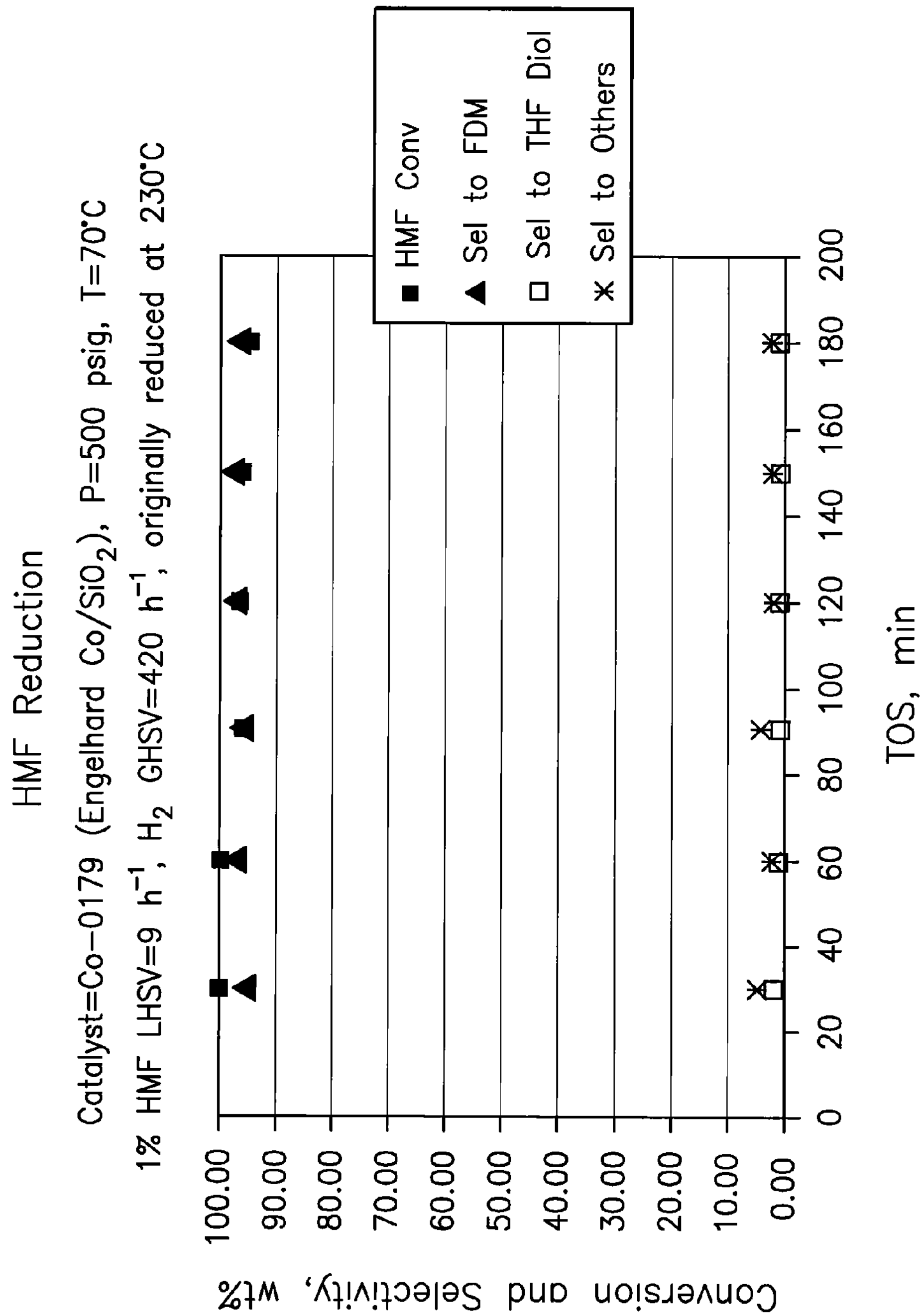

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=9 h-1, H2 GHSV=420 h-1, originally reduced at 230°C
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
TOS, min

FIG. 36

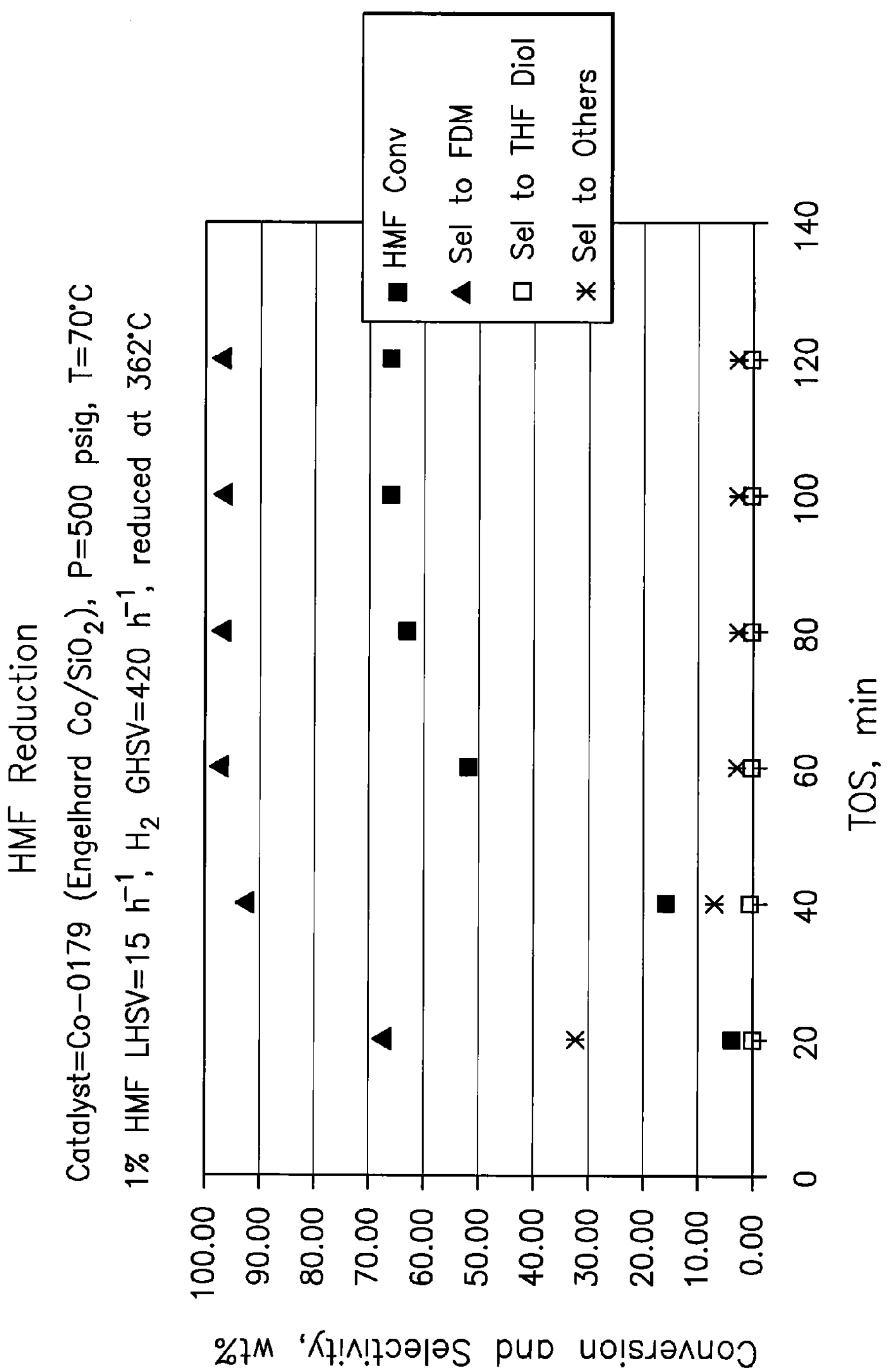

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1, reduced at 362°C
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others

FIG. 37

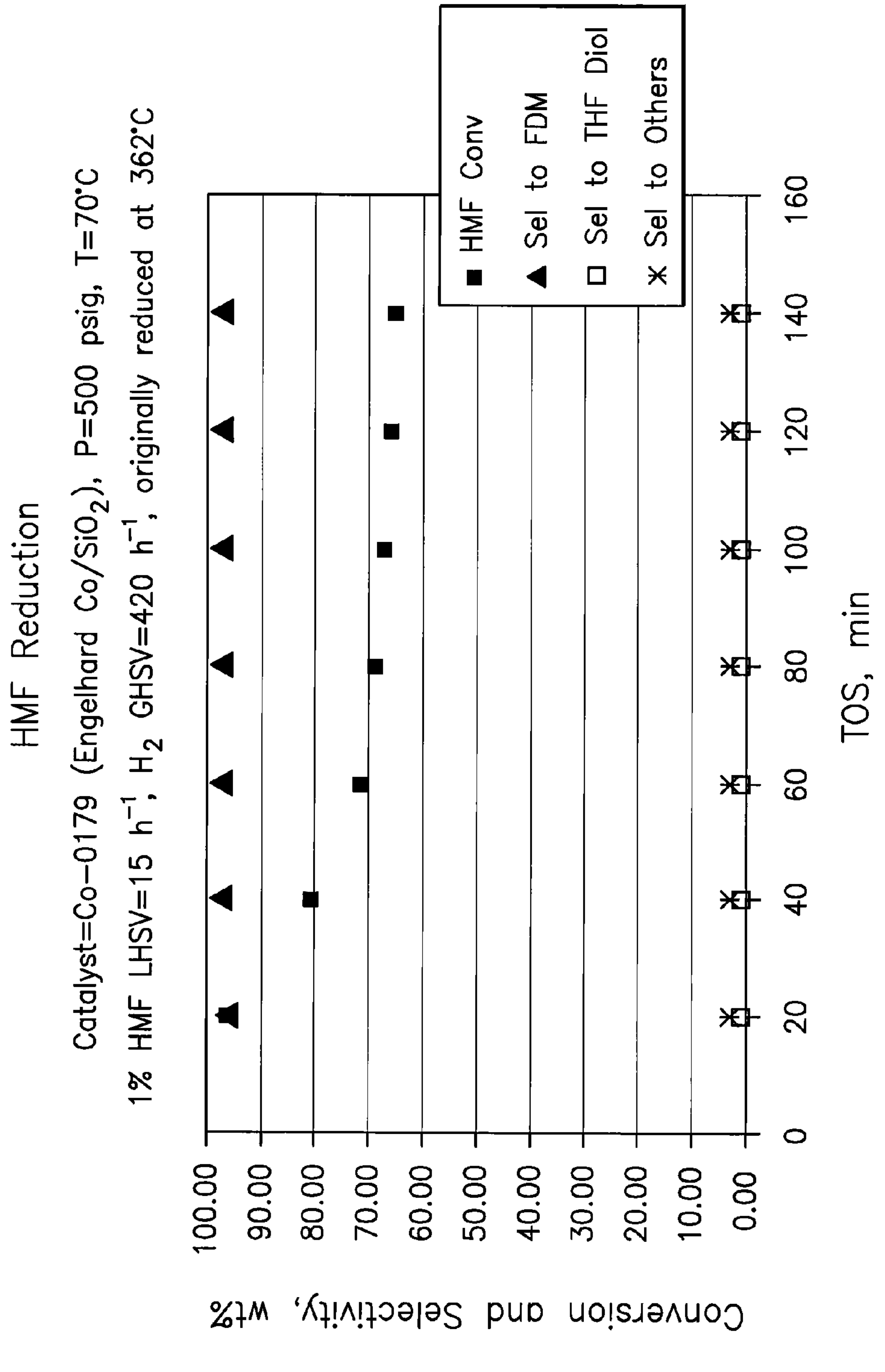

HMF Reduction
Catalyst=Co-0179 (Engelhard Co/SiO2), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1, originally reduced at 362°C
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to Others
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
TOS, min

FIG. 38

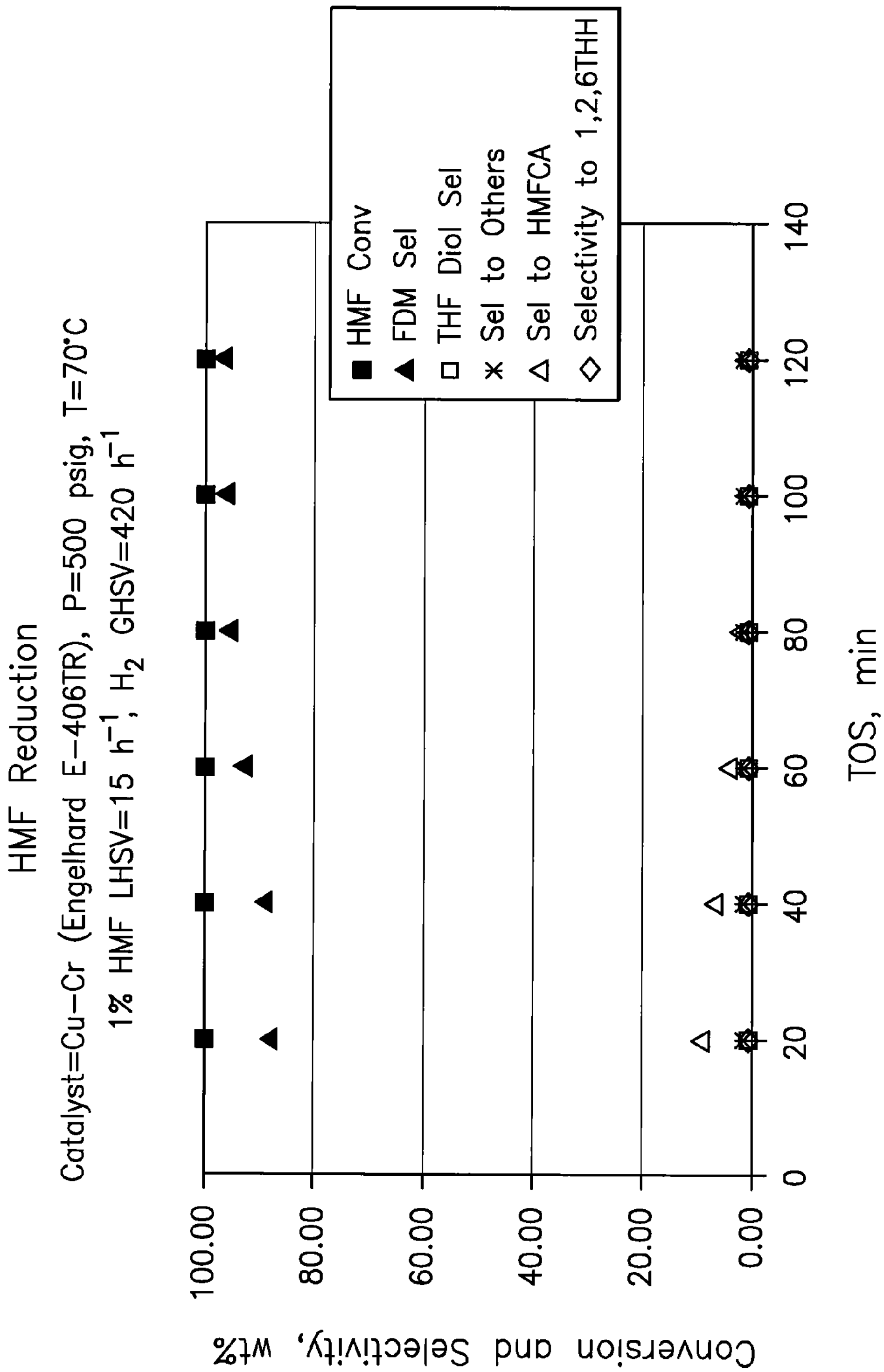

HMF Reduction
Catalyst=Cu–Cr (Engelhard E–406TR), P=500 psig, T=70°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to HMFCA
Selectivity to 1,2,6THH

FIG. 39

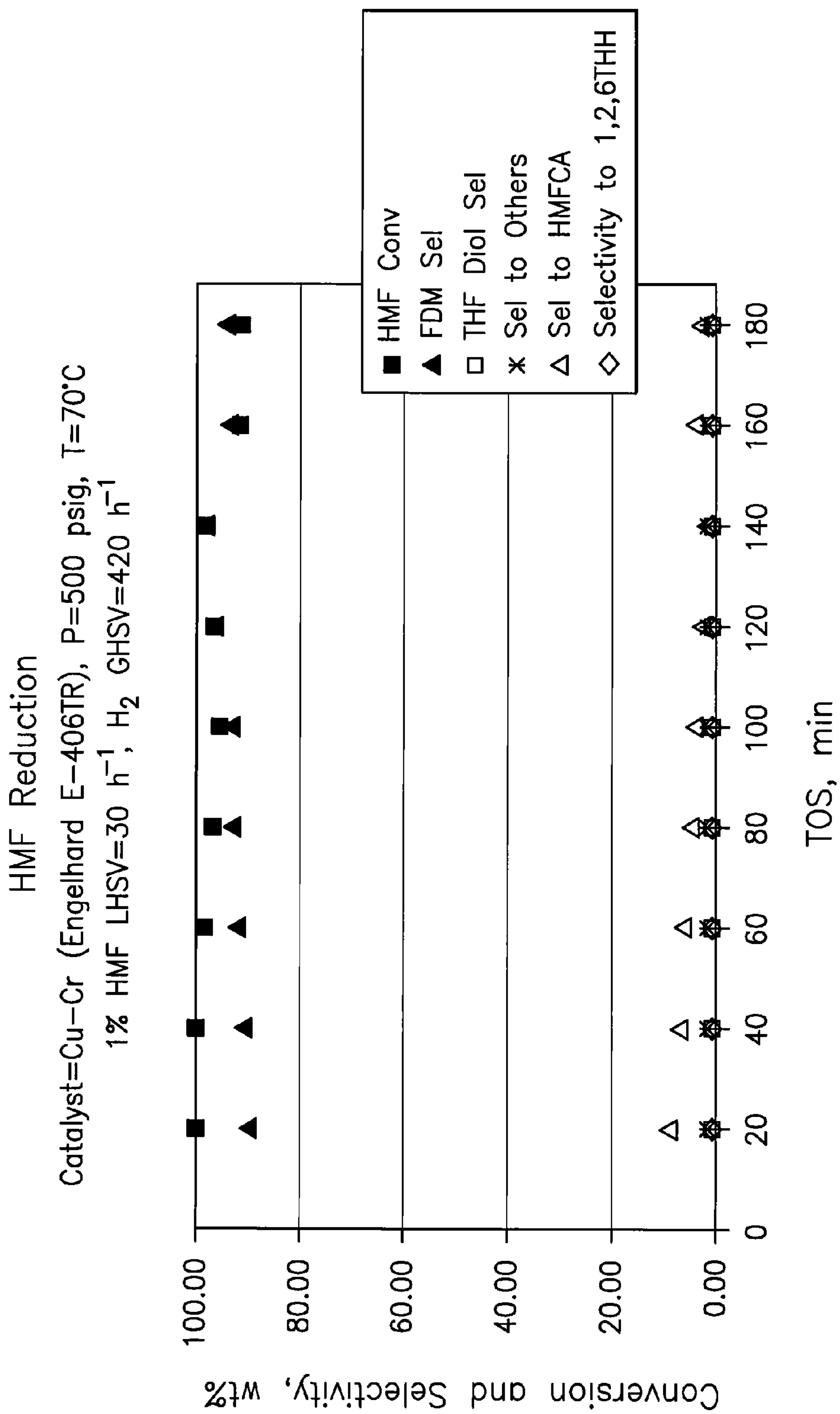

HMF Reduction
Catalyst=Cu-Cr (Engelhard E-406TR), P=500 psig, T=70°C
1% HMF LHSV=30 h-1, H2 GHSV=420 h-1
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
160
180
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to HMFCA
Selectivity to 1,2,6THH

FIG. 40

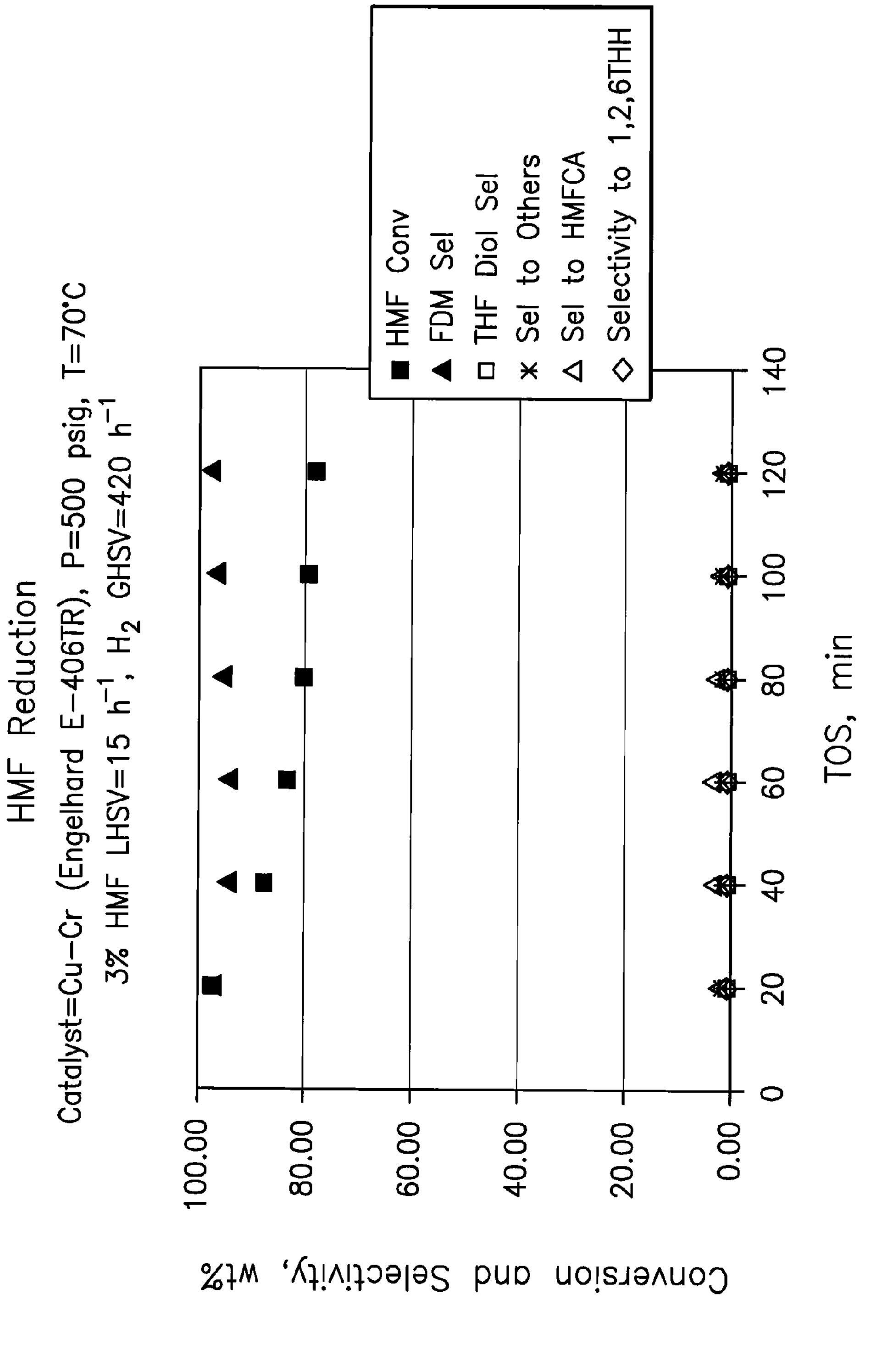

HMF Reduction
Catalyst=Cu–Cr (Engelhard E–406TR), P=500 psig, T=70°C
3% HMF LHSV=15 h⁻¹, H2 GHSV=420 h⁻¹
Conversion and Selectivity, wt%
100.00
80.00
60.00
40.00
20.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to HMFCA
Selectivity to 1,2,6THH

Fig. 41

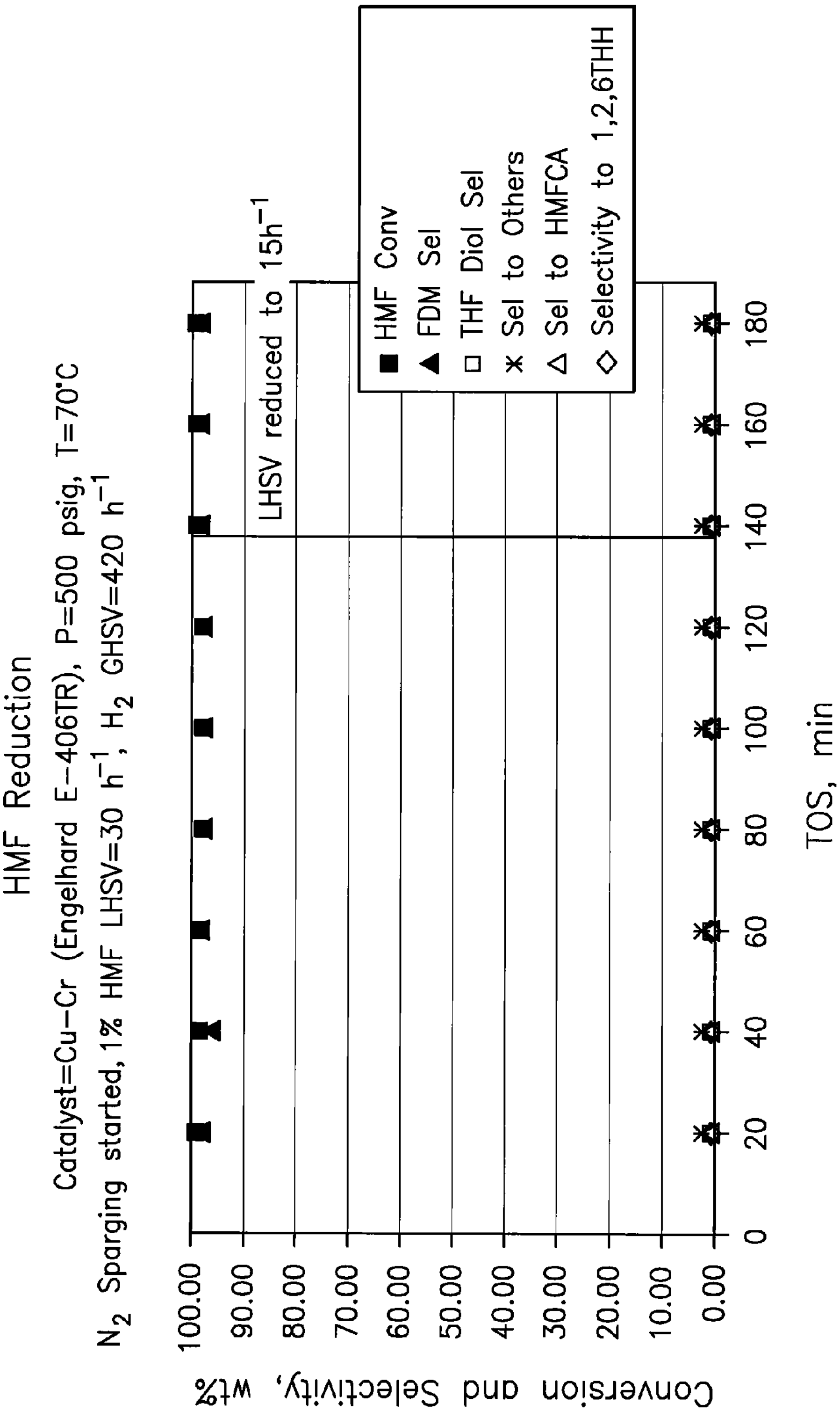

HMF Reduction
Catalyst=Cu–Cr (Engelhard E–406TR), P=500 psig, T=70°C
N2 Sparging started, 1% HMF LHSV=30 h-1, H2 GHSV=420 h-1
LHSV reduced to 15h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to HMFCA
Selectivity to 1,2,6THH
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
TOS, min

