FIGURE 9

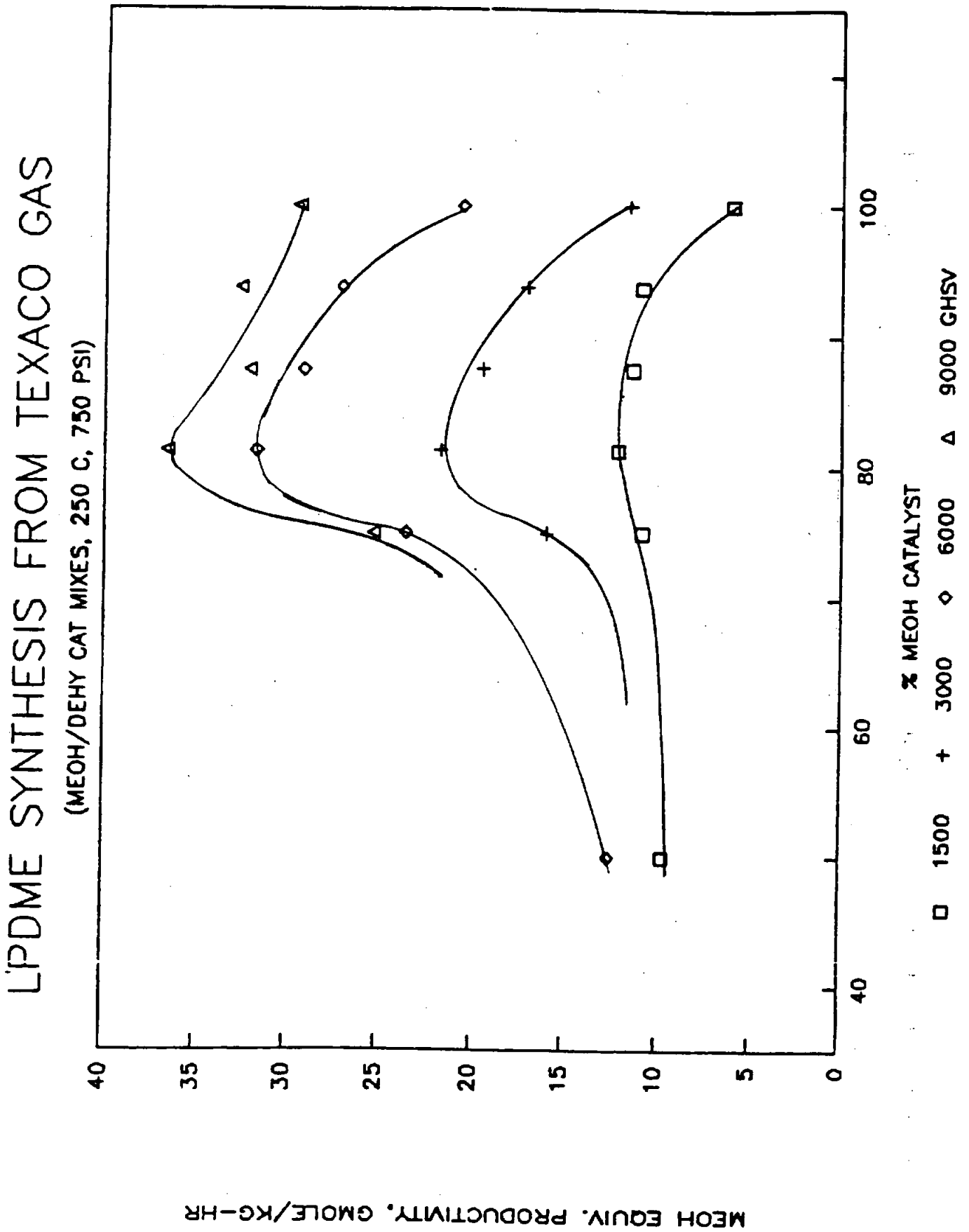

LPDME SYNTHESIS FROM TEXACO GAS
(MEOH/DEHY CAT MIXES, 250 C, 750 PSI)
MEOH EQUIV. PRODUCTIVITY, GMOLE/KG-HR
0
5
10
15
20
25
30
35
40
40
60
80
100
% MEOH CATALYST
□ 1500 + 3000 ◇ 6000 △ 9000 GHSV