Fig. 42

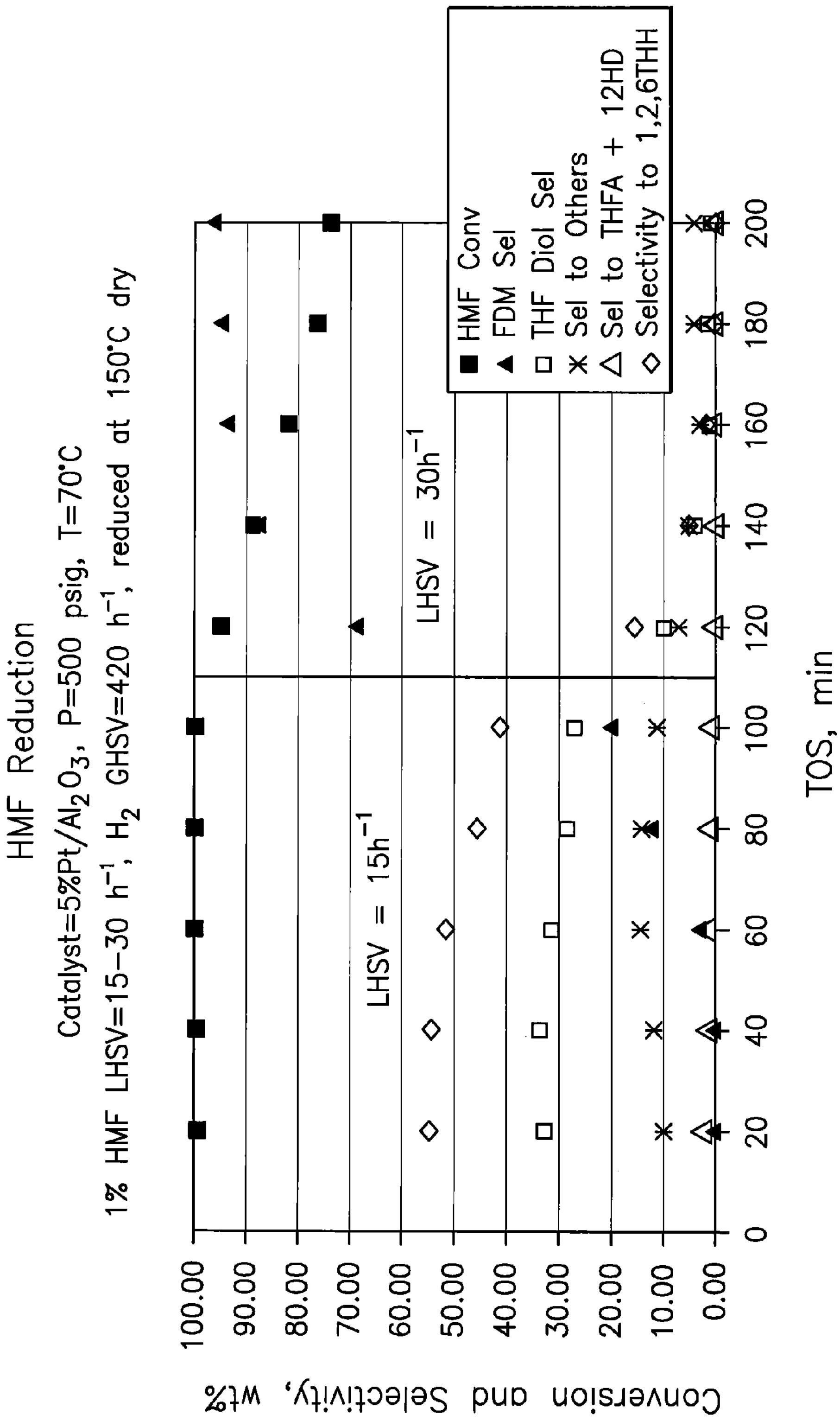

HMF Reduction
Catalyst=5%Pt/Al2O3, P=500 psig, T=70°C
1% HMF LHSV=15–30 h-1, H2 GHSV=420 h-1, reduced at 150°C dry
LHSV = 15h-1
LHSV = 30h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
TOS, min

FIG. 44

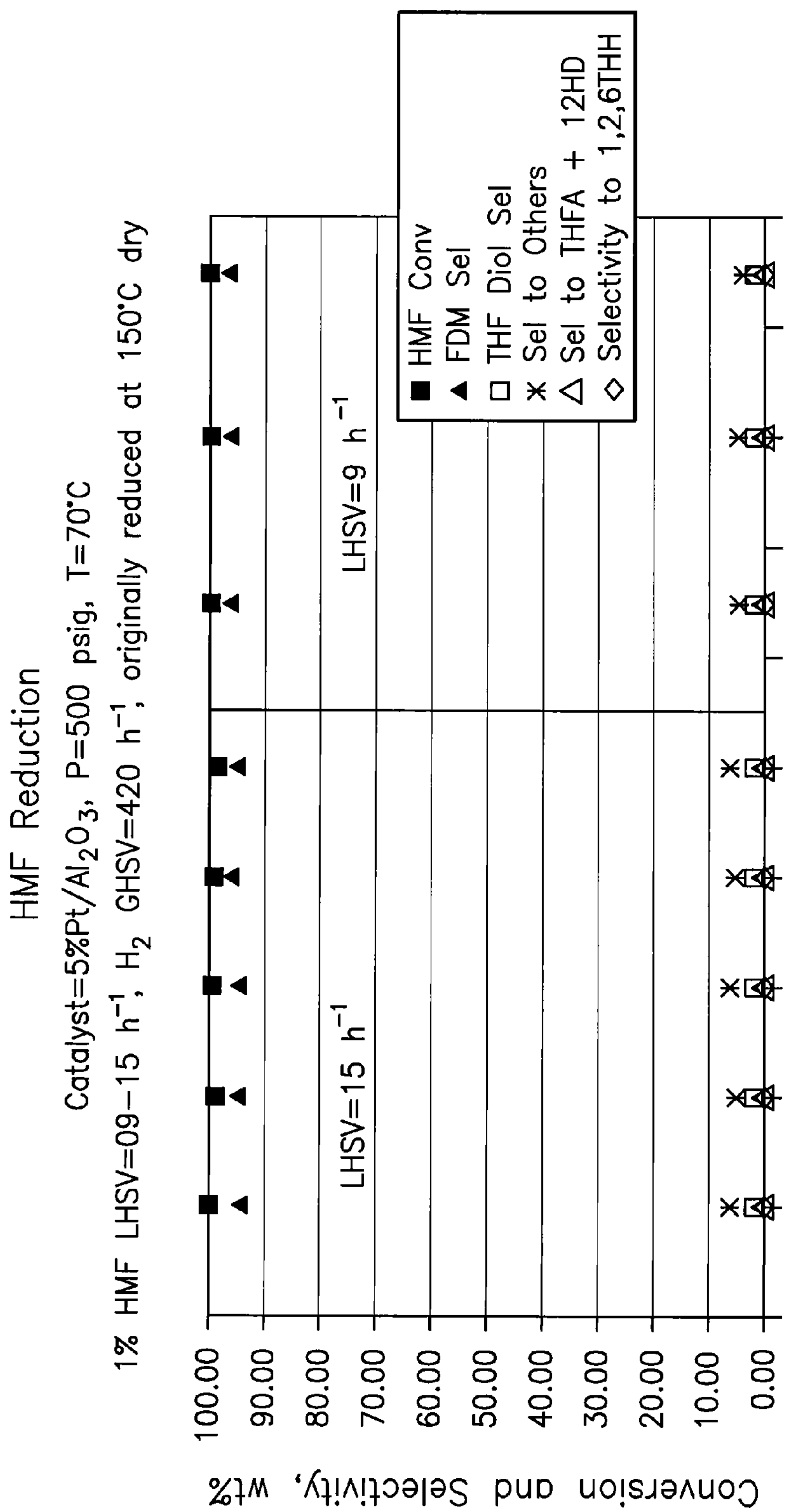

HMF Reduction
Catalyst=5%Pt/Al2O3, P=500 psig, T=70°C
1% HMF LHSV=09-15 h-1, H2 GHSV=420 h-1, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
TOS, min
LHSV=15 h-1
LHSV=9 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

Fig. 44

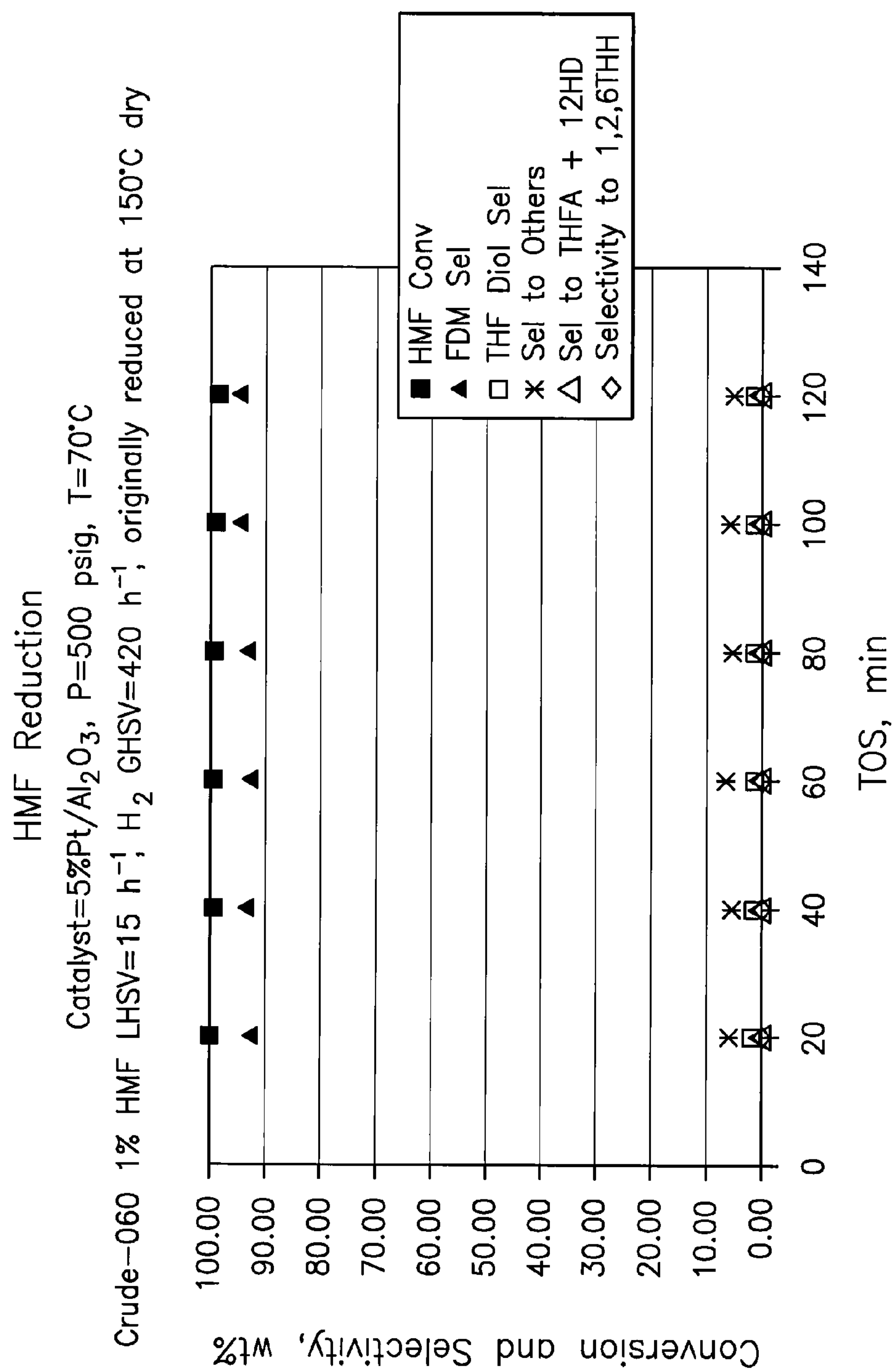

HMF Reduction
Catalyst=5%Pt/Al_2O_3, P=500 psig, T=70°C
Crude-060 1% HMF LHSV=15 h^{-1}, H_2 GHSV=420 h^{-1}, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

Fig. 45

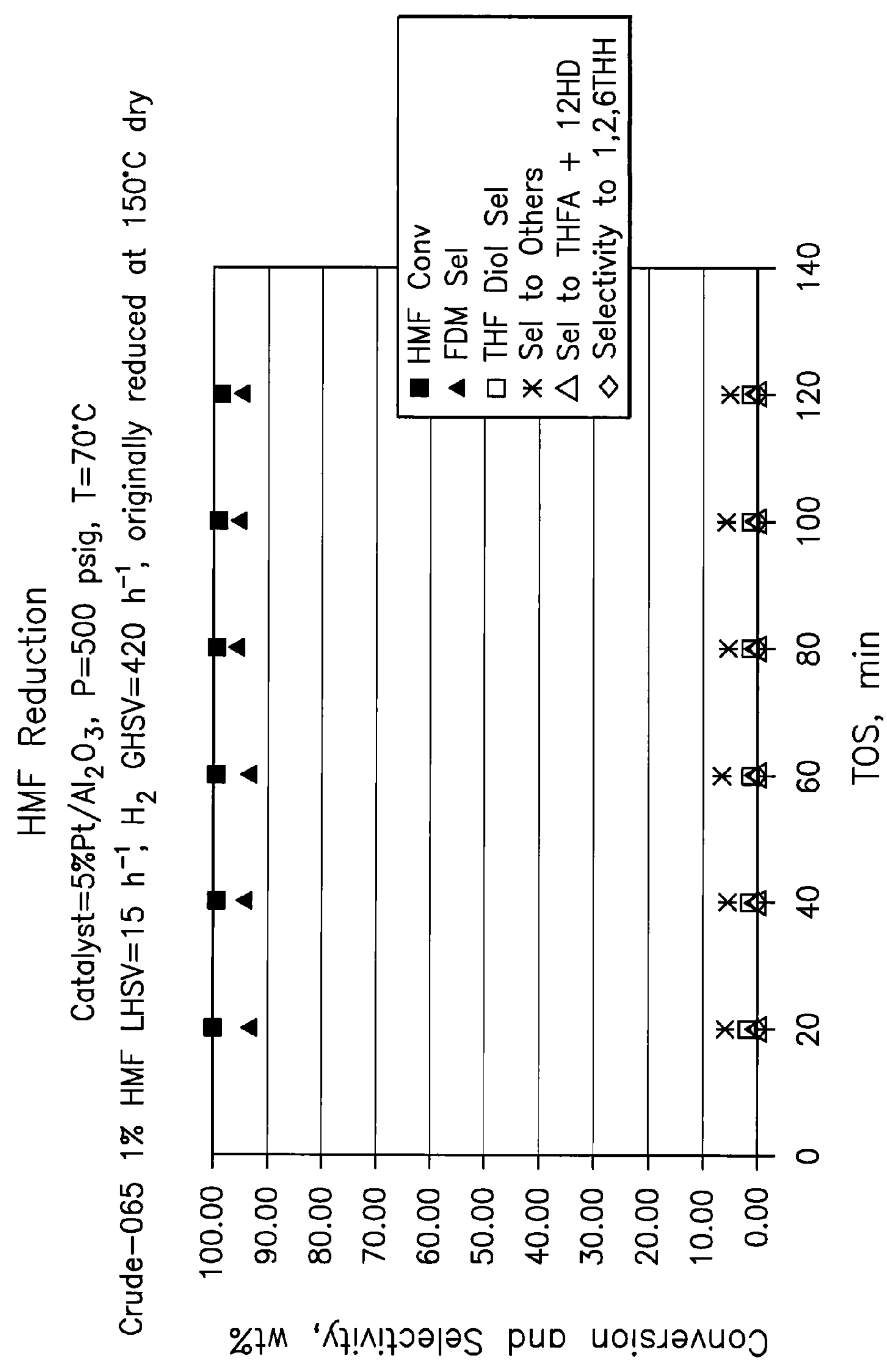

HMF Reduction
Catalyst=5%Pt/Al_2O_3, P=500 psig, T=70°C
Crude-065 1% HMF LHSV=15 h^{-1}, H_2 GHSV=420 h^{-1}, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

Fig. 46

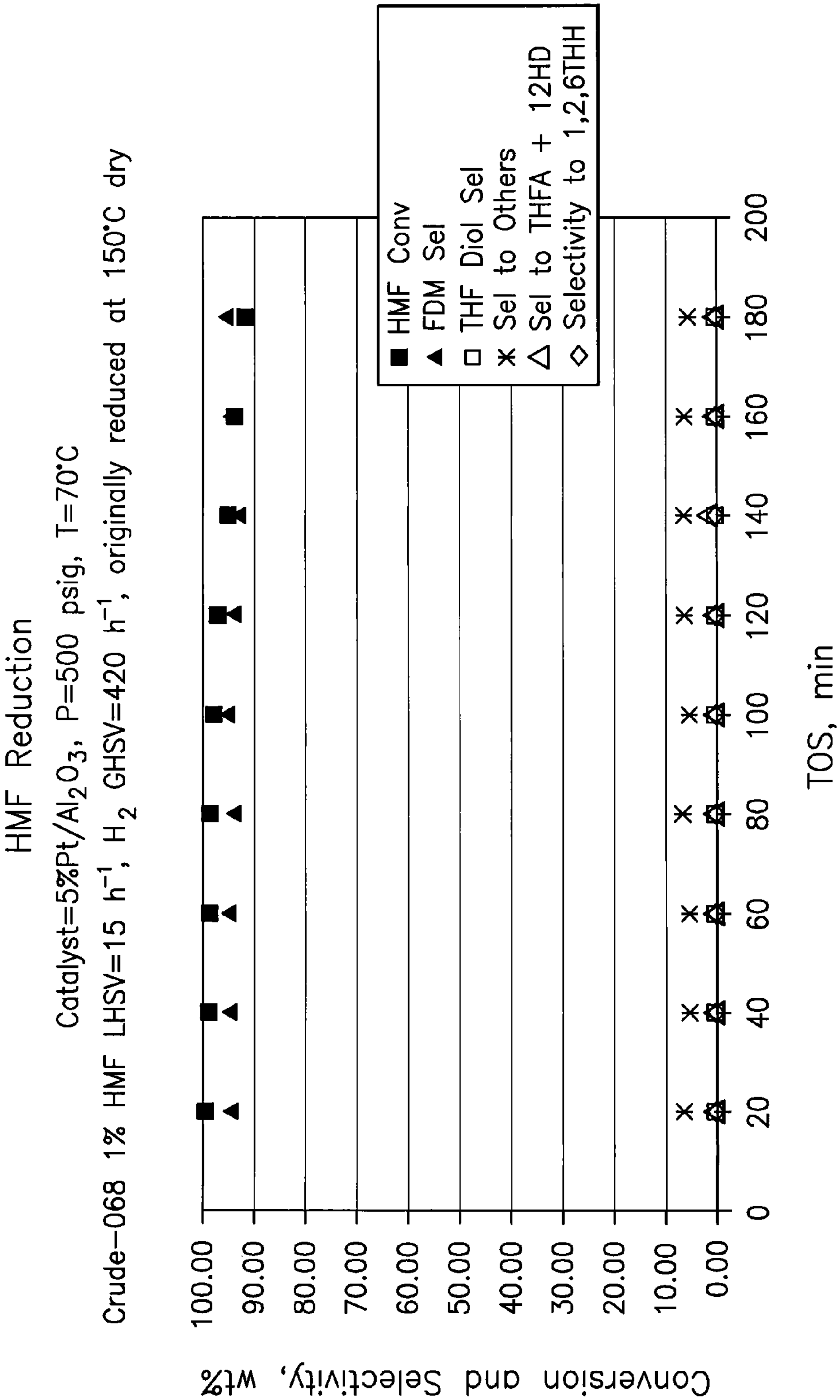

HMF Reduction
Catalyst=5%Pt/Al_2O_3, P=500 psig, T=70°C
Crude–068 1% HMF LHSV=15 h^{-1}, H_2 GHSV=420 h^{-1}, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
TOS, min
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

FIG. 72

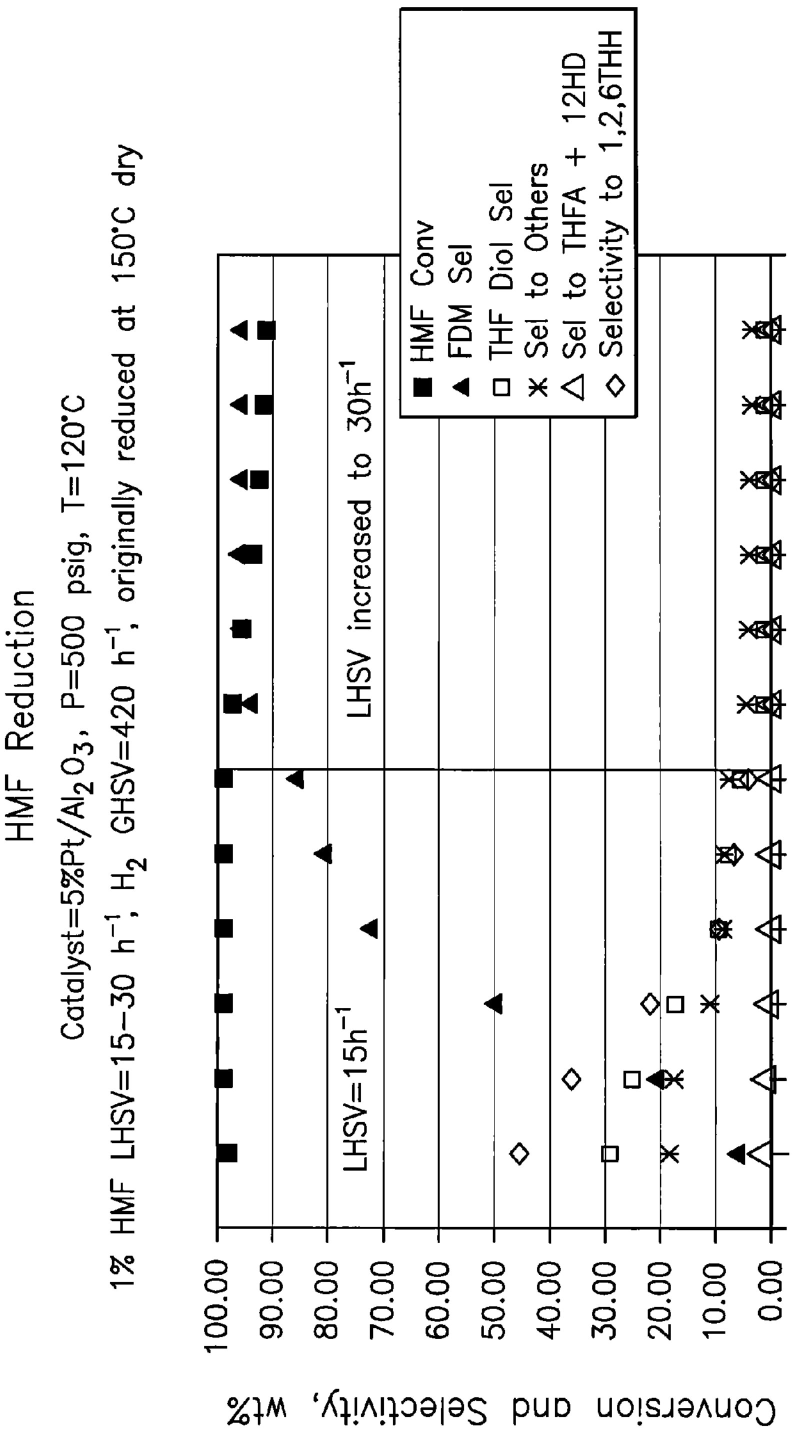

HMF Reduction
Catalyst=5%Pt/Al_2O_3, P=500 psig, T=120°C
1% HMF LHSV=15–30 h^{-1}, H_2 GHSV=420 h^{-1}, originally reduced at 150°C dry
LHSV=15h^{-1}
LHSV increased to 30h^{-1}
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
220
240
260
TOS, min

FIG. 48

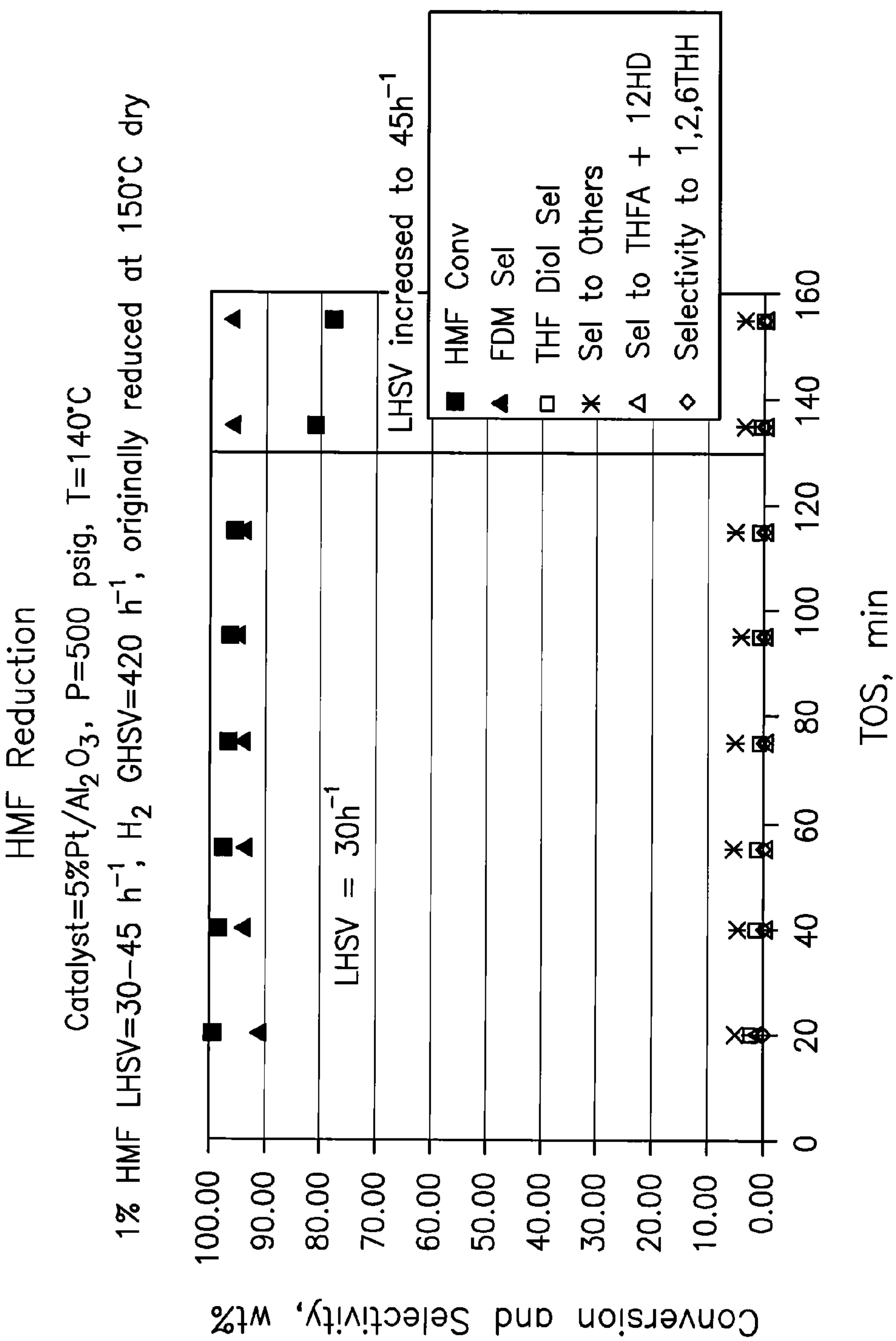

HMF Reduction
Catalyst=5%Pt/Al2O3, P=500 psig, T=140°C
1% HMF LHSV=30−45 h−1, H2 GHSV=420 h−1, originally reduced at 150°C dry
LHSV = 30h−1
LHSV increased to 45h−1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
TOS, min

FIG. 49

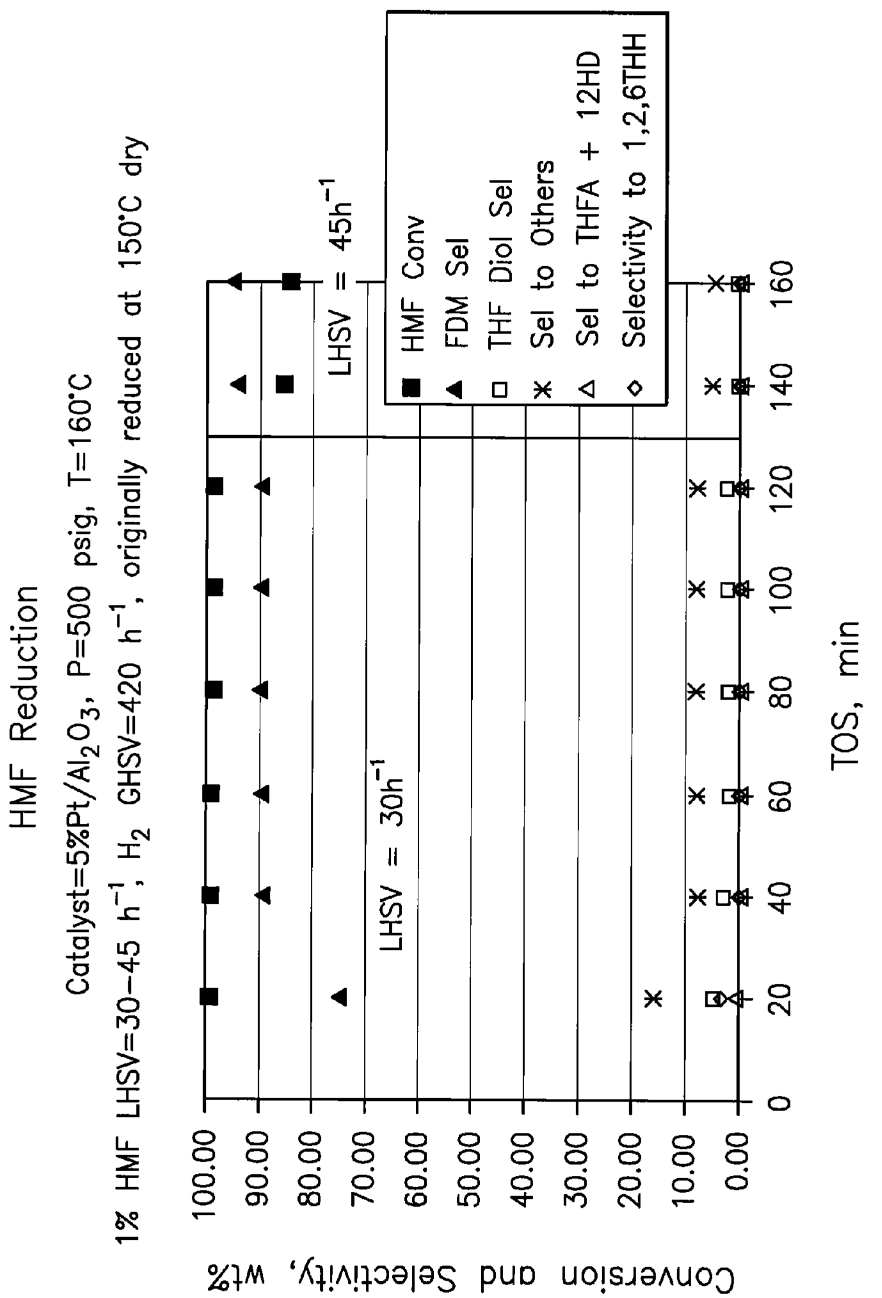

HMF Reduction
Catalyst=5%Pt/Al_2O_3, P=500 psig, T=160°C
1% HMF LHSV=30-45 h^{-1}, H_2 GHSV=420 h^{-1}, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
TOS, min
LHSV = 30h^{-1}
LHSV = 45h^{-1}
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

Fig. 50

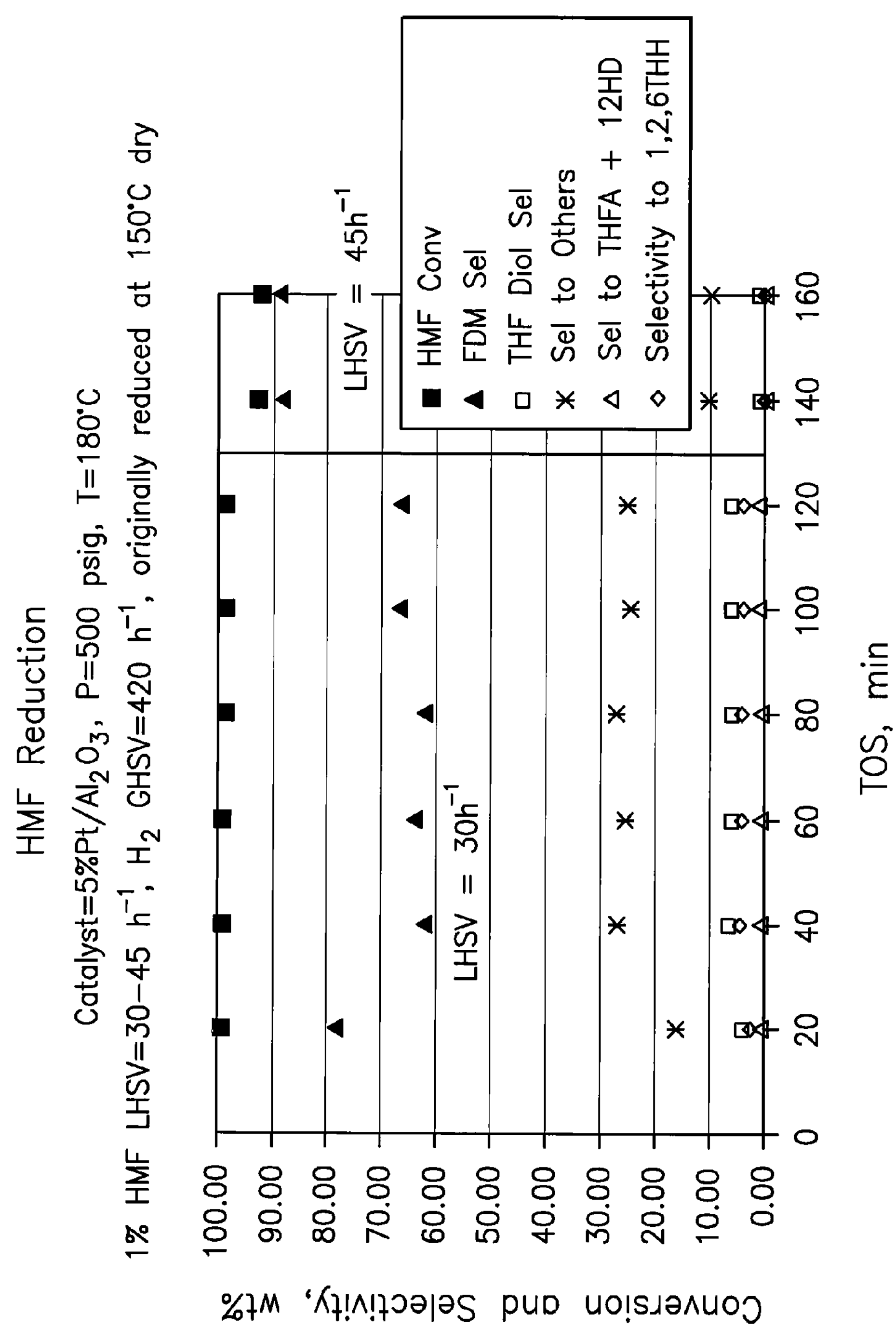

HMF Reduction
Catalyst=5%Pt/Al2O3, P=500 psig, T=180°C
1% HMF LHSV=30-45 h-1, H2 GHSV=420 h-1, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
TOS, min
LHSV = 30h-1
LHSV = 45h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

FIG. 51

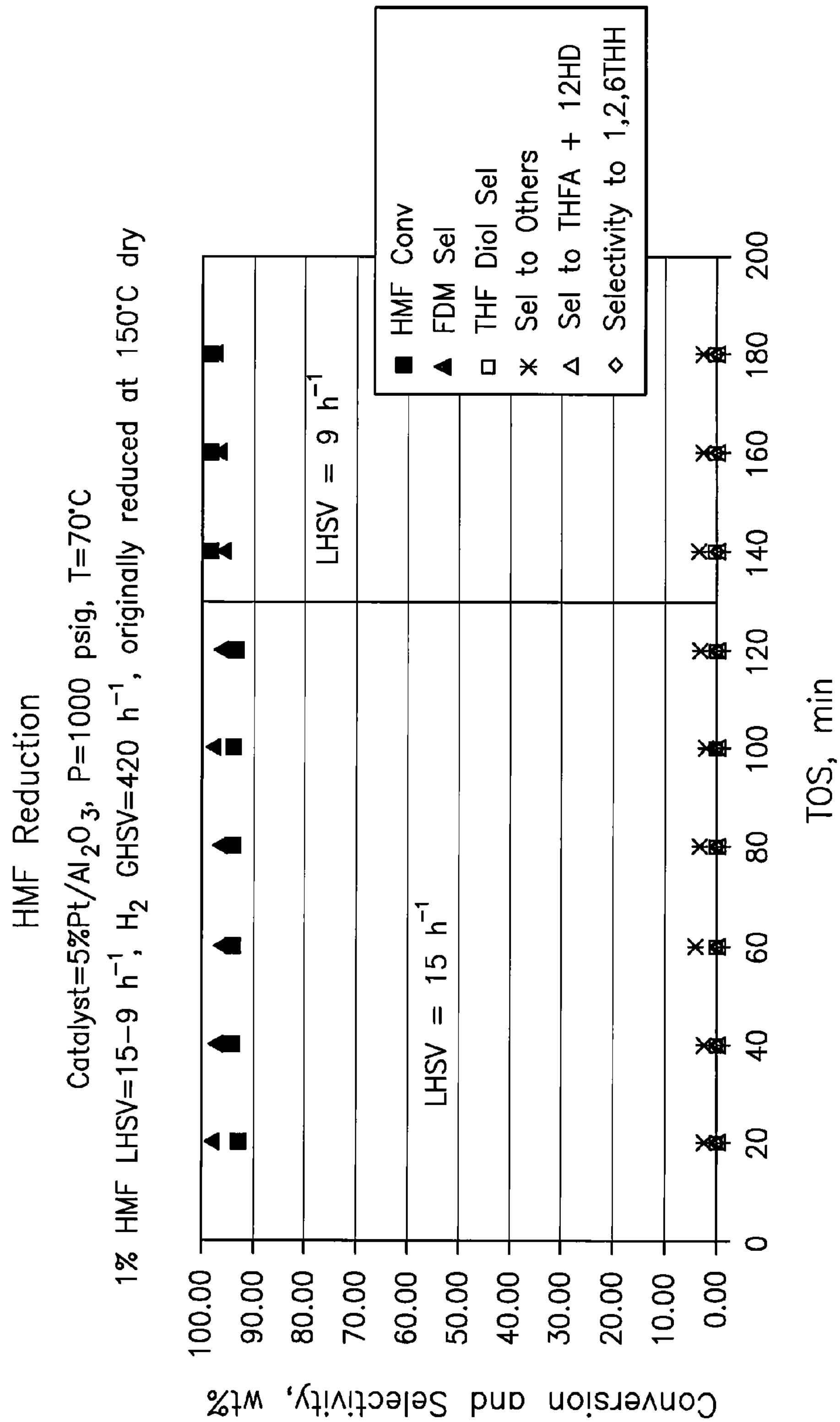

HMF Reduction
Catalyst=5%Pt/Al2O3, P=1000 psig, T=70°C
1% HMF LHSV=15-9 h-1, H2 GHSV=420 h-1, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
TOS, min
LHSV = 15 h-1
LHSV = 9 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

FIG. 52

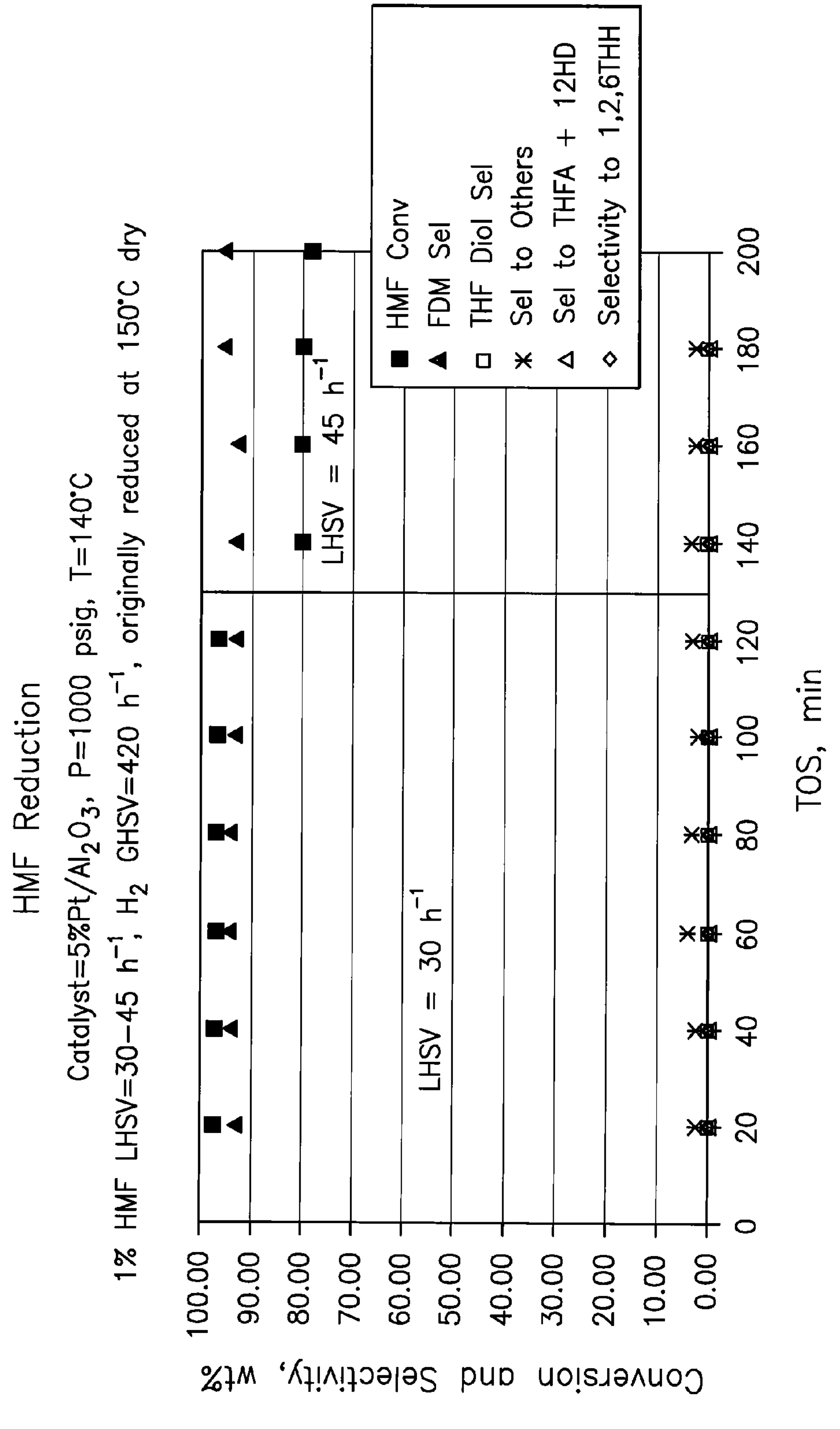

HMF Reduction
Catalyst=5%Pt/Al2O3, P=1000 psig, T=140°C
1% HMF LHSV=30-45 h-1, H2 GHSV=420 h-1, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
TOS, min
LHSV = 30 h-1
LHSV = 45 h-1
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

FIG. 53

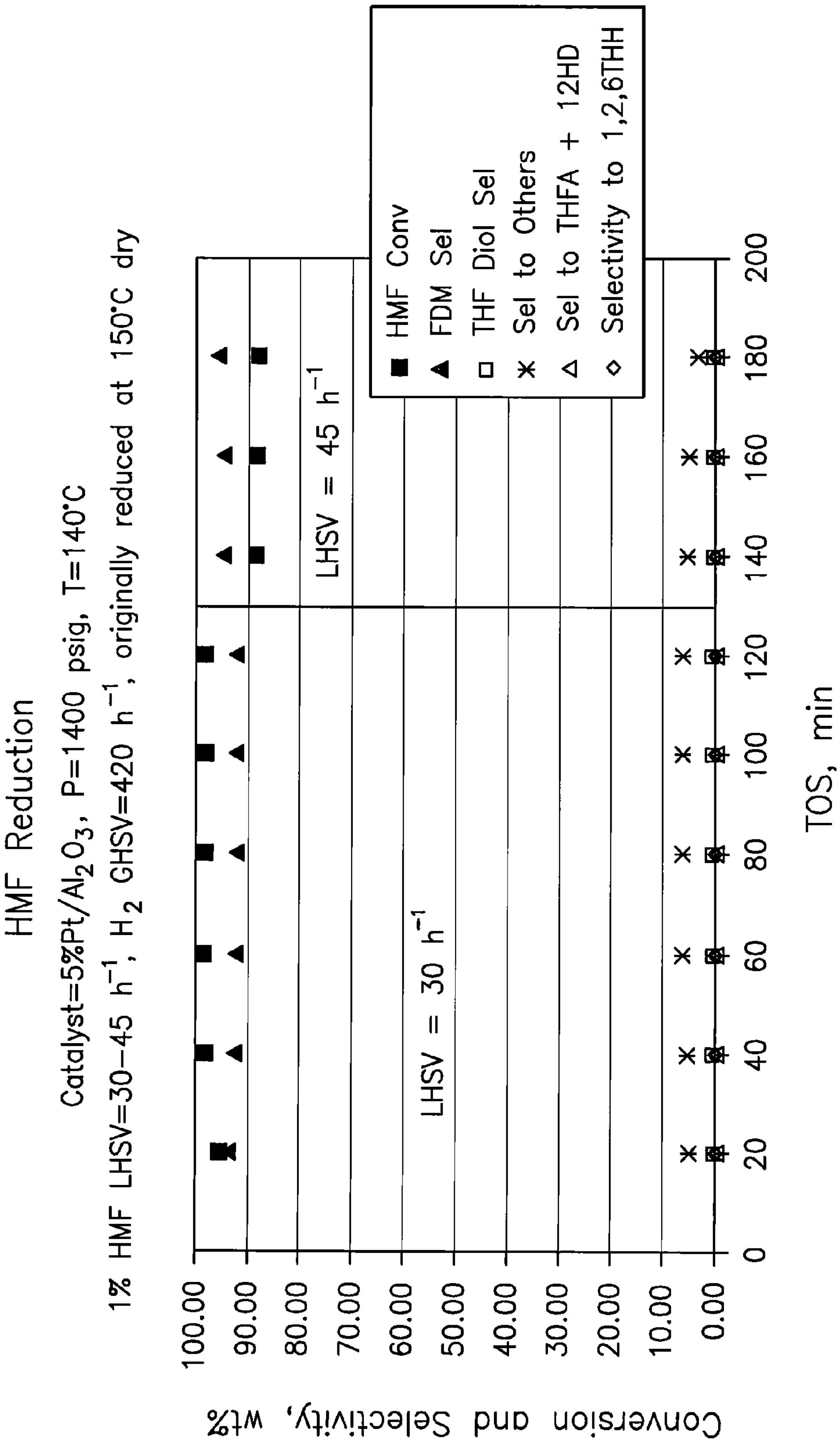

HMF Reduction
Catalyst=5%Pt/Al_2O_3, P=1400 psig, T=140°C
1% HMF LHSV=30–45 h^{-1}, H_2 GHSV=420 h^{-1}, originally reduced at 150°C dry
Conversion and Selectivity, wt%
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
TOS, min
LHSV = 30 h^{-1}
LHSV = 45 h^{-1}
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH

Fig. 54

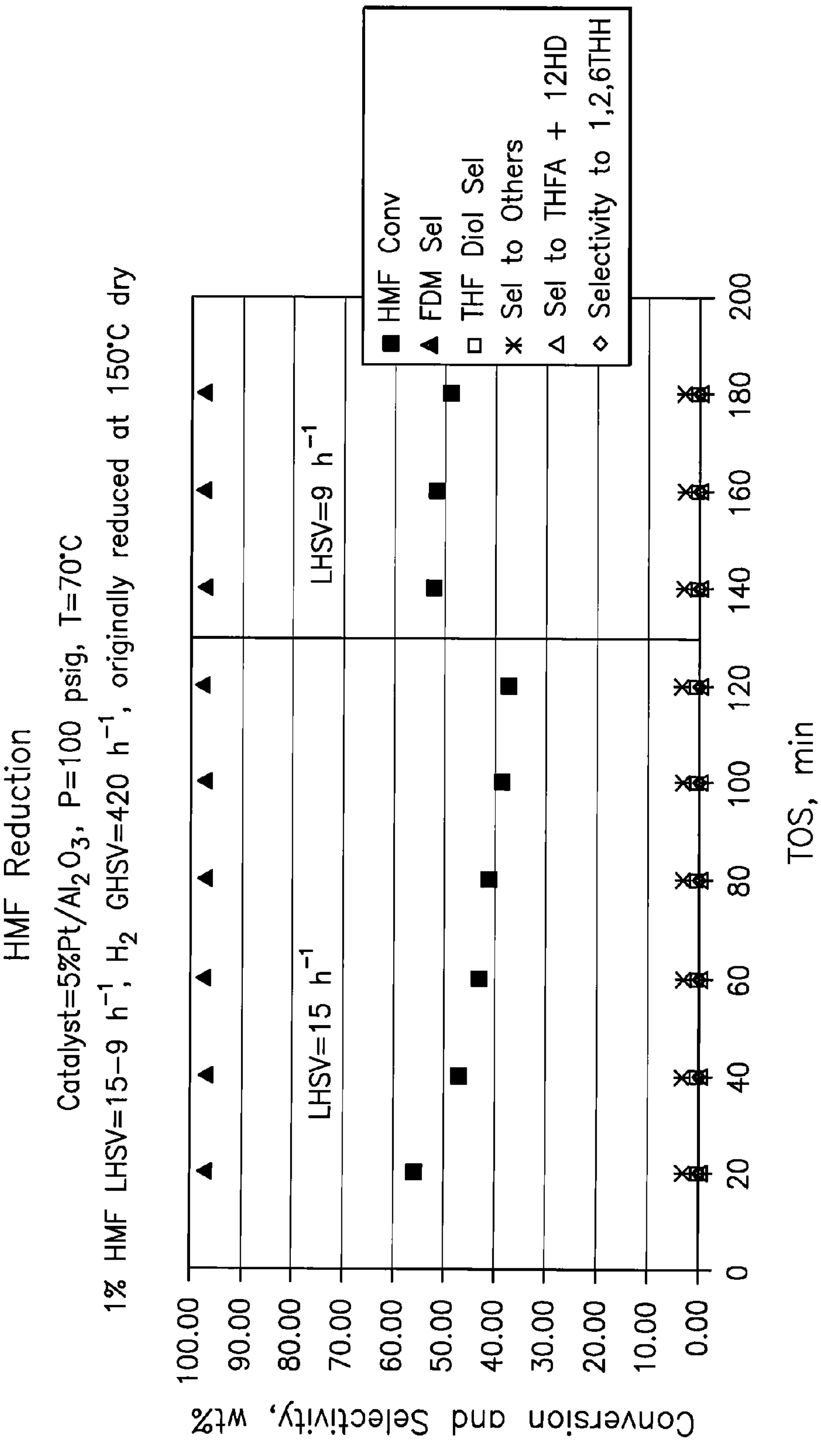

HMF Reduction
Catalyst=5%Pt/Al2O3, P=100 psig, T=70°C
1% HMF LHSV=15–9 h-1, H2 GHSV=420 h-1, originally reduced at 150°C dry
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
Sel to THFA + 12HD
Selectivity to 1,2,6THH
LHSV=15 h-1
LHSV=9 h-1
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
20
40
60
80
100
120
140
160
180
200
Conversion and Selectivity, wt%
TOS, min

FIG. 55

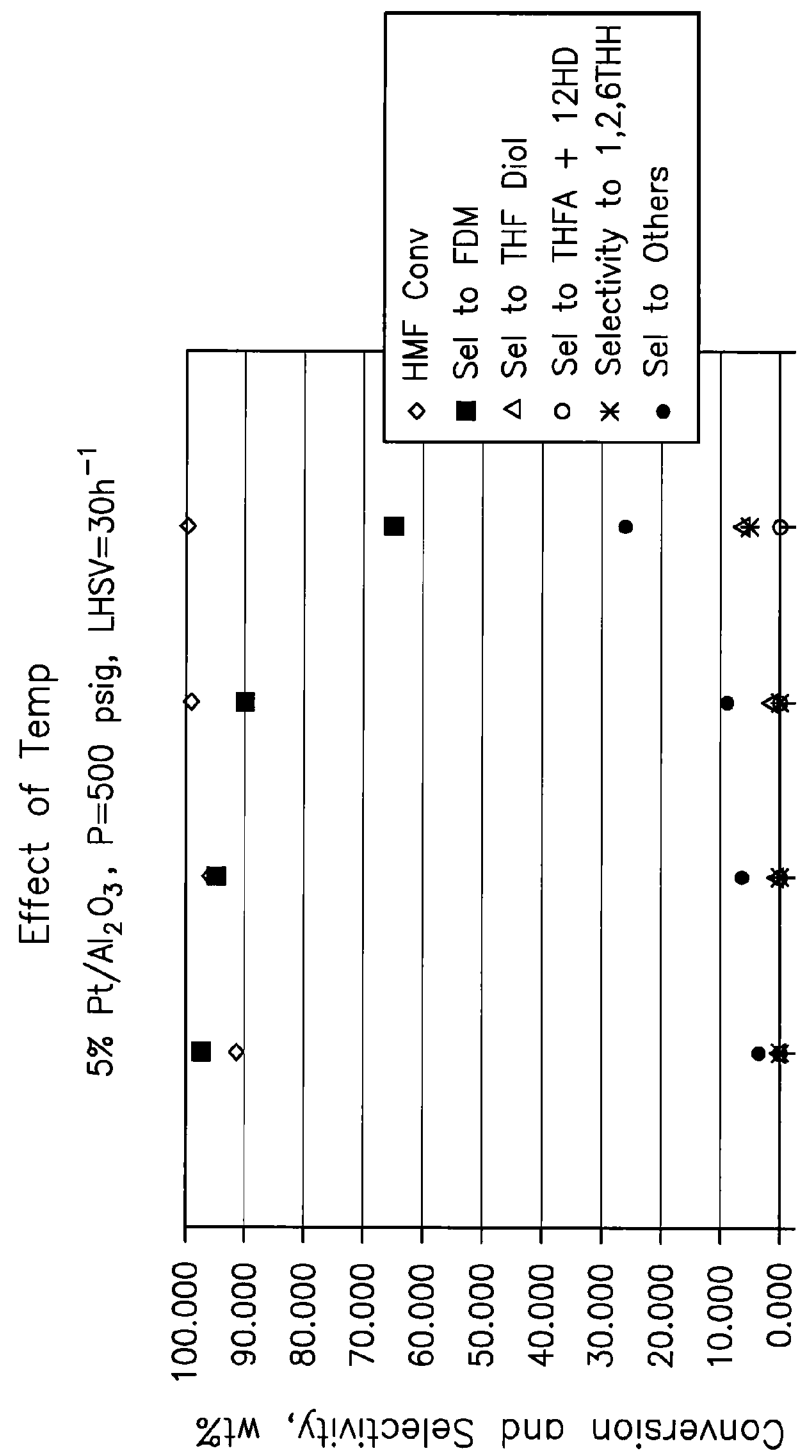

Effect of Temp
5% Pt/Al$_2$O$_3$, P=500 psig, LHSV=30h^{-1}
Conversion and Selectivity, wt%
100.000
90.000
80.000
70.000
60.000
50.000
40.000
30.000
20.000
10.000
0.000
100
120
140
160
180
200
Temp. °C
HMF Conv
Sel to FDM
Sel to THF Diol
Sel to THFA + 12HD
Selectivity to 1,2,6THH
Sel to Others

Fig. 56

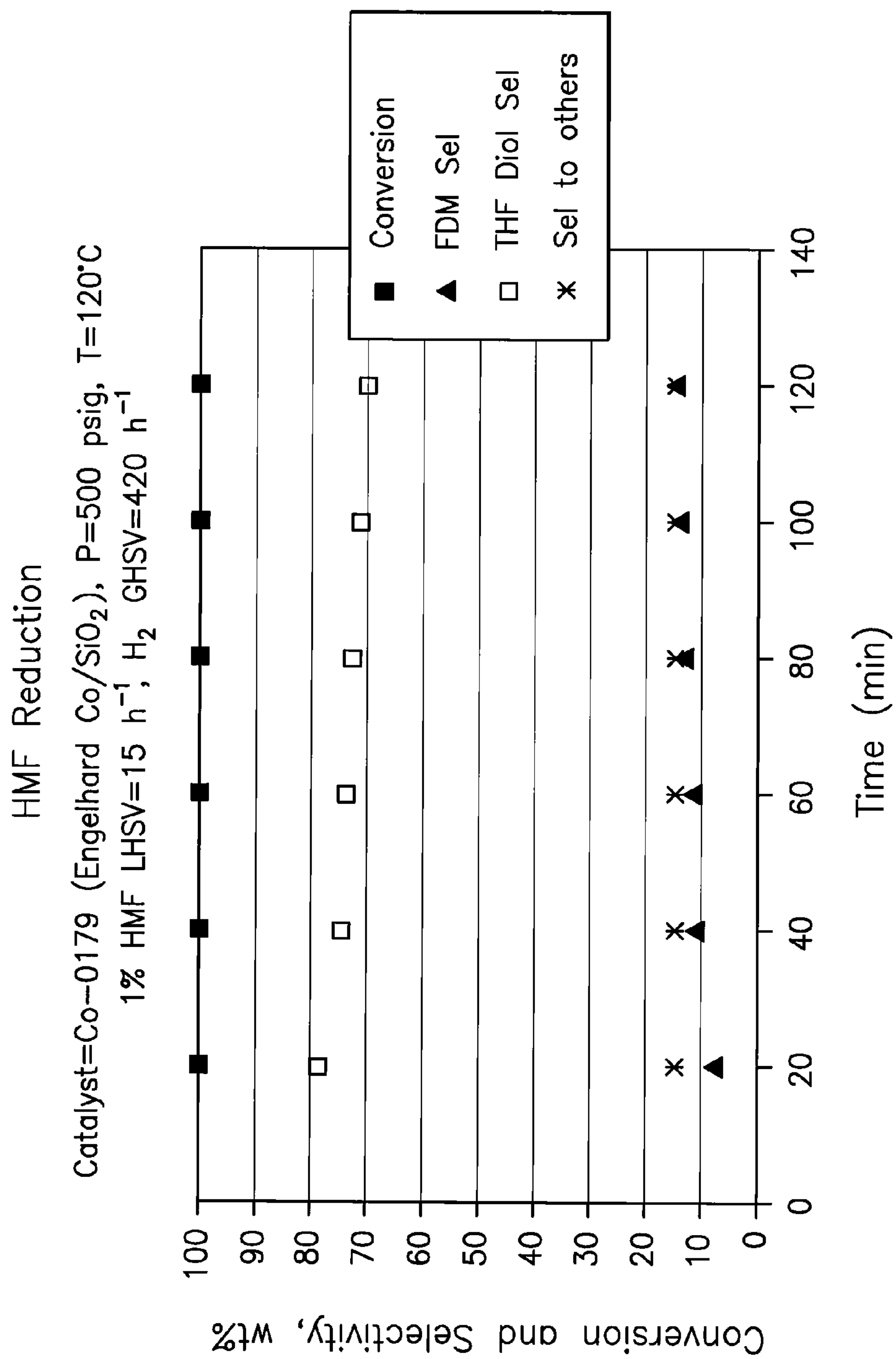

HMF Reduction
Catalyst=Co–0179 (Engelhard Co/SiO2), P=500 psig, T=120°C
1% HMF LHSV=15 h-1, H2 GHSV=420 h-1
Conversion
FDM Sel
THF Diol Sel
Sel to others
Conversion and Selectivity, wt%
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
Time (min)

Fig. 57

FDM Reduction to THF Diol

Catalyst=Ni/SiO_2 Catalyst (SudCehmie C46-7-03RS, Longer-Bed), P=500 psig, T=70°C
1% FDM LHSV=$15h^{-1}$, H_2 GHSV=$210h^{-1}$, originally reduced at 300°C dry

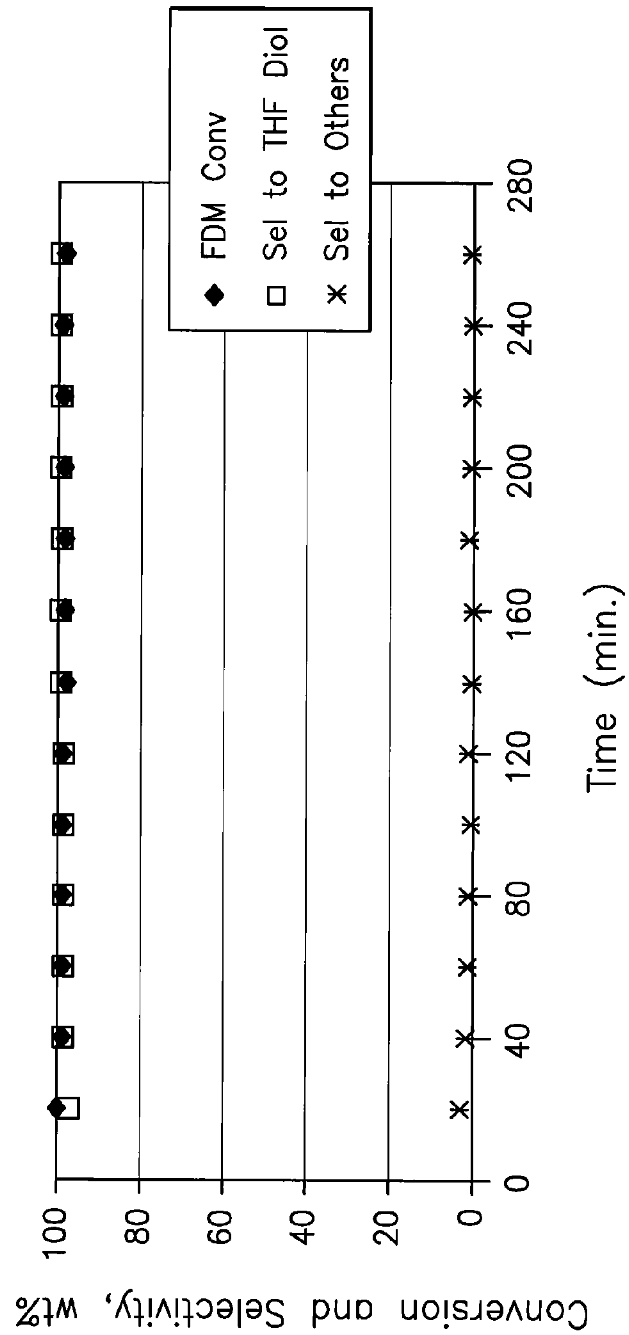


FIG 58

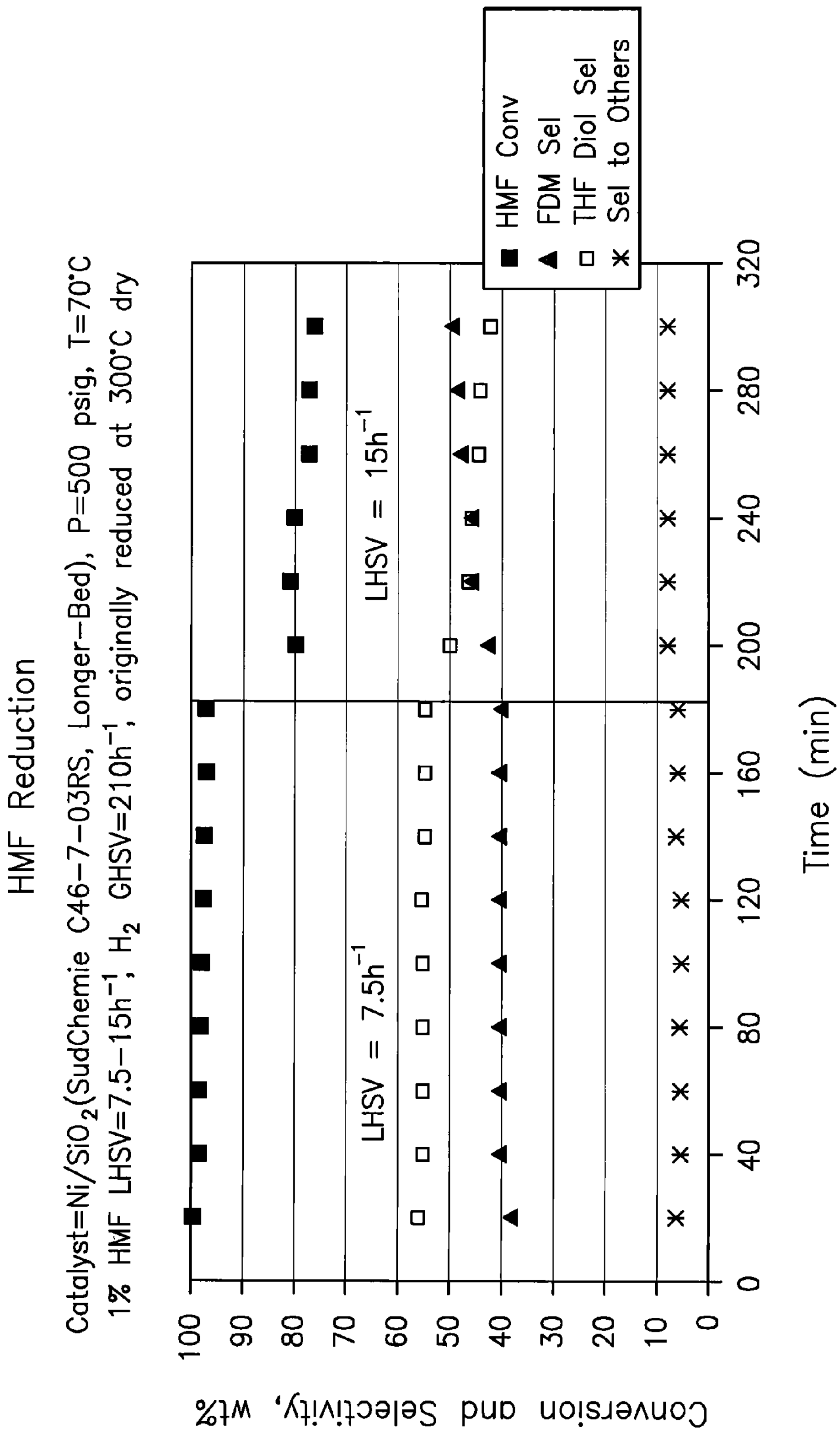
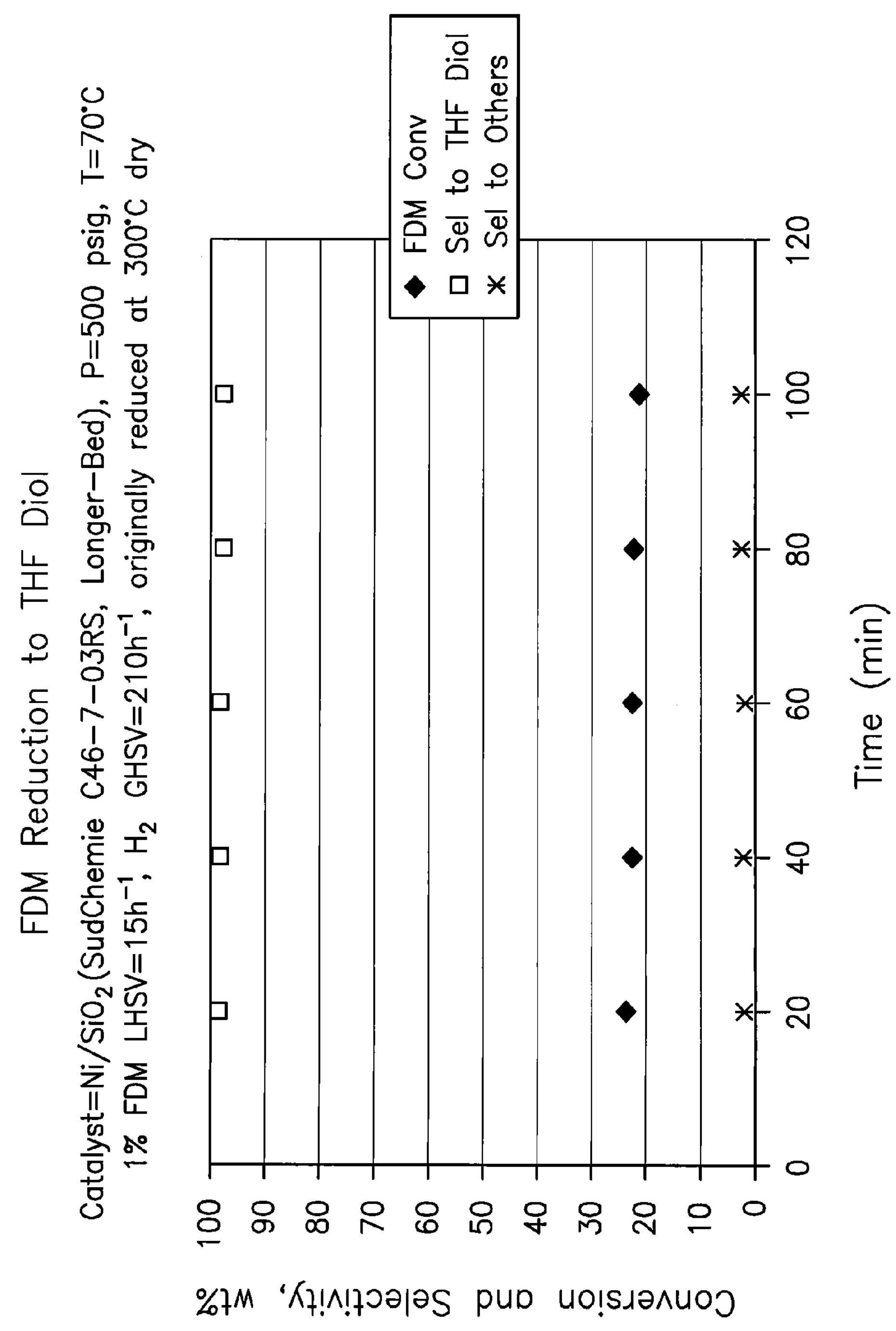

HMF Reduction
Catalyst=Ni/SiO2(SudChemie C46-7-03RS, Longer-Bed), P=500 psig, T=70°C
1% HMF LHSV=7.5-15h-1, H2 GHSV=210h-1, originally reduced at 300°C dry
HMF Conv
FDM Sel
THF Diol Sel
Sel to Others
LHSV = 7.5h-1
LHSV = 15h-1
Conversion and Selectivity, wt%
Time (min)
100
90
80
70
60
50
40
30
20
10
0
40
80
120
160
200
240
280
320

Fig. 59



FDM Reduction to THF Diol
Catalyst=Ni/SiO2(SudChemie C46-7-03RS, Longer-Bed), P=500 psig, T=70°C
1% FDM LHSV=15h-1, H2 GHSV=210h-1, originally reduced at 300°C dry
Conversion and Selectivity, wt%
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
Time (min)
FDM Conv
Sel to THF Diol
Sel to Others

FIG. 60

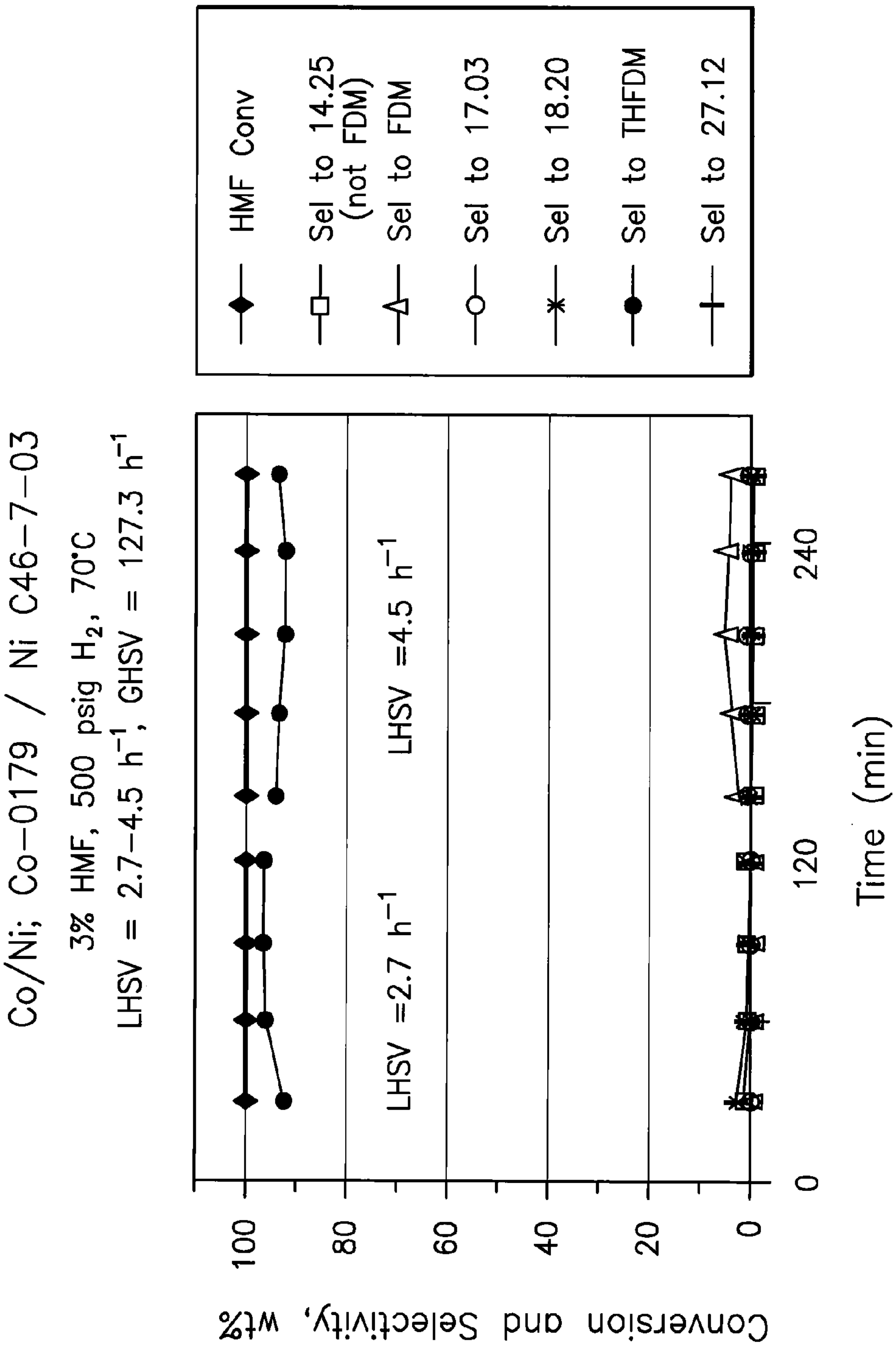

Co/Ni; Co−0179 / Ni C46−7−03
3% HMF, 500 psig H2, 70°C
LHSV = 2.7−4.5 h-1, GHSV = 127.3 h-1
LHSV =2.7 h-1
LHSV =4.5 h-1
Conversion and Selectivity, wt%
0
20
40
60
80
100
0
120
240
Time (min)
HMF Conv
Sel to 14.25 (not FDM)
Sel to FDM
Sel to 17.03
Sel to 18.20
Sel to THFDM
Sel to 27.12

FIG. 61

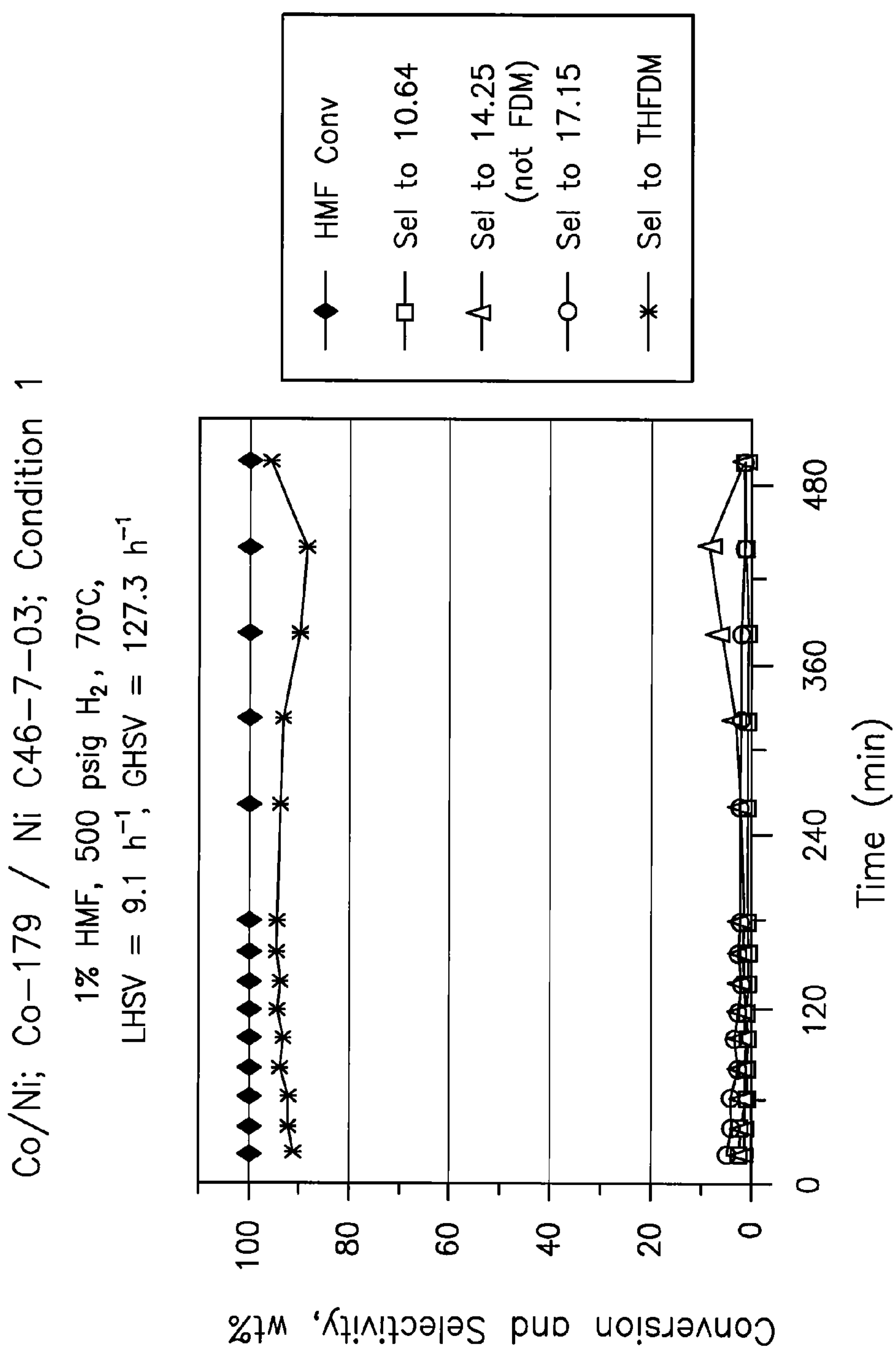

Co/Ni; Co-179 / Ni C46-7-03; Condition 1
1% HMF, 500 psig H2, 70°C,
LHSV = 9.1 h-1, GHSV = 127.3 h-1
HMF Conv
Sel to 10.64
Sel to 14.25 (not FDM)
Sel to 17.15
Sel to THFDM
Conversion and Selectivity, wt%
0
20
40
60
80
100
0
120
240
360
480
Time (min)

FIG. 62

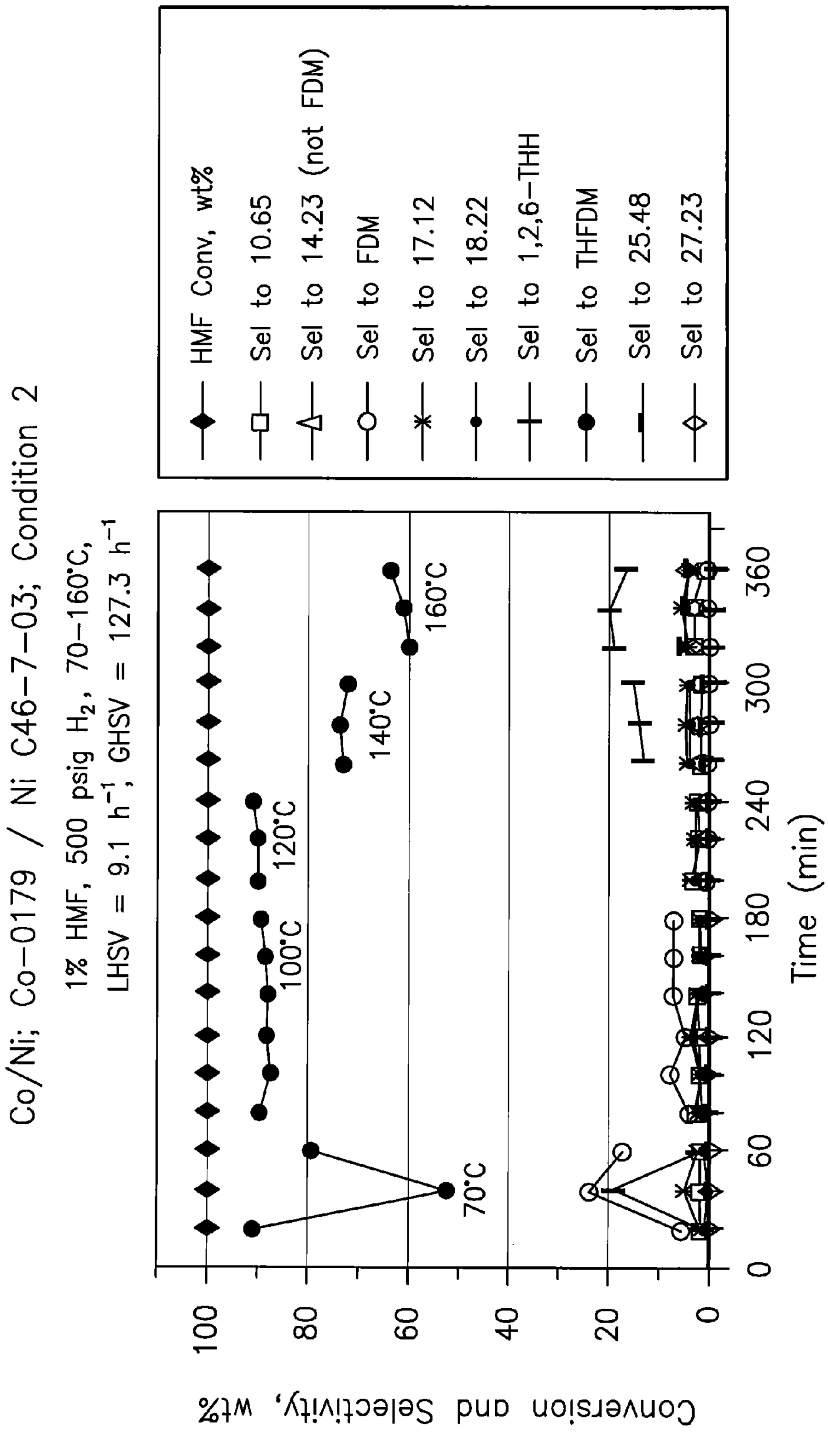
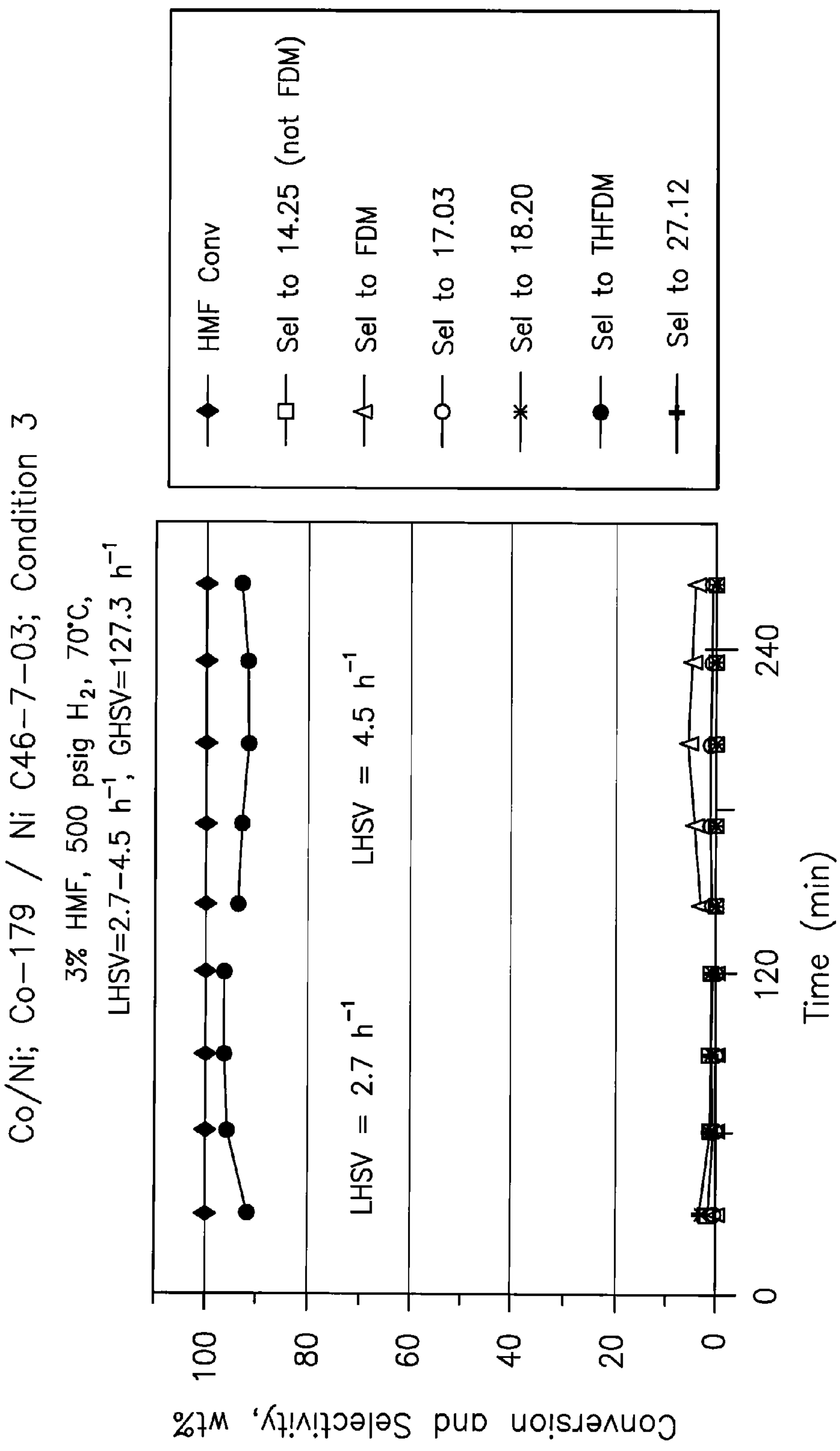

Co/Ni; Co-0179 / Ni C46-7-03; Condition 2
1% HMF, 500 psig H_2, 70-160°C,
LHSV = 9.1 h^{-1}, GHSV = 127.3 h^{-1}
Conversion and Selectivity, wt%
100
80
60
40
20
0
Time (min)
0
60
120
180
240
300
360
70°C
100°C
120°C
140°C
160°C
HMF Conv, wt%
Sel to 10.65
Sel to 14.23 (not FDM)
Sel to FDM
Sel to 17.12
Sel to 18.22
Sel to 1,2,6-THH
Sel to THFDM
Sel to 25.48
Sel to 27.23

FIG. 63



Co/Ni; Co–179 / Ni C46–7–03; Condition 3
3% HMF, 500 psig H2, 70°C,
LHSV=2.7–4.5 h-1, GHSV=127.3 h-1
LHSV = 2.7 h-1
LHSV = 4.5 h-1
Conversion and Selectivity, wt%
Time (min)
0
20
40
60
80
100
0
120
240
HMF Conv
Sel to 14.25 (not FDM)
Sel to FDM
Sel to 17.03
Sel to 18.20
Sel to THFDM
Sel to 27.12

Fig. 64

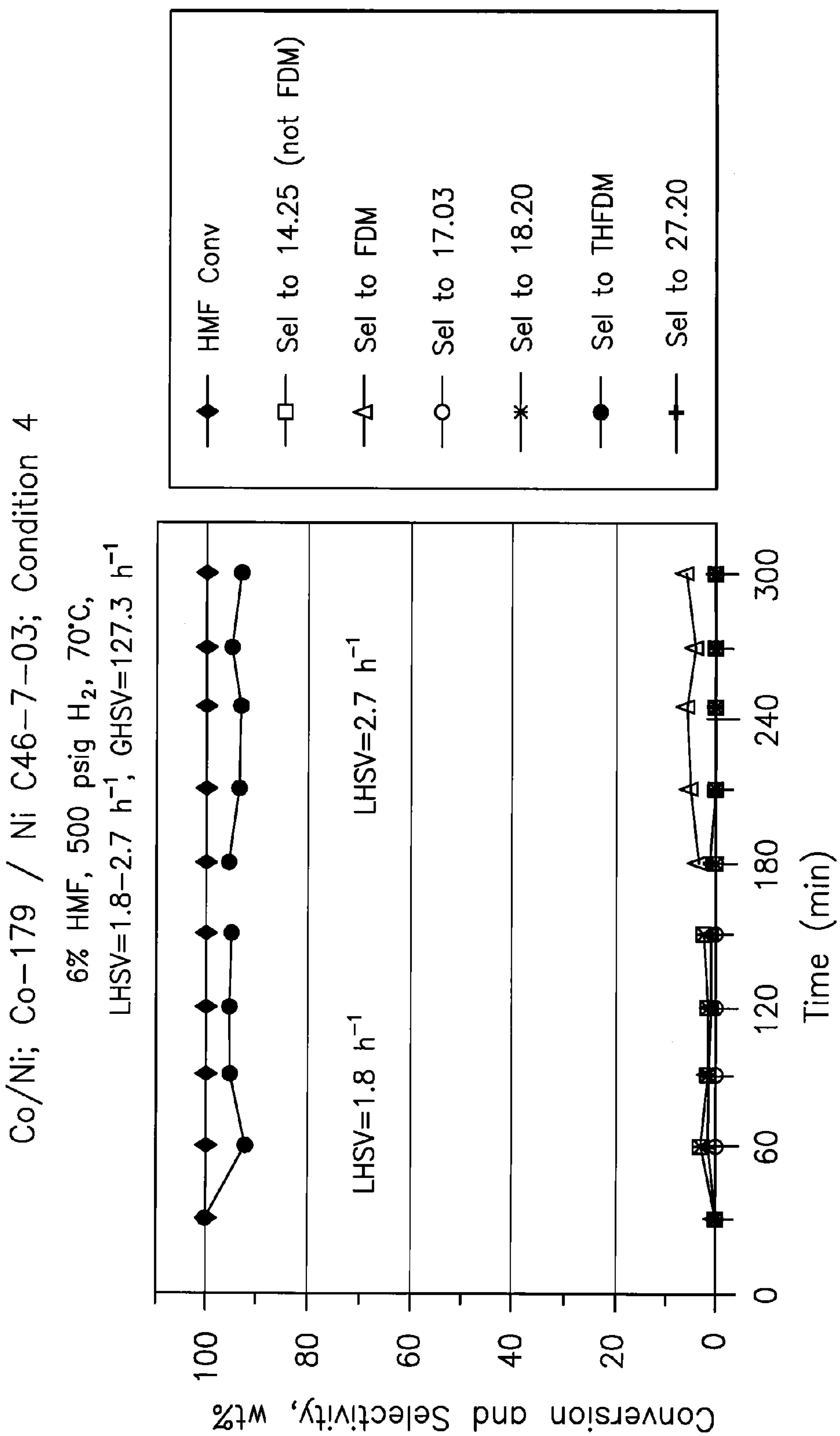

Co/Ni; Co-179 / Ni C46-7-03; Condition 4
6% HMF, 500 psig H_2, 70°C,
LHSV=1.8-2.7 h^{-1}, GHSV=127.3 h^{-1}
HMF Conv
Sel to 14.25 (not FDM)
Sel to FDM
Sel to 17.03
Sel to 18.20
Sel to THFDM
Sel to 27.20
LHSV=1.8 h^{-1}
LHSV=2.7 h^{-1}
Conversion and Selectivity, wt%
100
80
60
40
20
0
0
60
120
180
240
300
Time (min)

Fig. 65

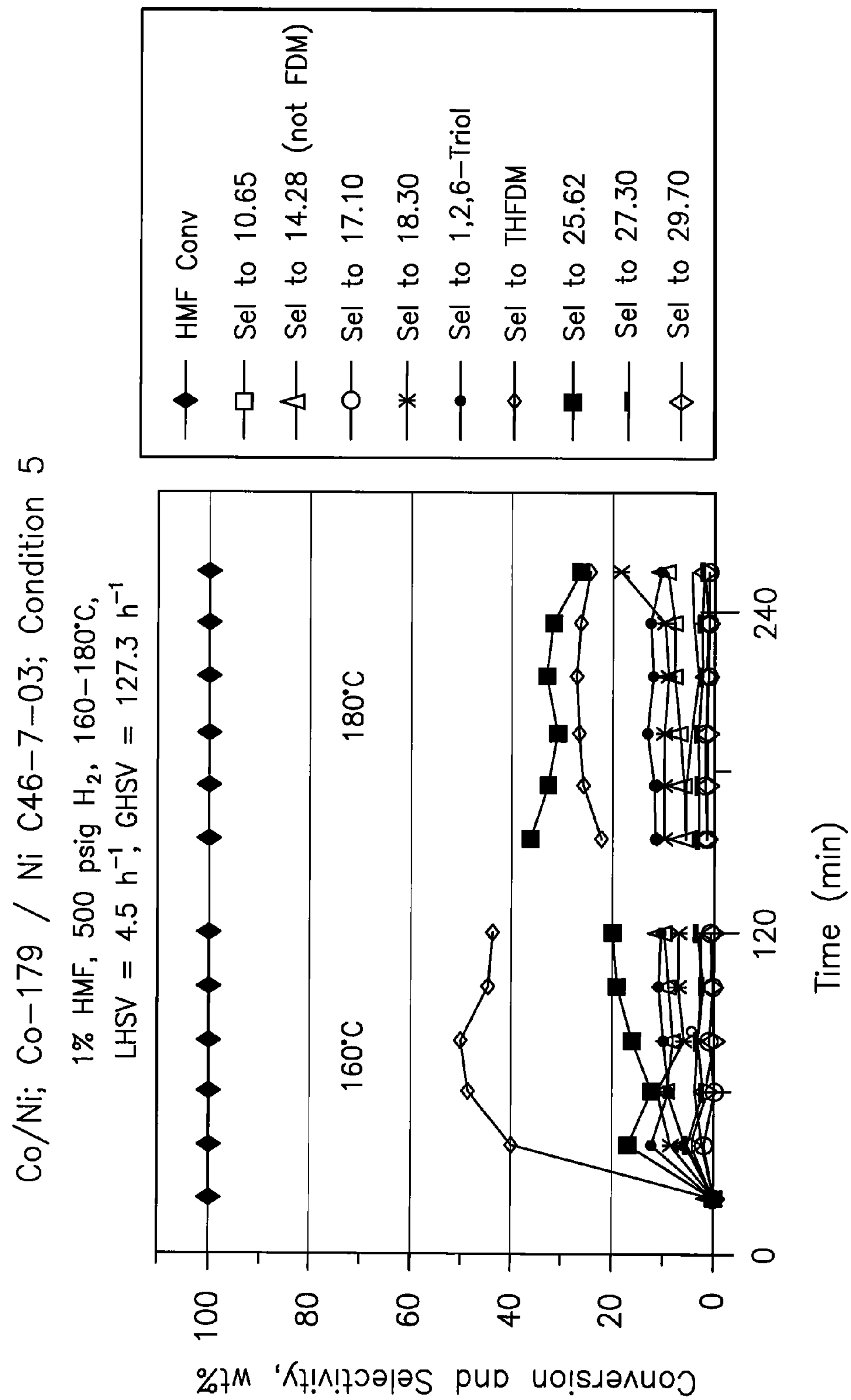

Co/Ni; Co-179 / Ni C46-7-03; Condition 5
1% HMF, 500 psig H_2, 160-180°C,
LHSV = 4.5 h^{-1}, GHSV = 127.3 h^{-1}
Conversion and Selectivity, wt%
0
20
40
60
80
100
0
120
240
Time (min)
160°C
180°C
HMF Conv
Sel to 10.65
Sel to 14.28 (not FDM)
Sel to 17.10
Sel to 18.30
Sel to 1,2,6-Triol
Sel to THFDM
Sel to 25.62
Sel to 27.30
Sel to 29.70

FIG. 66

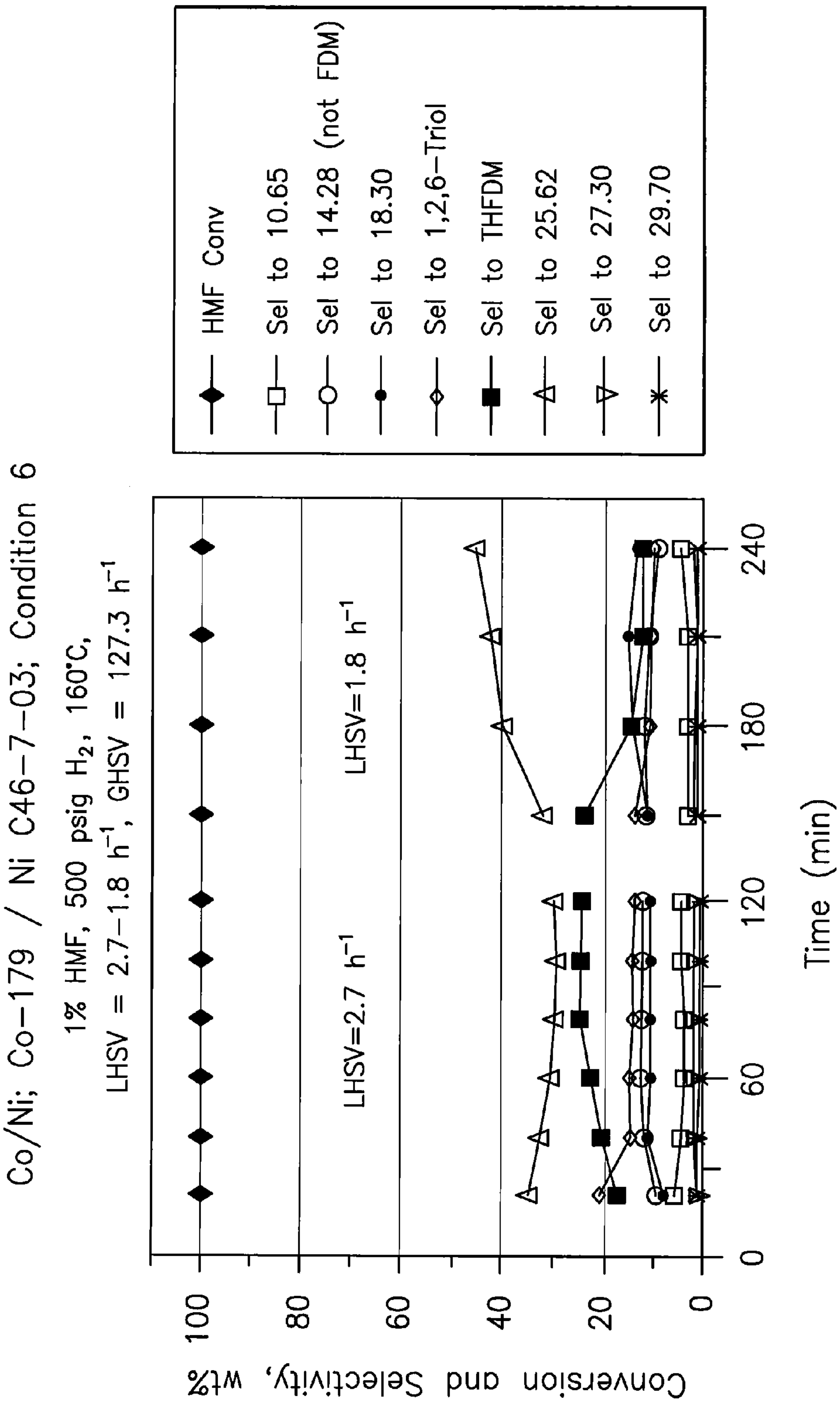

Co/Ni; Co−179 / Ni C46−7−03; Condition 6
1% HMF, 500 psig H_2, 160°C,
LHSV = 2.7−1.8 h^{-1}, GHSV = 127.3 h^{-1}
LHSV=2.7 h^{-1}
LHSV=1.8 h^{-1}
Conversion and Selectivity, wt%
Time (min)
0
20
40
60
80
100
0
60
120
180
240
HMF Conv
Sel to 10.65
Sel to 14.28 (not FDM)
Sel to 18.30
Sel to 1,2,6−Triol
Sel to THFDM
Sel to 25.62
Sel to 27.30
Sel to 29.70

FIG. 67

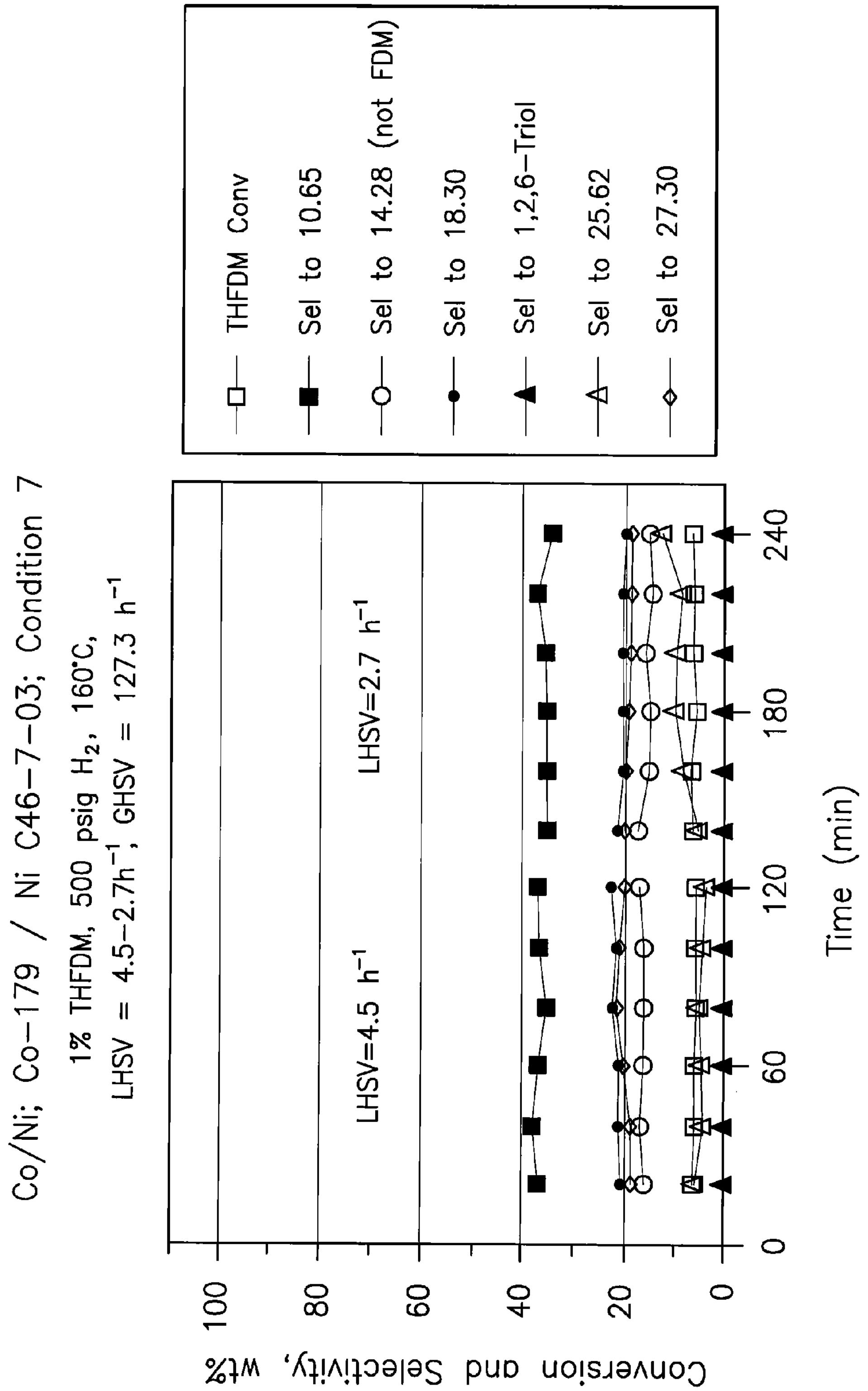

Co/Ni; Co–179 / Ni C46–7–03; Condition 7
1% THFDM, 500 psig H_2, 160°C,
LHSV = 4.5–2.7h^{-1}; GHSV = 127.3 h^{-1}
THFDM Conv
Sel to 10.65
Sel to 14.28 (not FDM)
Sel to 18.30
Sel to 1,2,6–Triol
Sel to 25.62
Sel to 27.30
LHSV=4.5 h^{-1}
LHSV=2.7 h^{-1}
Conversion and Selectivity, wt%
0
20
40
60
80
100
0
60
120
180
240
Time (min)

FIG. 68

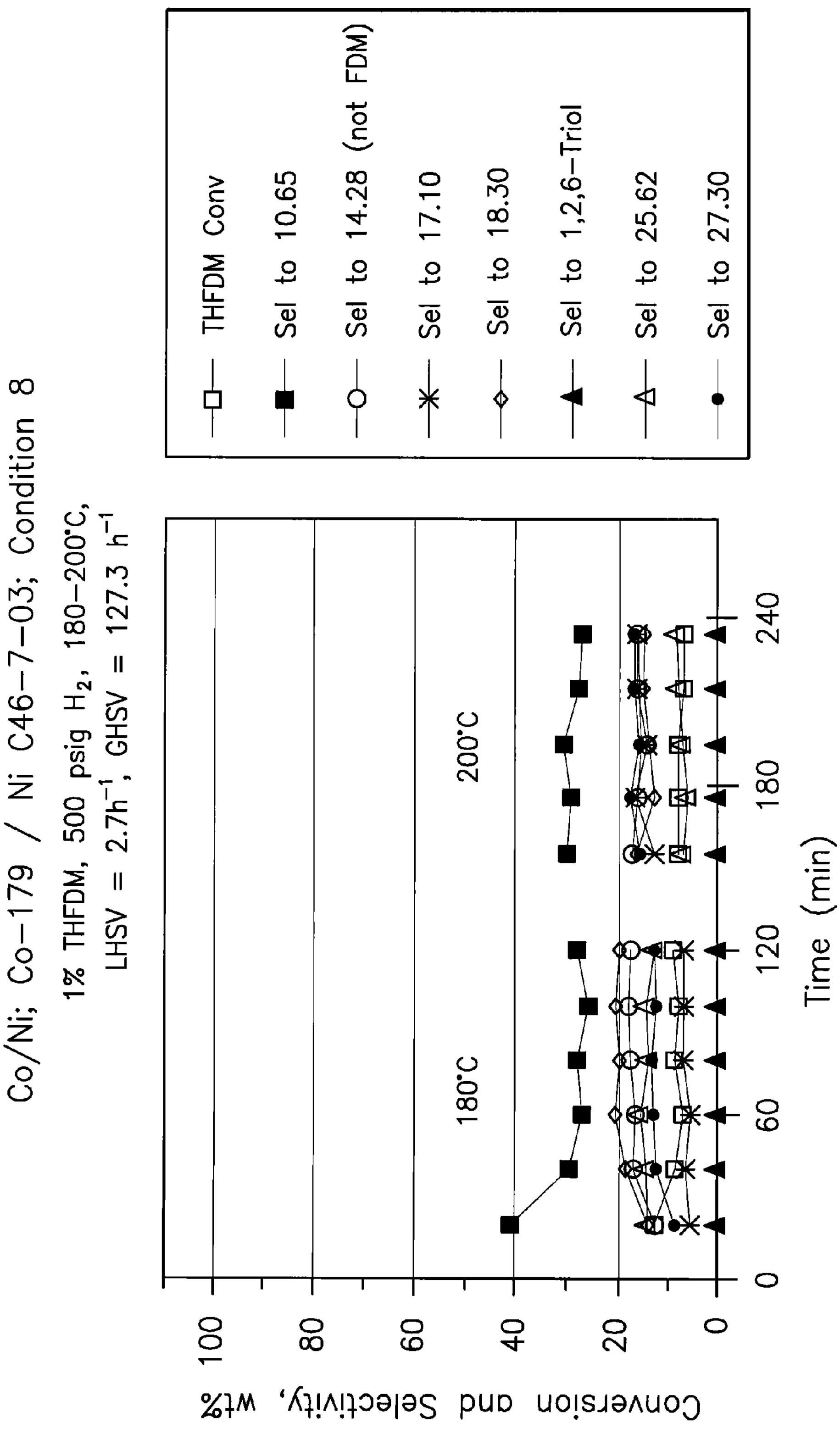

Co/Ni; Co−179 / Ni C46−7−03; Condition 8
1% THFDM, 500 psig H2, 180−200°C,
LHSV = 2.7h−1, GHSV = 127.3 h−1
180°C
200°C
Conversion and Selectivity, wt%
Time (min)
0
20
40
60
80
100
0
60
120
180
240
THFDM Conv
Sel to 10.65
Sel to 14.28 (not FDM)
Sel to 17.10
Sel to 18.30
Sel to 1,2,6−Triol
Sel to 25.62
Sel to 27.30

FIG. 69

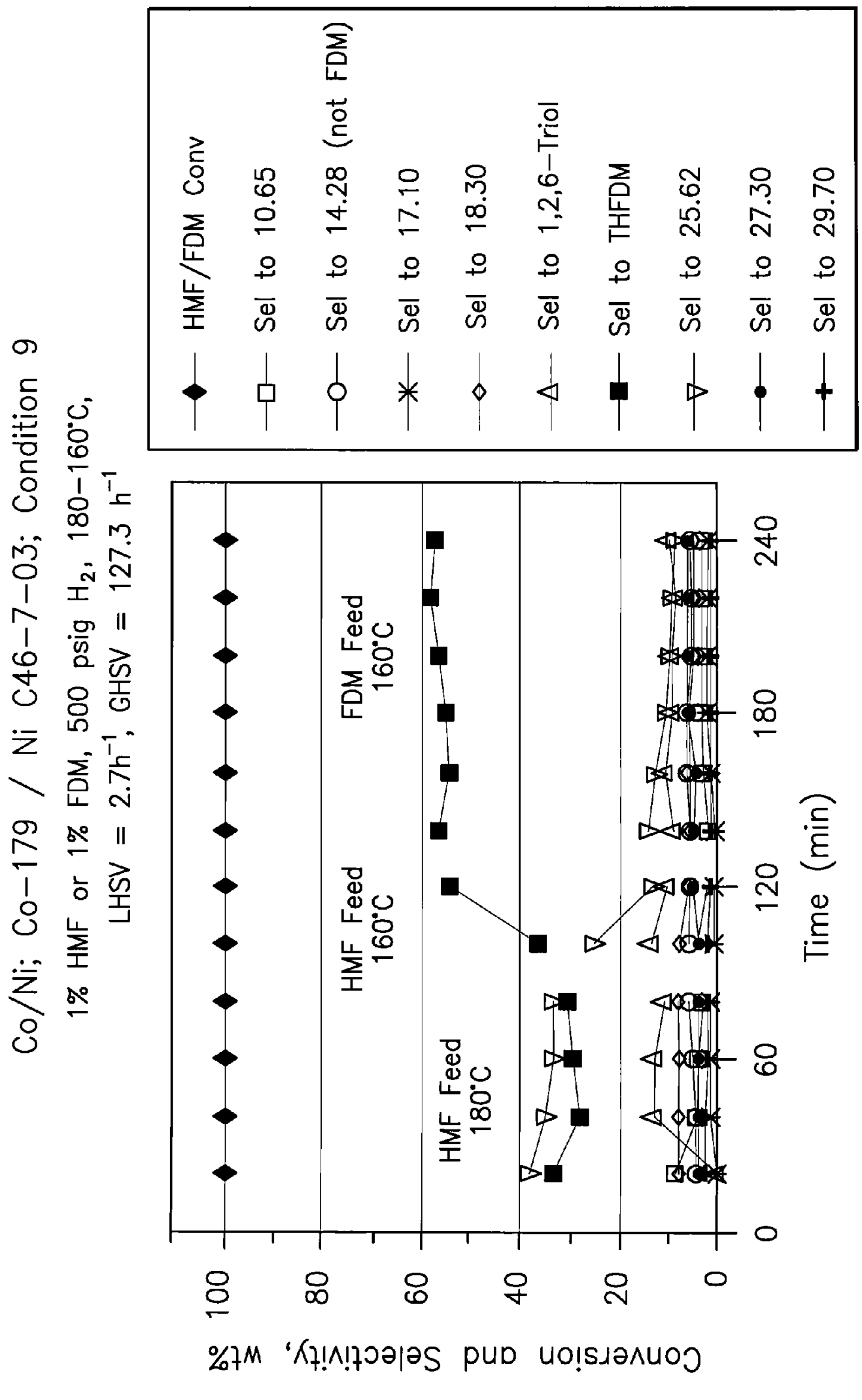

Co/Ni; Co-179 / Ni C46-7-03; Condition 9
1% HMF or 1% FDM, 500 psig H2, 180-160°C,
LHSV = 2.7h-1, GHSV = 127.3 h-1
HMF/FDM Conv
Sel to 10.65
Sel to 14.28 (not FDM)
Sel to 17.10
Sel to 18.30
Sel to 1,2,6-Triol
Sel to THFDM
Sel to 25.62
Sel to 27.30
Sel to 29.70
HMF Feed
180°C
HMF Feed
160°C
FDM Feed
160°C
Conversion and Selectivity, wt%
0
20
40
60
80
100
0
60
120
180
240
Time (min)

Fig. 70

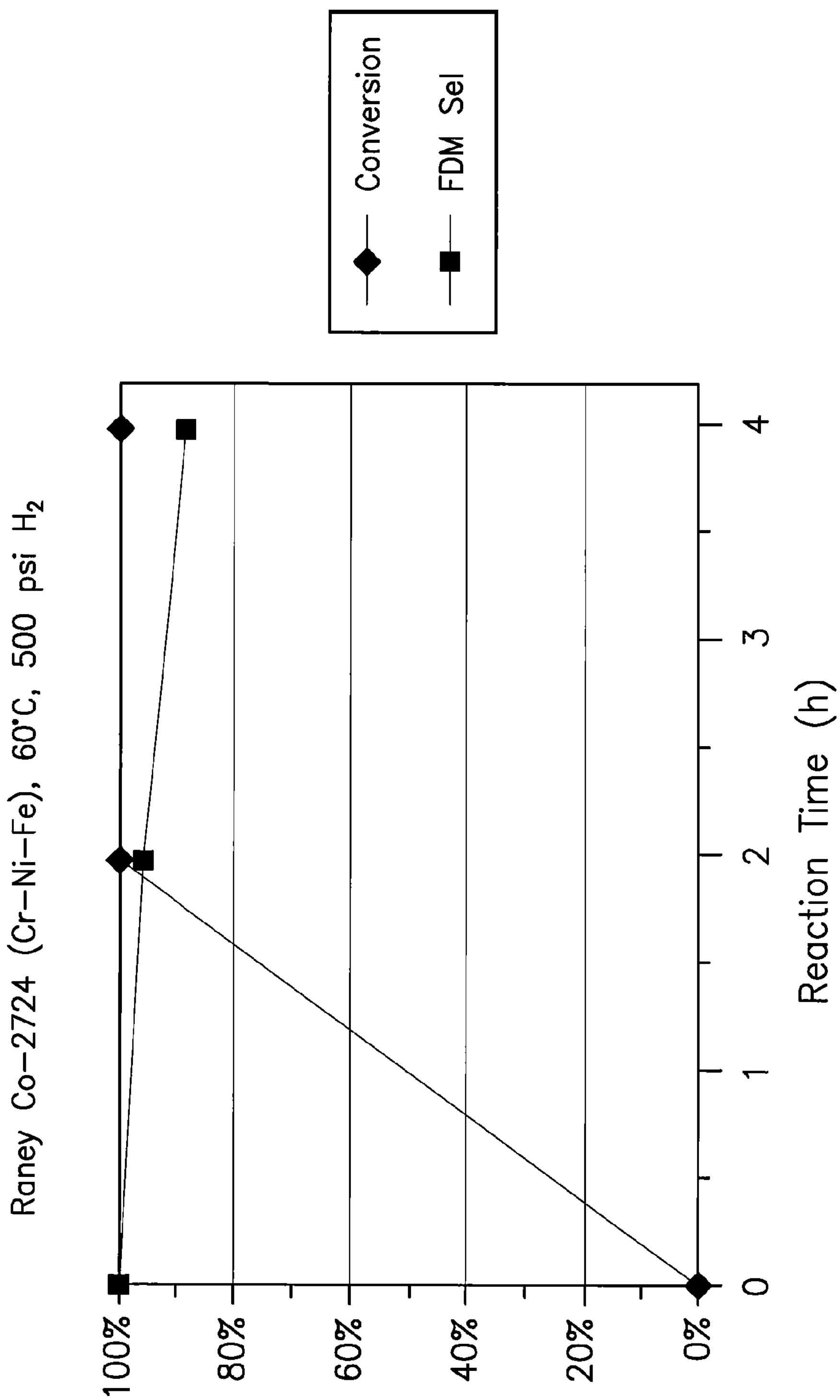

Raney Co-2724 (Cr-Ni-Fe), 60°C, 500 psi H2
Conversion
FDM Sel
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)

Fig 71

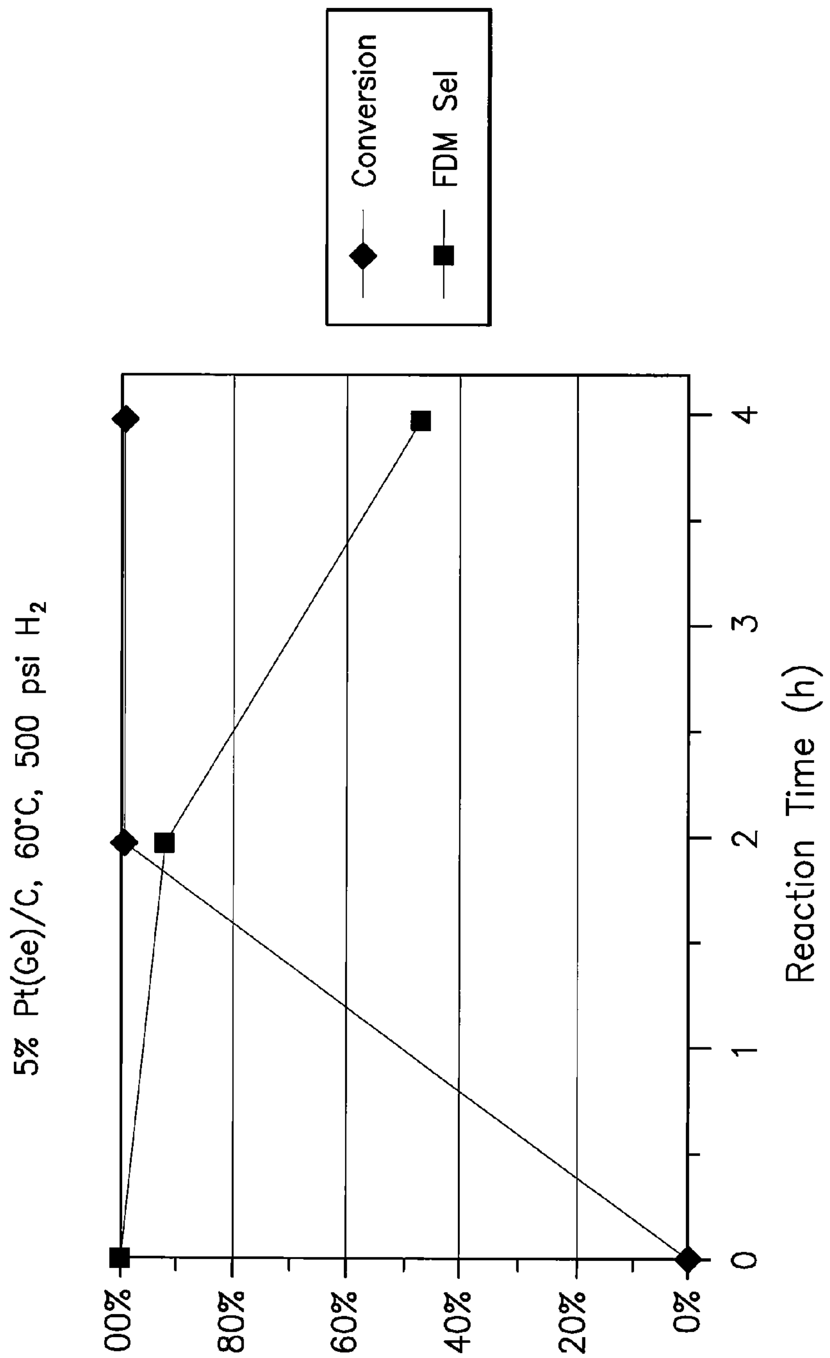

5% Pt(Ge)/C, 60°C, 500 psi H_2
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)
Conversion
FDM Sel

Fig. 72

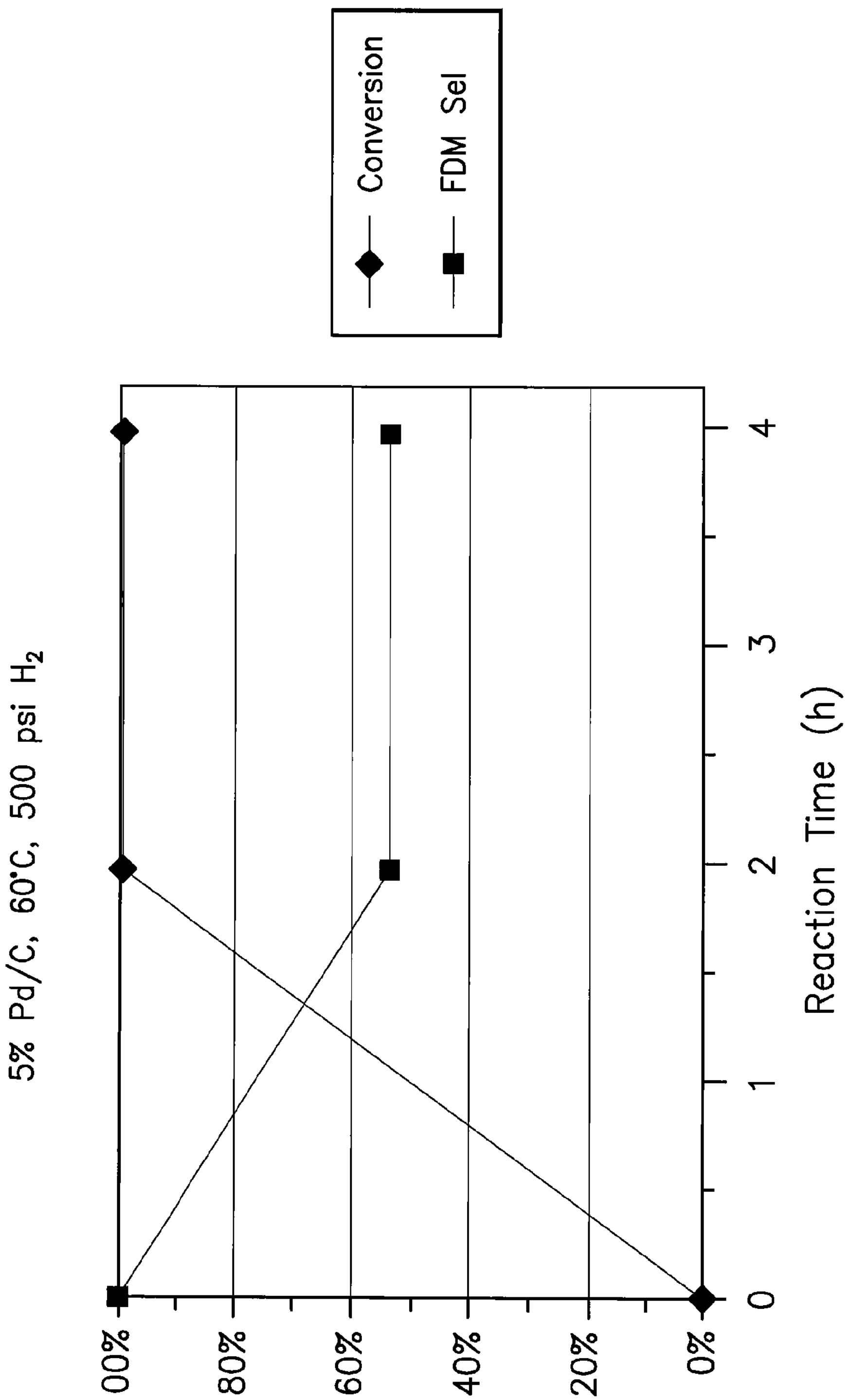

5% Pd/C, 60°C, 500 psi H2
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)
Conversion
FDM Sel

FIG. 73

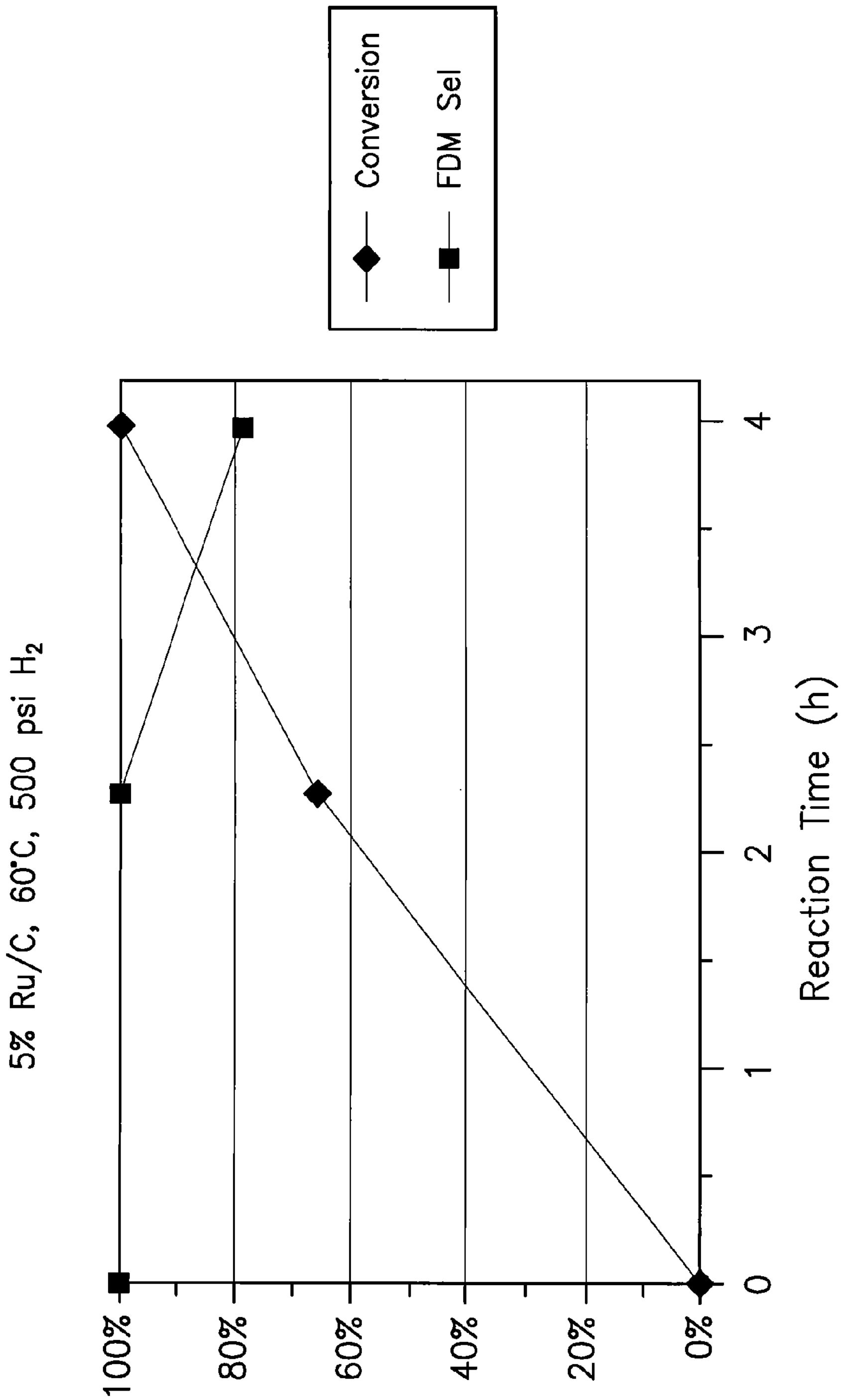

5% Ru/C, 60°C, 500 psi H_2
Conversion
FDM Sel
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)

FIG. 74

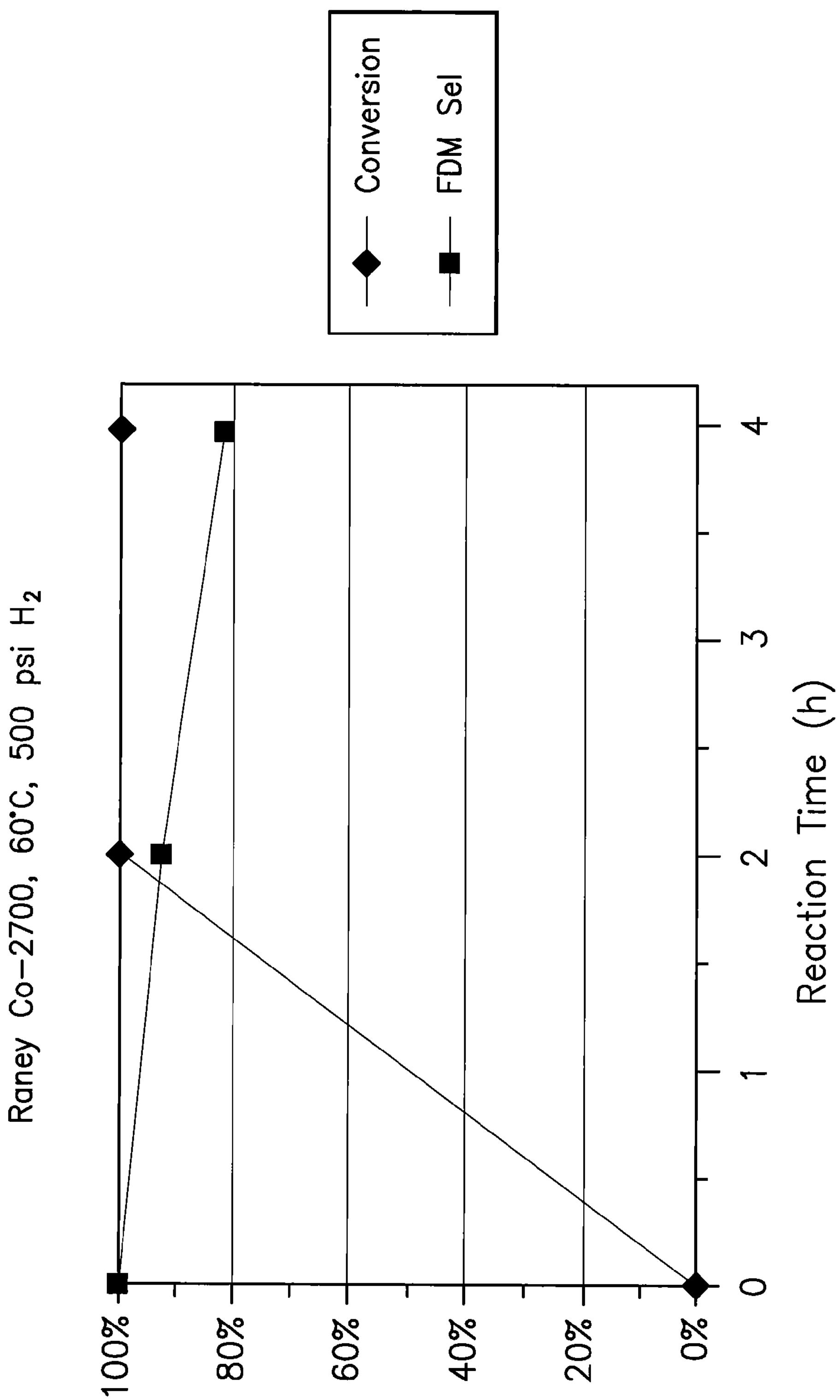

Raney Co-2700, 60°C, 500 psi H2
Conversion
FDM Sel
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)

Fig. 75

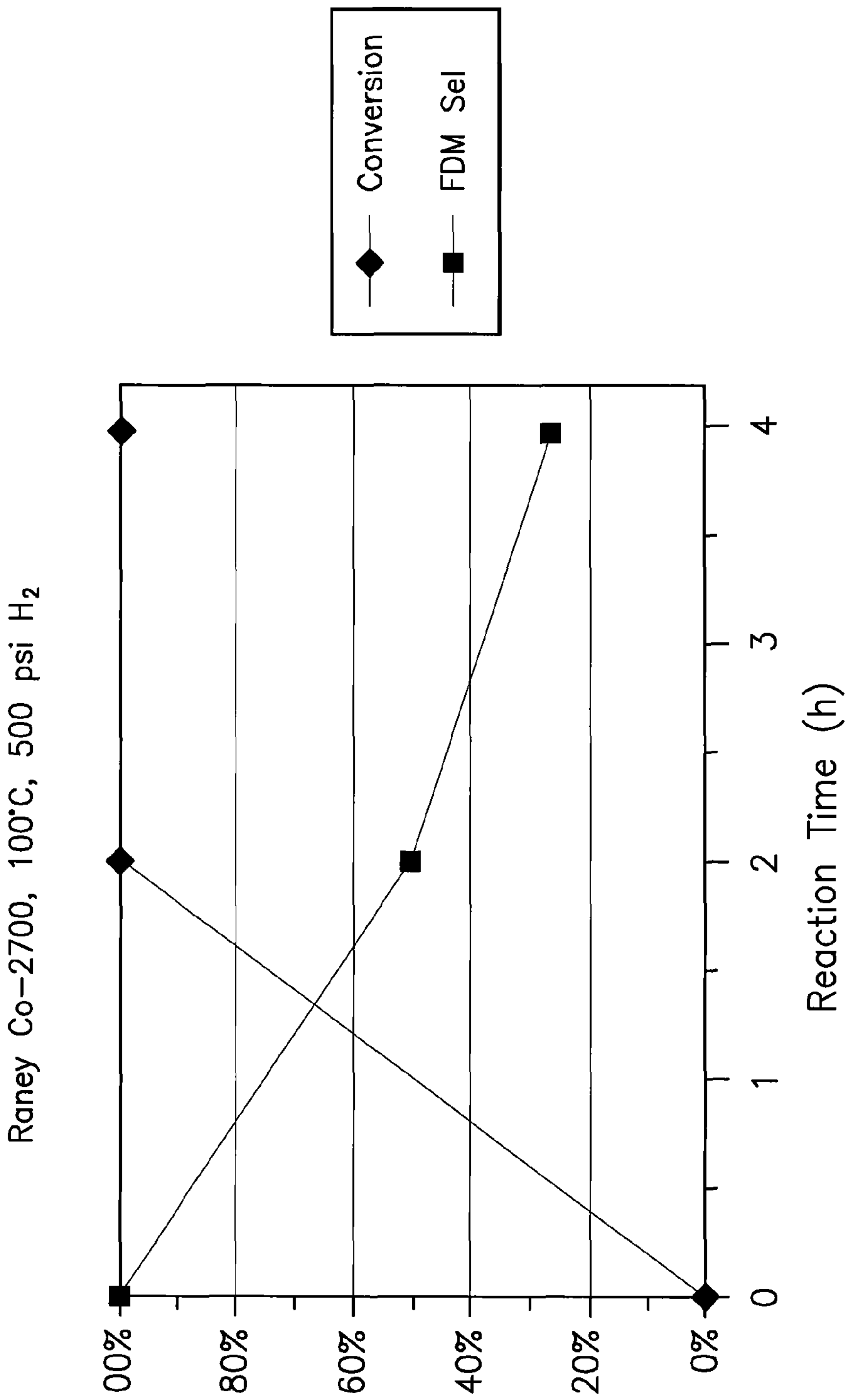

Raney Co−2700, 100°C, 500 psi H_2
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)
Conversion
FDM Sel

Fig. 76

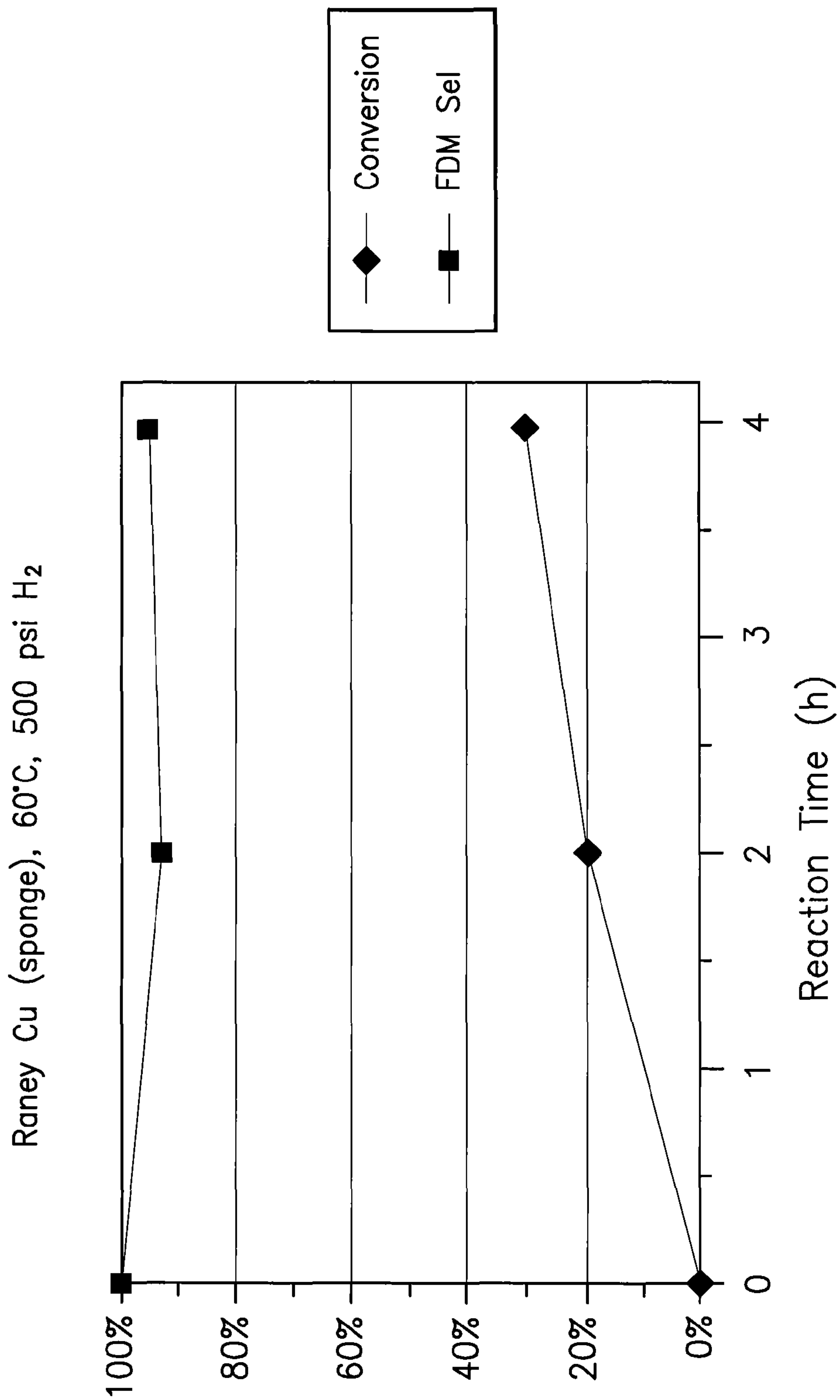

Raney Cu (sponge), 60°C, 500 psi H_2
Conversion
FDM Sel
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)

FIG. 77

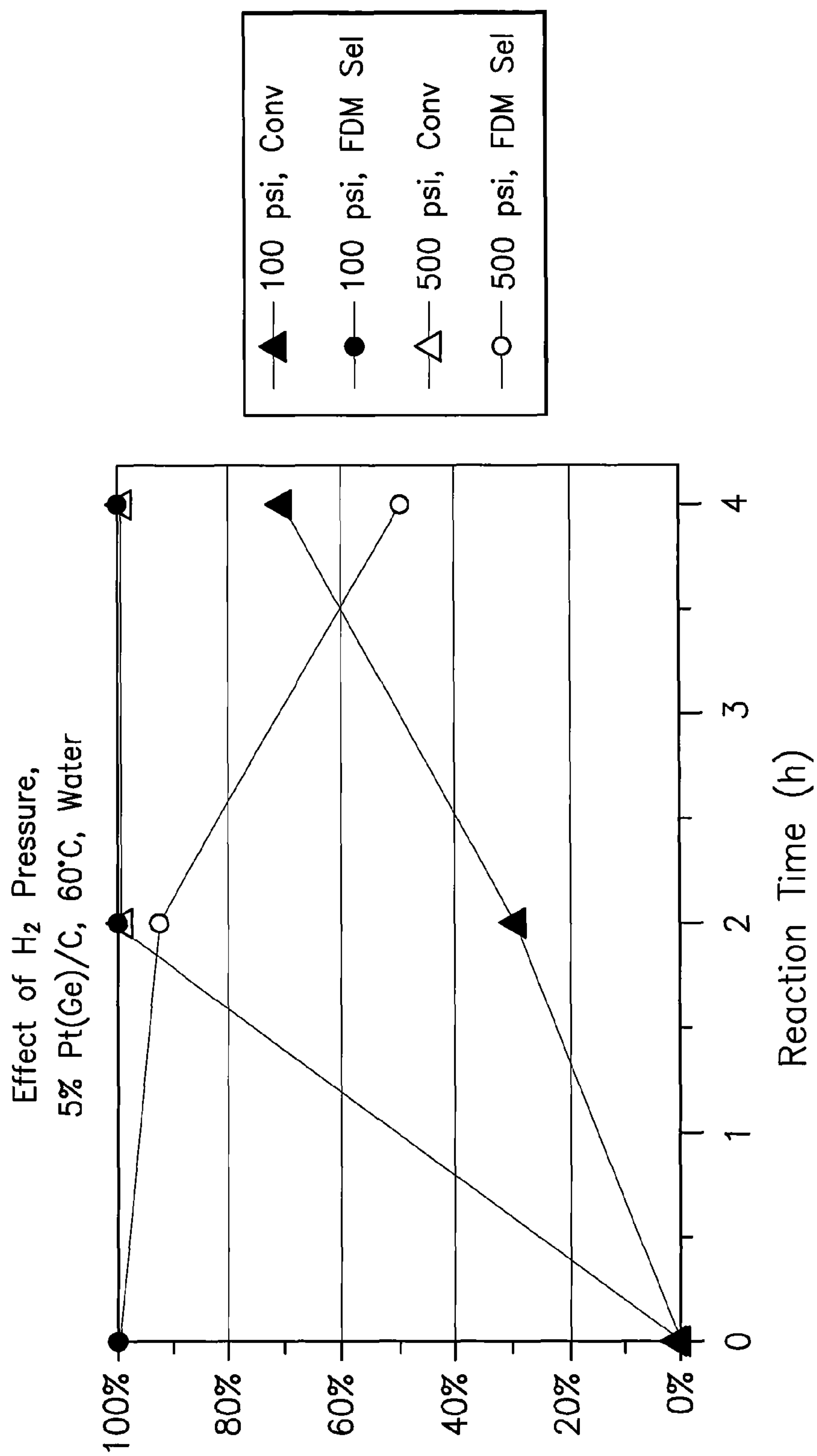

Effect of H_2 Pressure,
5% Pt(Ge)/C, 60°C, Water
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)
100 psi, Conv
100 psi, FDM Sel
500 psi, Conv
500 psi, FDM Sel

FIG. 78

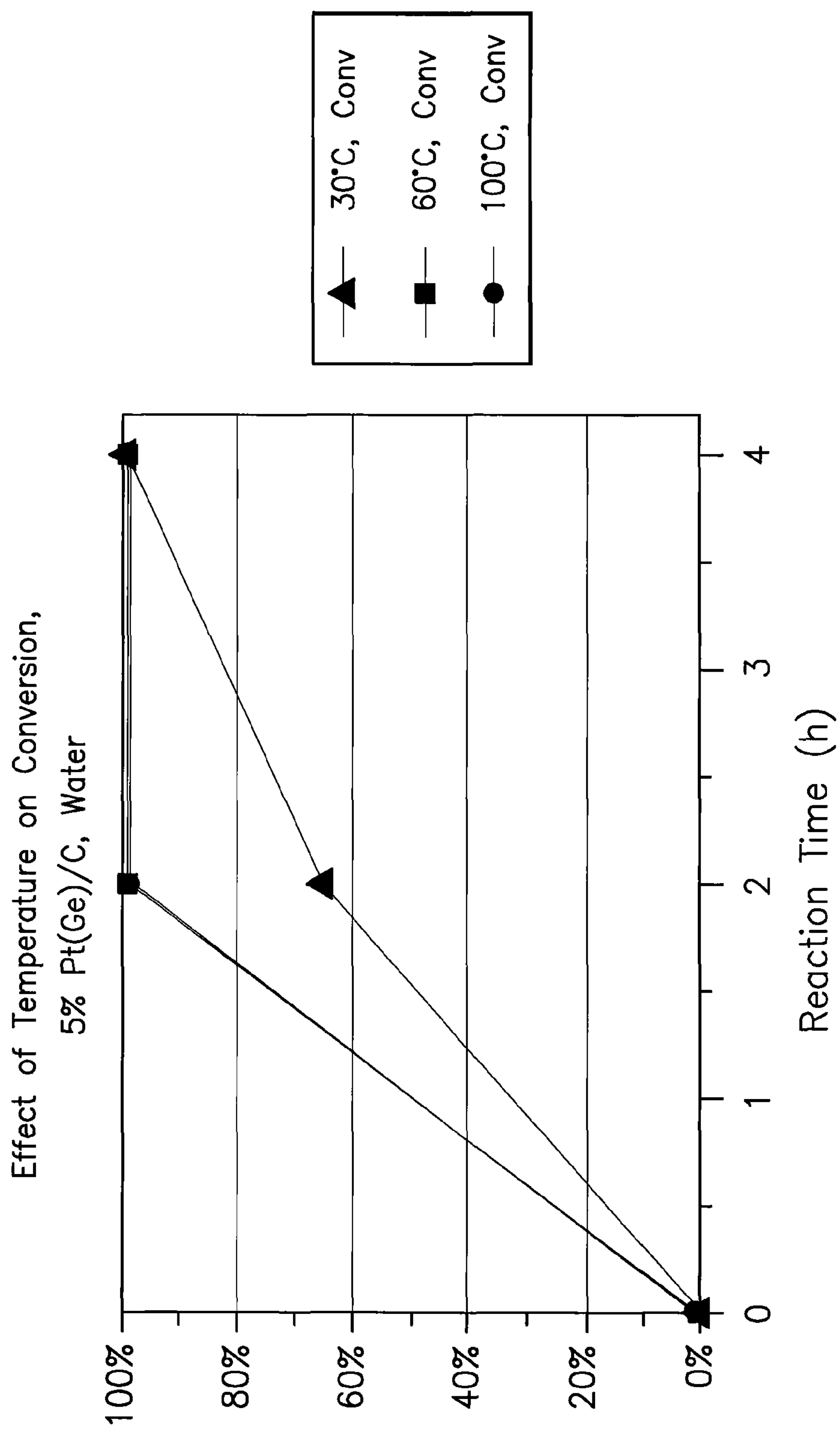

Effect of Temperature on Conversion,
5% Pt(Ge)/C, Water
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)
30°C, Conv
60°C, Conv
100°C, Conv

FIG. 79

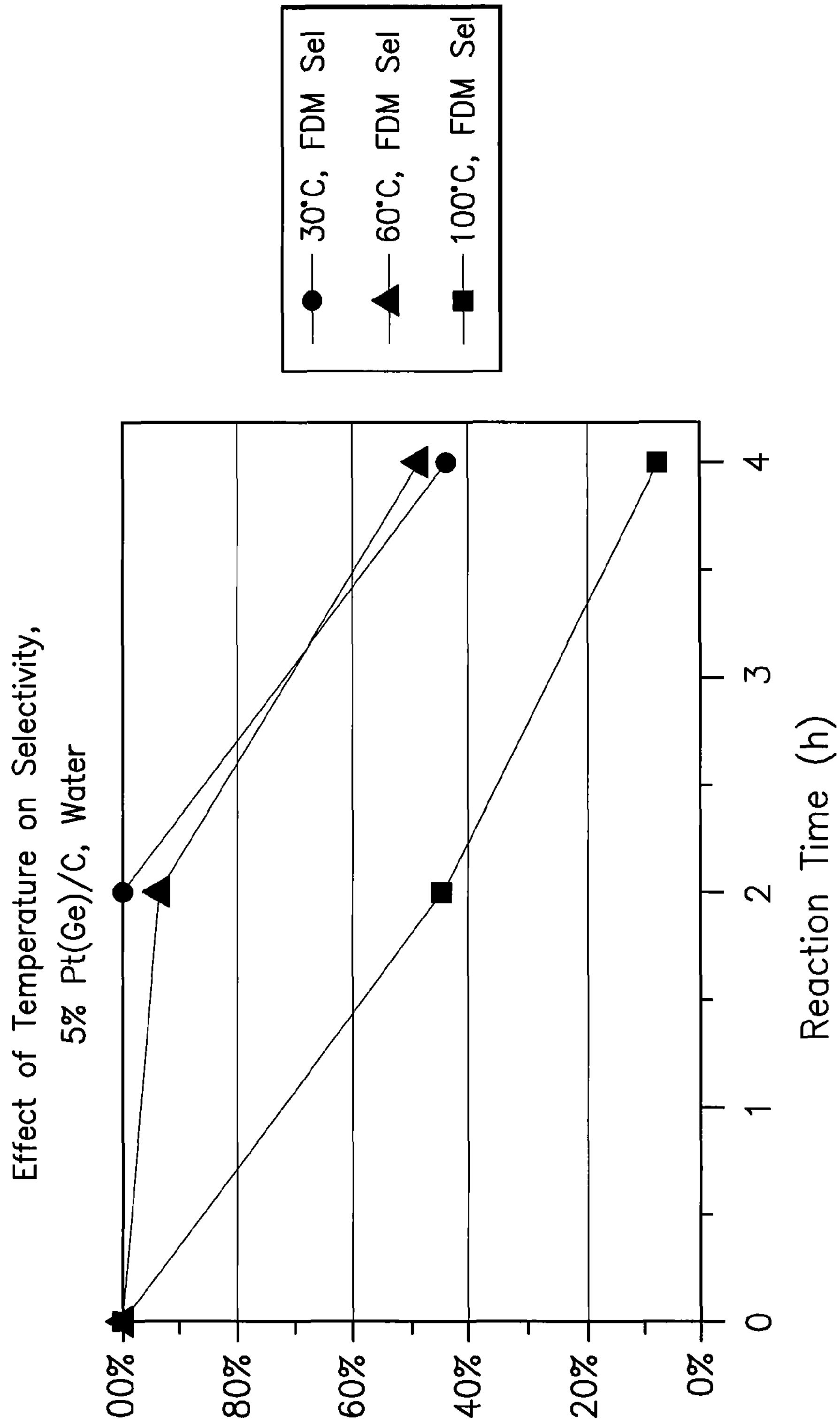

Effect of Temperature on Selectivity,
5% Pt(Ge)/C, Water
30°C, FDM Sel
60°C, FDM Sel
100°C, FDM Sel
100%
80%
60%
40%
20%
0%
0
1
2
3
4
Reaction Time (h)

FIG. 80

HYDROXYMETHYLFURFURAL REDUCTION METHODS AND METHODS OF PRODUCING FURANDIMETHANOL

RELATED PATENT DATA

This patent is a divisional of U.S. patent application Ser. No. 11/760,634 entitled Hydroxymethylfurfural Reduction Methods and Methods of Producing Furandimethanol which was filed Jun. 8, 2007 now U.S. Pat. No. 7,994,347 and claims priority under 35 U.S.C. §119 to U.S. Provisional Application No. 60/804,409, which was filed Jun. 9, 2006, the entirety of both of which are incorporated by reference herein.

TECHNICAL FIELD

The invention pertains to hydroxymethylfurfural reduction methods, methods of producing furandimethanol, and methods of producing tetrahydrofuran dimethanol.

BACKGROUND OF THE INVENTION

Hydroxymethylfurfural (HMF) is a compound which can be produced from various hexoses or hexose-comprising materials. HMF can in turn be converted into a variety of derivatives, many of which are currently or are quickly becoming commercially valuable. Of particular interest is a reduction product furandimethanol (FDM). Another reduction product of interest is tetrahydrofuran dimethanol (THF dimethanol, alternatively referred to as THF-diol or THFDM). FDM and THF dimethanol are useful in adhesives, sealants, composites, coatings, binders, foams, curatives, polymer materials, solvents, resins or as monomers, for example.

Conventional methodology for production of FDM and/or THF dimethanol from HMF typically results in low yields, and/or low selectivity and can therefore be cost prohibitive. Additionally, conventional methodology often utilizes one or more environmentally unfriendly compound or solvent, or utilizes harsh reaction conditions. Accordingly, it is desirable to develop alternative methods for production of FDM and/or THF dimethanol from HMF.

SUMMARY OF THE INVENTION

In one aspect the invention encompasses a method of reducing HMF where a starting material containing HMF in a solvent comprising water is provided into a reactor. H_2 is provided into a reactor and the starting material is contacted with a catalyst containing at least one metal selected from Ni, Co, Cu, Pd, Pt, Ru, Ir, Re and Rh. The contacting is conducted at a reactor temperature of less than or equal to 250° C.

In one aspect the invention encompasses a method of hydrogenating HMF. An aqueous solution containing HMF and fructose is provided into a reactor and H_2 is provided into the reactor. A hydrogenation catalyst is provided in the reactor. The HMF is selectively hydrogenated relative to the fructose at a temperature at or above about 30° C.

In one aspect the invention pertains to a method of producing tetrahydrofuran dimethanol (THFDM) A feed comprising HMF is provided into a reactor containing a first and a second catalyst. The feed is contacted with the first catalyst to produce furan dimethanol (FDM). The FDM is contacted with the second catalyst to produce THFDM.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

FIG. **1** shows conversion of HMF and selective production of furandimethanol and tetrahydrofuran diol (THF diol) as a function of time on stream (TOS) utilizing a continuous flow reactor with a cobalt supported on SiO_2 catalyst and a base set of parameters in accordance with one aspect of the invention.

FIG. **2** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at an increased liquid hourly space velocity (LHSV) relative to FIG. **1**.

FIG. **3** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at a decreased pressure relative to FIG. **1**.

FIG. **4** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at a decreased temperature relative to FIG. **1**.

FIG. **5** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at a decreased temperature relative to FIG. **1**.

FIG. **6** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at a decreased pressure relative to that of FIG. **1**.

FIG. **7** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at decreased pressure and temperature relative to that of FIG. **1**.

FIG. **8** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** and an increased HMF feed concentration relative to that of FIG. **1**.

FIG. **9** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at an increased HMF feed concentration and decreased pressure relative to that of FIG. **1**.

FIG. **10** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at an increased HMF feed concentration and a decreased pressure with increased temperature relative to that of FIG. **1**.

FIG. **11** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at an increased temperature relative to FIG. **1**.

FIG. **12** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **1** at an increased pressure relative to that of FIG. **1**.

FIG. **13** shows HMF conversion and product selectivity as a function of temperature utilizing the catalyst of FIG. **1**.

FIG. **14** shows HMF conversion and product selectivity as a function of pressure utilizing the catalyst of FIG. **1**.

FIG. **15** shows HMF conversion and product selectivity as a function of time on stream utilizing an 0.8% palladium supported on carbon catalyst in a continuous flow reactor utilizing a base set of reaction parameters in accordance with one aspect of the invention.

FIG. **16** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **15** at a decreased LHSV relative to FIG. **15**.

FIG. **17** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **15** at an increased temperature and decreased LHSV relative to FIG. **15**.

FIG. **18** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **15** at an increased pressure and decreased LHSV relative to FIG. **15**.

FIG. **19** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **15** at reduced pressure and increased temperature and decreased LHSV relative to FIG. **15**.

FIG. **20** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **15** at an increased temperature and decreased LHSV relative to FIG. **15**.

FIG. **21** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **15** at a decreased H_2 gas hourly space velocity (GHSV), increased temperature, and decreased LHSV relative to FIG. **15**.

FIG. **22** shows HMF conversion and product selectivity as a function of time on stream for a continuous flow reactor utilizing a Pt on SiO_2 support (in-house prep) catalyst and a base set of reaction parameters in accordance with one aspect of the invention.

FIG. **23** shows HMF conversion and product selectivity as a function of time on stream for a continuous flow reaction utilizing another Co/SiO_2 catalyst and a base set of reaction of parameters in accordance with another aspect of the invention.

FIG. **24** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **23** at a decreased pressure and decreased temperature relative to FIG. **23**.

FIG. **25** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **23** at a decreased pressure and decreased temperature with an increased HMF feed concentration relative to FIG. **23**.

FIG. **26** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** at an increased temperature relative to FIG. **23**.

FIG. **27** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** at the parameters used in FIG. **23**.

FIG. **28** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** utilizing an increased LHSV relative to FIG. **23**.

FIG. **29** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** utilizing an increased HMF feed concentration relative to FIG. **23**.

FIG. **30** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **23** and the parameters of FIG. **23** where the catalyst was pretreated by dry reduction at 150° C.

FIG. **31** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** after 150° C. dry reduction utilizing the parameters of FIG. **23**.

FIG. **32** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** reduced at 150° C. at a decreased LHSV.

FIG. **33** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** reduced at 150° C. at a decreased LHSV relative to FIG. **23**.

FIG. **34** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** reduced at 150° C. at an increased reactor temperature relative to FIG. **23**.

FIG. **35** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** reduced at 230° C.

FIG. **36** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** originally reduced at 230° C. utilizing a decreased LHSV relative to FIG. **23**.

FIG. **37** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** reduced at a temperature of 362° C.

FIG. **38** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **23** originally reduced at 362° C.

FIG. **39** shows HMF conversion and product selectivity as a function of time on stream utilizing a Cu—Cr catalyst and a base set of reaction parameters in accordance with another aspect of the invention.

FIG. **40** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **39** and an increased LHSV relative to FIG. **39**.

FIG. **41** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **39** at an increased HMF feed concentration relative to FIG. **39**.

FIG. **42** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **39** at an increased LHSV over a portion of the run and N_2 sparging.

FIG. **43** shows HMF conversion and product selectivity as a function of time on stream for a 5% Pt/Al_2O_3 catalyst reduced at 150° C. at a base set of reaction parameters with varied LHSV.

FIG. **44** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **43** originally reduced at 150° C. at a decreased LHSV relative to FIG. **43**.

FIG. **45** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **43** and a crude HMF feed.

FIG. **46** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **43** and a second crude HMF feed.

FIG. **47** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **43** and a third crude HMF feed.

FIG. **48** shows HMF conversion and product selectivity as a function of time on stream utilizing the catalyst of FIG. **43** at an increased reactor temperature relative to FIG. **43**.

FIG. **49** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **43** at an increased reactor temperature and at an increased LHSV relative to FIG. **43**.

FIG. **50** shows HMF conversion and product selectivity as a function of time on stream of the catalyst of FIG. **43** at an increased reactor temperature and increased LHSV relative to FIG. **43**.

FIG. **51** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **43** at an increased reactor temperature and at an increased LHSV relative to FIG. **43**.

FIG. **52** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **43** at an increased pressure and decreased LHSV relative to FIG. **43**.

FIG. **53** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **43** at an increased pressure, an increased temperature and at an increased LHSV relative to FIG. **43**.

FIG. **54** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **43** at an increased pressure, an increased temperature and at an increased LHSV relative to FIG. **43**.

FIG. **55** shows HMF conversion and product selectivity as a function of time on stream for the catalyst of FIG. **43** at a decreased pressure and decreased LHSV relative to FIG. **43**.

FIG. **56** shows HMF conversion and product selectivity as a function of temperature for the catalyst of FIG. **43**.

FIG. **57** shows HMF conversion and product selectivity as a function of time on stream utilizing a continuous flow reactor and a Co/SiO_2 catalyst at 120° C.

FIG. 58 shows FDM conversion and product selectivity as a function of time on stream for a continuous flow reactor utilizing a Ni/SiO_2 catalyst at 70° C.

FIG. 59 shows HMF conversion and product selectivity as a function of time on stream for a continuous flow reactor utilizing a Ni/SiO_2 catalyst at 70° C. at varied LHSV.

FIG. 60 shows a repeat of FDM conversion and product selectivity as a function of time on stream for a continuous flow reactor utilizing a Ni/SiO_2 catalyst at 70° C., after the run shown in FIG. 59.

FIG. 61 shows HMF conversion and product selectivity for a staged bed (segregated catalysts) continuous flow reactor utilizing Co/SiO_2 and Ni/SiO_2 catalysts.

FIG. 62 shows HMF conversion as a function of time on stream for a staged bed continuous flow reactor utilizing segregated Co/SiO_2 and Ni/SiO_2 catalysts and a base set of reaction conditions in accordance with one aspect of the invention.

FIG. 63 shows HMF conversion as a function of time on stream utilizing the system of FIG. 62 and increased temperatures relative to FIG. 62.

FIG. 64 shows HMF conversion as a function of time on stream utilizing the system of FIG. 62 and increased feed concentration and increased LHSV relative to FIG. 62.

FIG. 65 shows HMF conversion as a function of time on stream utilizing the system of FIG. 62 with increased feed concentration and decreased LHSV relative to FIG. 62.

FIG. 66 shows HMF conversion as a function of time on stream utilizing the system of FIG. 62 with increased temperatures and decreased LHSV relative to FIG. 62.

FIG. 67 shows HMF conversion as a function of time on stream utilizing the system of FIG. 62 with increased temperature and decreased LHSV relative to FIG. 62.

FIG. 68 shows tetrahyrofuran dimethanol (THFDM) conversion as a function of time on stream utilizing the system of FIG. 62 and increased temperature with decreased LHSV relative to FIG. 62.

FIG. 69 shows THFDM conversion as a function of time on stream utilizing the system of FIG. 62 and increased temperature with decreased LHSV relative to FIG. 62.

FIG. 70 shows HMF or FDM conversion as a function of time on stream utilizing the system of FIG. 62 and increased temperature with decreased LHSV relative to FIG. 62.

FIG. 71 shows HMF conversion and product selectivity as a function of reaction time for a batch reaction utilizing RANEY® cobalt (Cr—Ni—Fe).

FIG. 72 shows HMF conversion and product selectivity as a function of reaction time for a batch reactor utilizing 5% Pt (Ge)/C catalyst.

FIG. 73 shows HMF conversion and product selectivity as a function of reaction time for a batch reactor utilizing a 5% Pd/C catalyst.

FIG. 74 shows HMF conversion and product selectivity as a function of reaction time for a batch reactor utilizing a 5% Ru/C catalyst.

FIG. 75 shows HMF conversion and product selectivity as a function of reaction time for a batch reactor utilizing a RANEY® cobalt catalyst at 60° C.

FIG. 76 shows HMF conversion and product selectivity as a function of reaction time for the catalyst of FIG. 75 at an increased temperature relative to FIG. 75.

FIG. 77 shows HMF conversion and product selectivity as a function of reaction time for a batch reactor utilizing a RANEY® copper sponge catalyst.

FIG. 78 shows HMF conversion and product selectivity as a function of reaction time at two different reactor pressures for a batch reactor utilizing 5% Pt (Ge)/C catalyst.

FIG. 79 shows HMF conversion as a function of reaction time at three different temperatures utilizing a 5% Pt (Ge)/C catalyst.

FIG. 80 shows FDM product selectivity as a function of reaction time at three different temperatures utilizing the 5% Pt (Ge)/C catalyst of FIG. 79.

The following acronyms are used: FDM=Furan-2,5-dimethanol; GHSV=Gas hourly space velocity; 12HD=1,2-hexanediol; HMF=5-Hydroxymethyl-2-furaldehyde; HMFCA=5-Hydroxymethyl-2-furancarboxylic acid; LHSV=Liquid hourly space velocity; THFA=Tetrahydrofurfuryl alcohol; THF-diol=Tetrahydrofuran-2,5-dimethanol (THFDM); THFDM=Tetrahydrofuran-2,5-dimethanol (THF-diol); 1,2,6-THH=1,2,6-trihydroxyhexane; 1,2,6-Triol=1,2,6-trihydroxyhexane; TOS=Time on Stream

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

In general, the methodology of the invention encompasses production of furandimethanol (FDM), production of tetrahydrofuran dimethanol (THF dimethanol), or both. More specifically, selective reduction of the aldehyde group on HMF, or both aldehyde groups on alternative starting material diformyl furan (DFF), can be conducted to selectively produce FDM. In particular instances, THF dimethanol is produced as a byproduct. Alternatively, reaction parameters and/or the reaction catalyst can be altered to increase production of, or to selectively produce THF dimethanol. The reaction methodology involves providing HMF or DFF in aqueous solution or within an aqueous mixture. However, the invention contemplates conducting reduction reactions in the presence of one or more organic solvents. In general, the reaction mixture is exposed to a catalyst in accordance with the invention which promotes a reduction of the aldehyde group, and in particular instances the carbon-carbon double bond(s), in water solvent and under relatively mild reaction conditions as compared to conventional methodology. It is to be understood that the invention additionally includes use of alternative starting compounds for reduction utilizing methodology in accordance with the invention, such as HMF derivatives with similarly reducible groups including but not limited to formyl, acid, ester or amide groups.

For aqueous reactions, the relatively mild reaction conditions of reduction methodology in accordance with the invention typically comprise a reaction temperature of less than or equal to 250° C., and in particular instances the reaction temperature will be less than or equal to 100° C. The reduction reaction is performed in the presence of H_2. Typically the H_2 pressure will be at least 1 atm (14.7 psi) and less than or equal to 1400 psi, more typically between 200-500 psi. Although not limited to a particular pH, the HMF reduction is typically conducted at a pH of about neutral.

For methodology of the invention that utilize fixed-bed continuous flow operation, additional parameters such as liquid and gas flow rates, and feed concentration can be adjusted and in some aspects can affect overall yield.

In one aspect, catalysts of the present invention can comprise at least one of the catalyst metals selected from the group consisting of Pd, Pt, Ru, Rh, Ni, Ir, Cu, Re and Co. In particular instances, catalysts comprising Pd, Pt, Co, Rh, Ir, Cu and/or Ni, can be combination catalysts which additionally include one or more metals selected from the group consisting of Ca, Cr, Mn, Re, Fe, Ru, Rh, Ir, Ni, Pd, Pt, Ag, Au, In, Ge, Cu, Sn, S, Cd, Ga, Al, Mo, Zn and Bi. In particular embodiments, the catalyst can preferably comprise both In and Ir. In alternative aspects, a Cu-chromite catalyst can be preferred.

Where catalysts comprising these metals or combinations of metals are utilized for HMF/HMF-derivative reduction, the catalyst metal can typically be supported by one or more support materials. Such support materials can be, for example, carbon support materials including but not limited to activated carbon support materials, and various inorganic supports such as metal oxide support materials including but not limited to Zr-oxides, Ti-oxides, Al-oxides, Si-oxides, etc. Various exemplary catalysts of the type described above which were utilized for conducting reduction methodology in accordance with the invention are set forth in Tables 1 and 2. Table 1 presents commercially available catalysts while Table 2 presents catalysts prepared in-house for use in the reduction reactions. It is to be understood that the listed catalysts are exemplary and are not intended to limit the scope of the invention.

TABLE 1

Exemplary commercially available catalysts for HMF reduction

Catalyst Composition	Manufacturer	Lot No/Sample ID
5% Pd, 0.5% Cu/C	Engelhard	787A-15-409-1
10%/Pd/C	Degussa	CC1-2155
5% Pd, 1% Sn/C	Engelhard	SOC 98186
5% Pd, 0.15% Fe/C	Engelhard	787A-8-157-1
5% Pd, 0.5% Fe/C	Engelhard	787A-15-417-1
5% Pd/C	Engelhard	39658
5% Pd, 5% Re/C	Engelhard	6758-17-03
5% Pd, 5% Re/C	Engelhard	6555-38-1
5% Pt(Ge)/C	Engelhard	43932
5% Pt(S)/C	Engelhard	787A-15-321-1
1.5% Pt, 0.15% Cu/C	Engelhard	787A-8-153-1
1.5% Pt, 0.15% Sn/C	Engelhard	787A-8-152-1
1.5% Pt, 0.15% Bi/C	Engelhard	787A-8-151-1
1.5% Pt, 0.15% Ru/C	Engelhard	787A-8-150-1
3% Pt/Al_2O_3	Engelhard	6849-14-1
3% Pt/C	Engelhard	43931
Escat 288	Engelhard	324230
5% Ru/C	AlfaAesar	C10J23
2.5% Ru/C	Engelhard	6818-13-2
5% Ru/ZrO_2	Engelhard	712A-4-294-1
5% Ru/C	Johnson Matthey	072183
3% Ru/TiO_2 (rutile)	Degussa	H7709x/o
3% Ru/TiO_2	Degussa	CC4-251A
5% Rh/C	Heraeus	K-0319
5% Rh/C	Engelhard	43671
Ni powder	Mallinckrodt	S-96-674
2.5% Ni, 2.5% Re/C	Engelhard	6757-43-2
4% Ni, 4% Re/C	Engelhard	6818-15-3
Cu/Cr	SudChemie	G-22/2
Cu/Cr/Mn	United Catalyst (SudChemie)	G-89, 4171-S
Cu-chromite	Engelhard	S-02-245
1.5% Pt, 0.15% Cu on C	Engelhard	787a-8-153-1
10% Re on Al_2O_3	Davicat	Al2301
10% Re on Al_2O_3	Davicat	Al2400
0.5% Pd on C	Degussa	E181
5% Rh on C	Degussa	G106
5% Ru on ZrO_2	Engelhard	Ru on ZrO_2
0.7% Ru on C	Engelhard	47038
5% Pd, 1% Sn on C	Engelhard	5% Pd 1% Sn
2.5% Ni, 2.5% Re on C	Engelhard	6757-43-2
5% Pd, 5% Re on C	Engelhard	6758-17-02
2.5% Co, 2.5% Re on C	Engelhard	6818-15-1
2% Ni, 2.5% Re on C	Engelhard	6818-20-4
Supported 40% Co	Engelhard	Co-0124
Supported 40% Co	Engelhard	Co-0138
Supported 40% Co	Engelhard	Co-0164

TABLE 1-continued

Exemplary commercially available catalysts for HMF reduction

Catalyst Composition	Manufacturer	Lot No/Sample ID
40% Co on SiO_2	Engelhard	Co-0179
Supported 50% Ni	Engelhard	Ni-3210 T
Supported 50% Ni	Engelhard	Ni-3288 E
Supported Cu	Engelhard	Cu-1186 t 1/8 lot #60"
0.8% Pd on C	Engelhard	Escat 132
0.5% Pd on C	Engelhard	Escat 138
0.5% Pt on C	Engelhard	Escat 238
5% Pt on C	Engelhard	Escat 288
Supported Cu	Sud Chemie	G-132 1/16 ext."
Supported Cu	Girdler	G-9 CuMn tab.
Supported Cu	Harshaw	Cu-2501 G4-6
5% Rh on C	Engelhard	Italiana 43664
Supported Cu	Katalco	ICI MeOH cat. CuZnAl
55% Ni on SiO_2	Sud Chemie	C46-7-03 RS
40% Co on SiO_2 + ZrO_2	Sud Chemie	G62aExt
40% Co on SiO_2	Sud Chemie	G62aRS
40% Co on SiO_2 + ZrO_2	Sud Chemie	G67aRS Ext
Supported 50% Ni	Sud Chemie	G69bRS
Supported Cu	Sud Chemie	G-99b-13 EF tab.
Supported Cu	Sud Chemie	T-4489 rs 3 × 3 tab
40% Co on SiO_2	United Catalysts	G62RS
Supported Cu	United Catalysts	G-89 CuCrMn
Supported Cu	United Catalysts	T-4489 CuAl
Raney ® 2700-Co	W.R. Grace & Co	Lot# 7865
Raney ® 2724-Co	W.R. Grace & Co	Lot# 8318
Raney ® Cu sponge	Strem Chemicals	Lot# 141625-S
Raney ® Ni catalyst	Activated Metals	A-5200

TABLE 2

Reduction catalysts prepared in-house.

Catalyst Composition	Catalyst Composition
5% Co on SiO_2	5.1% Ir on SiO_2
20% Co on SiO_2	2.6% Ir, 0.3% Ca on SiO_2
5% Co, 1% Ag on SiO_2	2.6% Ir, 0.7% Cd on SiO_2
20% Co, 4% Ag on SiO_2	2.6% Ir, 0.5% Ga on SiO_2
5% Co, 1.8% Au on SiO_2	2.6% Ir, 0.8% In on SiO_2
20% Co, 7.2% Au on SiO_2	2.6% Ir, 0.8% Sn on SiO_2
5% Co, 0.4% Ca on SiO_2	7% Ni, 0.5% Fe on C
20% Co, 1.6% Ca on SiO_2	Supported 20% Ni, 10% Mo
5% Co, 0.6% Cu on SiO_2	1% Pd on TiO_2 (rutile)
20% Co, 2.4% Cu on SiO_2	1.4% Pd on SiO_2
5% Co, 0.3% Fe on SiO_2	1.4% Pd, 0.3% Ca on SiO_2
20% Co, 1.2% Fe on SiO_2	1.4% Pd, 0.7% Cd on SiO_2
5% Co, 0.9% Ir on SiO_2	Pd, Fe on C
20% Co, 3.5% Ir on SiO_2	1.4% Pd, 0.5% Ga on SiO_2
5% Co, 0.3% Mn on SiO_2	1.4% Pd, 0.8% In on SiO_2
20% Co, 1.2% Mn on SiO_2	1.4% Pd, 0.8% Sn on SiO_2
5% Co, 0.3% Ni on SiO_2	Pt on C
20% Co, 1.2% Ni on SiO_2	2.6% Pt on SiO_2
5% Co, 0.5% Pd on SiO_2	5% Pt on SiO_2
20% Co, 2% Pd on SiO_2	5% Pt on Al_2O_3
5% Co, 0.9% Pt on SiO_2	2.6% Pt, 0.3% Ca on SiO_2
20% Co, 3.5% Pt on SiO_2	2.6% Pt, 0.7% Cd on SiO_2
5% Co, 0.5% Rh on SiO_2	2.6% Pt, 0.5% Ga on SiO_2
20% Co, 2% Rh on SiO_2	2.6% Pt, 0.8% In on SiO_2
0.65% Ir on SiO_2	2.6% Pt, 0.8% Sn on SiO_2
1.3% Ir on SiO_2	1.4% Rh on SiO_2
2.6% Ir on SiO_2	1.4% Rh, 0.8% In on SiO_2
5.1% Ir on SiO_2	1.4% Rh, 0.8% Sn on SiO_2

For preparation of the catalysts presented in Table 2, support material was manually weighed into a vial, impregnated with the first metal solution and allowed to dry in air at ambient pressure overnight. Where a second metal was utilized, a second metal solution was then added. Optionally, the vial could be exposed to a flow of air (100 mL/min) and heated to 400° C. for 4 h with a ramp of about 5° C./min. The vial was then placed in a catalyst reduction reactor and reduced at 250-300° C. with a ramp of 1-2° C./min and held for 2-4 h under a flow of H_2 (100 mL/min). After reduction, the catalyst reduction reactor was sealed under an N_2 environment and moved to a glovebox where the catalyst could be loaded into the conversion reactor.

Each of the catalysts listed in Tables 1 and 2 was tested batch-wise under mild conditions (typical conditions: 500 psi H_2 and 60° C. for a reaction time of 1 hour) and/or in a fixed-bed continuous flow reactor. Of the listed catalysts tested batch-wise, Co, Pd, Ir and Pt catalysts resulted in the highest yields of FDM. Test reactions were also conducted batch wise at temperatures as low as 30° C. and showed good conversion of HMF. The batch testing additionally included experiments conducted as low as 100 psi H_2, also showing good conversion. Selectivity of HMF to FDM is often highest upon just reaching approximately 100% conversion of HMF, with continued reaction times sometimes resulting in over-reduction.

Reactions were also performed utilizing various of the catalysts presented in the Tables in fixed-bed reactor systems. Such studies suggest that, of the catalysts tested, Pd, Pt, Co and Cu—Cr catalysts can be preferred for FDM production under the conditions utilized.

In addition to the catalysts described above, reaction methodology of the invention can alternatively be conducted utilizing RANEY® type metals such as RANEY® nickel, RANEY® cobalt or RANEY® copper.

With respect to the RANEY® type metals, RANEY® cobalt appears to be both highly active and selective for FDM production from HMF. RANEY® Ni is also able to catalyze reduction of HMF to FDM under the reaction conditions of the present invention. RANEY® copper also shows ability to produce FDM under the mild reaction conditions, however such metal is less reactive and gives a different product distribution than was observed for RANEY® cobalt or RANEY® Ni catalyzed reductions.

Example 1

Selective Reduction of HMF Utilizing Pd/C

To 10 mL of water in a small pressure autoclave (45 mL total volume) was added 0.2289 g of dry Pd/C catalyst (commercially available 0.8% Pd on carbon). A magnetic stir bar was added and the vessel was sealed. The reactor was purged with N_2 and was pressure tested for leaks at 500 psi. After confirming an absence of leaks, the vessel was vented, the line was removed and 0.4513 g of HMF dissolved in 5 mL of water was added utilizing a small syringe and needle through the 1/16 inch fitting on the head of the vessel.

The vessel was then purged with N_2, purged with H_2 and pressurized to 500 psi H_2. The reaction vessel was isolated from the H_2 feed line by a valve downstream from the pressure gauge. The reactor was brought to a reaction temperature of 60° C. in less than 5 minutes. After 2 hours reaction time (measured from the point of reaching 60° C.) the pressure within the vessel was determined to be 330 psi. The vessel was then vented and purged with N_2 and the gas line removed to allow sampling of vessel contents. Approximately 1 mL of sample was removed utilizing an approximately 5 inch needle, and the sample was filtered utilizing a 0.2 micron syringe filter. The gas line was then reconnected and the vessel purged with N_2 followed by H_2 and was re-pressurized to 500 psi H_2.

Sampling was repeated after 4 hours and the reaction was stopped after removing the 4 hour sample. Each of the 2 hour and 4 hour samples was diluted by 50% and was analyzed by liquid chromatography (LC). The results showed that by 2 hours the HMF conversion was 100% with 51% selectivity to FDM due to over-reduction (as apparent by the presence of THF dimethanol).

Example 2

Reduction of HMF Utilizing RANEY® Metals

Reduction reactions were performed utilizing RANEY® cobalt, RANEY® copper and RANEY® nickel in independent reactions. The reduction reactions were performed at 60° C. and 500 psi H_2 for at least 2 hours. The experiment conducted utilizing RANEY® cobalt resulted in a 100% HMF conversion with 97% selectivity for FDM upon reacting for 2 hours. As indicated above, RANEY® copper was less reactive and resulted in a different product distribution.

Example 3

Reduction of HMF with Production of THF Dimethanol

A commercially available nickel powder catalyst (Mallinckrodt Specialty Chemical Company, Calsicat, S-96-674, #69F-093A, E-473P L, 12/6/96) was utilized. The catalyst was received and stored under water.

1 mL of catalyst slurry was placed in a glass liner and 9 mL of water added. A magnetic stir bar was added and the liner sealed in a 45 mL autoclave. The autoclave was purged and pressure/leak tested to 500 psi with hydrogen. The autoclave was vented and 0.45 grams of HMF dissolved in 5 mL of water was added. The reactor was purged again, and pressurized to 500 psi with hydrogen. The desired temperature of 60° C. was achieved upon heating for approximately 5 minutes and was maintained for 2 hours at which time the first sample was removed and analyzed by LC. HMF conversion was 99% with selectivity to FDM of 84%. Over reduction of FDM to THF dimethanol occurred with a selectivity to THF dimethanol of 10%.

After 4 hours at 60° C. a second sample was removed and analyzed. Conversion of HMF was 100% with more over reduction, selectivity to FDM dropped to 77% and selectivity to THF dimethanol increased to 17%. At 4 hours the temperature was increased to 100° C. and pressure increased to 950 psi hydrogen. After 3 hours of additional reaction under these conditions, FDM selectivity had dropped to 3% and THF dimethanol selectivity increased to 95%.

In fixed-bed continuous flow experiments using the same or similar catalysts and reaction conditions described above, alternative parameters such as gas and liquid flow rates, and feed concentrations were also independently varied to study the effect of such variations on conversion, yield and selectivity. A first set of studies was performed utilizing cobalt metal on SiO_2 support material with varying parameters including temperature, H_2 pressure, feed concentration, and flow rate parameters. The results of such studies are presented in a series of graphs set forth in FIGS. **1-14**.

Similar studies were performed utilizing a palladium metal on carbon support catalyst. For both the palladium and the cobalt catalyst studies, a fixed-bed reactor was utilized to allow sample flow rate to be studied. The results of independent variants of flow rate, reaction temperature, and pressure for the Pd/C catalyst studies are presented in FIGS. **15-21**. Tables 3 and 4 show the effect of pressure at 70° C. and 100° C. respectively utilizing the Pd/C catalyst.

TABLE 3

Pressure Effect (T = 70° C., data taken at TOS = 60 minutes)	P = 500 psig	P = 800 psig
HMFConv, wt %	57.29	51.71
FDM Sel, wt %	88.36	84.07
THF Diol Sel, wt %	3.78	5.68
Sel to Others, wt %	7.86	10.25

TABLE 4

Pressure Effect (T = 100° C., data taken at TOS = 60 minutes)	P = 200 psig	P = 500 psig
HMFConv, wt %	72.68	95.32
FDM Sel, wt %	91.19	87.93
THF Diol Sel, wt %	1.28	4.79
Sel to Others, wt %	7.53	7.28

Additional flow reactor studies were conducted utilizing alternative catalysts. Presented herewith are results of flow reactor studies conducted utilizing Pt/SiO_2 (FIG. **22**), an alternative Co/SiO_2 catalyst (FIGS. **23**-**38**), a copper-chromite catalyst (FIGS. **39**-**42**), or Pt/Al_2O_3 (FIGS. **43**-**56**). The enclosed sets of results for the alternative Co/SiO_2 catalyst, Cu-chromite, and Pt/Al_2O_3 include effects on conversion and product selectivity of varied reaction parameters including gas and liquid flow rates, HMF feed concentration, H_2 pressure, and/or temperature. Table 5 shows the effect of pretreatment temperature for the alternative Co/SiO_2 catalyst (Engelhard Co-0179). Table 6 shows the effect of pressure for continuous flow reaction utilizing the Pt/Al_2O_3 catalyst.

TABLE 5

Effect of Catalyst Pretreatment Temperature			
Condition #	1	13	9
Reaction Temp, ° C.	362	230	150
Con Conv, %	99.9	66.9	84.3
FDM Sel	68.7	93.2	88.3
THF Diol Sel	29.5	1.0	4.0
Others Sel	1.7	5.8	7.7

TABLE 6

Effect of Pressure (5% Pt/Al_2O_3)	70° C., LHSV = 15 h^{-1}		140° C., LHSV = 30 h^{-1}		
	P = 500 psig	P = 1000 psig	P = 500 psig	P = 1000 psig	P = 1400 psig
HMF Conv, wt %	91.63	93.68	96.21	96.66	98.46
Sel to FDM, wt %	95.10	96.06	94.22	93.33	92.82
Sel to THF Diol	0.49	0.10	0.53	0.73	1.14
Sel to Others	4.41	3.84	5.25	5.93	6.04

Example 4

Reduction of HMF with Production of FDM in a Fixed-Bed Continuous Flow Reactor

A tubular reactor made of ⅜ inch stainless-steel thick-wall tubing (0.065 inch wall thickness) was utilized. 2 mL (1.11 g) of dry Pt/Al_2O_3 catalyst (prepared with 5% Pt on 40-80 mesh alumina support) was reduced before testing at 150° C. at atmospheric pressure with a hydrogen flow of 20 mL/minute. The reactor was then cooled to 40° C. and water was introduced at a flow rate of 0.5 mL/min with a high pressure liquid pump.

The hydrogen gas flow was increased to approximately 120 mL/minute until the system pressure increased to 500 psig, at which time the hydrogen flow rate was decreased to 14 mL/minute. The temperature operating set point of the system was increased to 70° C. and upon achieving 70° C., a 1% feed solution of HMF (optionally purged with nitrogen) was fed to the catalyst bed at a rate of 0.5 mL/minute. At 20 minute reaction time intervals (measured from the time feed was started) liquid samples of the product exiting the reactor were collected for LC analysis. LC results for each sample taken showed 100% conversion of HMF and 95% selectivity to FDM.

After 1 hour and 40 minutes of testing the liquid feed rate of the 1% HMF solution was decreased to 0.3 mL/minute. Sampling and analysis was repeated at 20 minute intervals for an additional 1 hour and 40 min. The results indicate no observed over-reduction at this lower liquid flow rate (as apparent by the absence of THF dimethanol) and that HMF conversion remained at 100% with 95% selectivity to FDM.

As can be observed in the forgoing figures, under certain conditions products other than FDM can be selectively produced from HMF with particular catalysts. Further studies sere conducted to selectively produce non-FDM products utilizing HMF, FDM or tetrahydrofuran dimethanol (THFDM, THF diol) starting material.

The Co-179 catalyst in a continuous flow reactor at 70° C. resulted in high selectivity (>95%) to FDM (see FIGS. **28**, **29** and **36**), with only moderate selectivities to THFDM when the temperature is raised to 120° C. Referring to FIG. **57**, at about 100% HMF conversion at 120° C. a THFDM selectivity of about 70% was achieved. Reduction to THFDM was incomplete and significant by-products were observed at the higher temperature.

Referring to FIG. **58**, Ni/SiO_2 reduced FDM nearly quantitatively to THFDM at 70° C. However, under identical conditions utilizing HMF (FIG. **59**), only 80% HMF conversion was obtained and selectivity to THFDM was about 40%. When the feed was switched again to FDM, only about 20% FDM conversion was observed (FIG. **60**), indicating that HMF poisons the Ni catalyst.

A staged bed (segregated catalysts in the same bed) containing ⅓ cobalt catalyst and ⅔ nickel catalyst was tested for production of THFDM from HMF. The HMF feed first passed through the Co catalyst which primarily reduced the HMF to FDM, then through the Ni catalyst which primarily reduced the FDM to THFDM. Very high HMF conversion and selectivity to THFDM was obtained as shown in FIG. **61**. The Ni catalyst appeared to remain active for THFDM production when HMF was reduced first to FDM with the Co catalyst. HMF feed concentrations of 1%, 3%, and 6%, were tested, all giving similar conversions and selectivities.

Additional experiments were conducted utilizing the staged Co/Ni catalysts at high temperatures with either HMF or FDM feeds to examine polyol production (FIGS. **62**-**70**). Temperatures as high as 180° C. were evaluated. The major product was 1,2,6-hexanetriol but yields decreased with increased temperatures with production of may unknown products. One major by-product was identified as 2,5-hexanediol. When the feed was THFDM however, almost no ring-opening occurred. THFDM was quite stable up to 200° C. Ring-opened polyols therefore likely are formed via HMF or FDM, not via THFDM. FIGS. **62**-**70** show the results obtained under a variety of temperatures, feed (FDM vs. HMF) feed concentration and space velocity.

A batch-wise experiment was conducted to study the effect of organic solvent on the catalytic hydrogenation of HMF to FDM utilizing two different catalysts. Selectivity toward FDM production was compared for reactions conducted in ethanol and reactions conducted in water. As shown in Table 7, conversion and selectivity toward FDM are lower in ethanol than in water under the same reaction conditions and reaction times.

TABLE 7

Effect of Organic Solvent on HMF Reduction

		60° C. 500 psi H_2			100° C. 950 psi H_2		
		Time	Conversion	Selectivity	Time	Conversion	Selectivity
Co/SiO_2	H_2O	4 hr	100%	96%	1 hr	98%	83%
	EtOH	4 hr	1%	16%	1 hr	2%	49%
Pt/Al_2O_3	H_2O	2 hr	94%	98%	1 hr	89%	96%
	EtOH	2 hr	82%	98%	1 hr	53%	96%

The impact of various impurities on the hydrogenation of HMF was investigated in both batch-wise and flow reactor studies. Impurities included fructose, ethyl acetate, dimethylacetamide, methyl t-butyl ether, methyl iso-butyl ketone, levulinic acid, formic acid, acetic acid, sodium sulfate, and N-methyl pyrrolidinone. These impurities were found to be non-detrimental to HMF conversion within the accuracy of the experiments.

Of particular interest were the results with fructose impurity in batch experiments conducted between 60 and 100° C. and 500 psi for at least 2 h. Both Pt(Ge)/C (Engelhard #43932) and Co/SiO_2 (Sud Chemie G62aRS) catalysts converted HMF to reduced products without reducing fructose to sorbitol or mannitol, even at high HMF conversions. FDM can be formed in high yield. In the absence of HMF, fructose is easily reduced under these reaction conditions, suggesting that HMF either inhibits fructose reduction or is reduced at a faster rate. These results indicate that highly selective reduction of HMF is possible with the HMF precursor fructose present in the feed and that fructose need not be separated from the HMF solution prior to reduction.

Example 5

Reduction of HMF in the Presence of Fructose

Batch-wise experiments were conducted with an aqueous solution of 15 wt % each of HMF and fructose under 500 psi H_2 between 75 and 100° C. using Ge-promoted 5% Pt on carbon (Engelhard #43932) for at least 2 h. In a sample taken at 1 h, LC and ^{13}C NMR analysis showed that HMF was converted to FDM with good selectivity but that essentially no fructose was converted to sorbitol or mannitol even at high HMF conversion. Only trace amounts of levulinic and formic acids were formed.

FIGS. **71**-**80** show the results of a number of batchwise HMF conversion reactions utilizing RANEY® Co-2724 (FIG. **71**); 5% Pt(Ge)/C (FIG. **72**); 5% Pd/C (FIG. **73**); 5% Ru/C (FIG. **74**); RANEY® Co-2700 (FIGS. **75**-**76**); and RANEY® Cu (FIG. **77**) catalysts. The effect of H_2 pressure was investigated utilizing a 5% Pt(Ge)/C catalyst as shown in FIG. **78**. FIG. **79** shows the effect of temperature on HMF conversion using the Pt(Ge)/C catalyst, and FIG. **80** shows the effect of temperature on FDM selectivity for the Pt(Ge)/C catalyst.

Reaction methods of the invention for selective reduction of HMF to produce FDM and/or THF dimethanol have many advantages relative to conventional technologies. The reaction temperature of the inventive methodology is relatively low, thereby reducing unwanted side reactions and decomposition of reactants and/or products, and allowing increased selectivity. The hydrogen pressure is also low resulting in reduced operating costs. Since the solvent utilized is water rather than an organic solvent, the methodology is relatively less expensive and more environmentally friendly than many conventional processes. The reaction rates obtained through the methodology of the invention are high, allowing highly efficient continuous flow reactors to be utilized.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

The invention claimed is:

1. A method of producing tetrahydrofuran dimethanol (THFDM), comprising:

providing a continuous flow reactor having a first catalyst and a second catalyst, the first catalyst comprising one or both of Ni and/or Co; and the second catalyst comprising one or both of Ni and/or Co;

providing a feed comprising hydroxymethyl furfural (HMF) into the reactor;

contacting the feed with the first catalyst to produce furan dimethanol (FDM); and

contacting the FDM with the second catalyst to produce THFDM.

2. The method of claim **1** wherein the feed comprises from about 1% to about 6% HMF.

3. The method of claim **1** wherein the THFDM is the majority product.

4. The method of claim **1** wherein the first catalyst comprises Co.

5. The method of claim **1** wherein the composition of the first catalyst is different than the composition of the second catalyst.

6. The method of claim **1** wherein the first catalyst comprises Co and the second catalyst comprises Ni.

7. The method of claim **1** wherein the second catalyst comprises Ni.

8. The method of claim **1** wherein either one or both of the first and second catalyst are maintained at a temperature below 250° C. during the contacting.

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