FIGURE 10

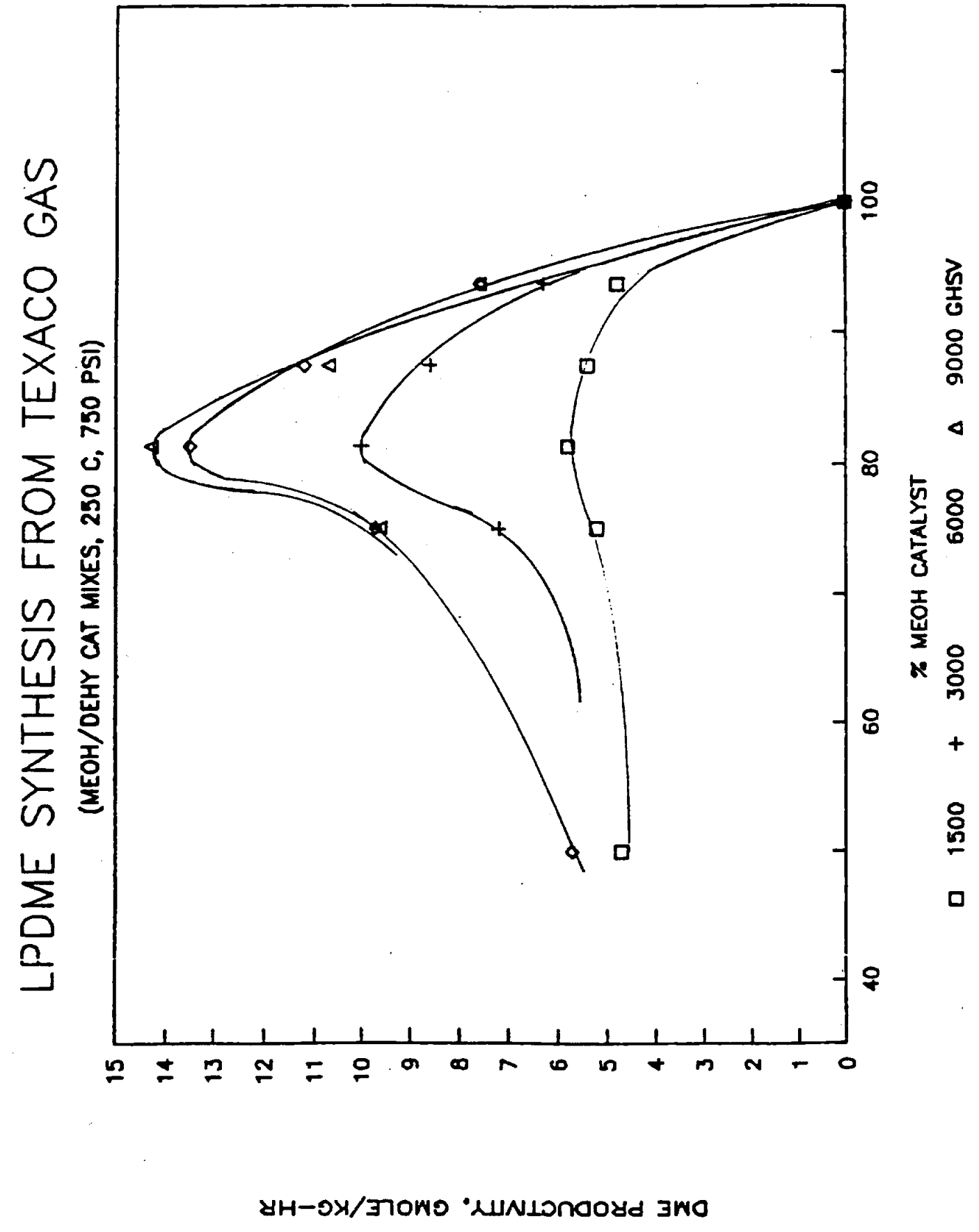

LPDME SYNTHESIS FROM TEXACO GAS
(MEOH/DEHY CAT MIXES, 250 C, 750 PSI)
DME PRODUCTIVITY, GMOLE/KG-HR
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
40
60
80
100
% MEOH CATALYST
□ 1500 + 3000 6000 Δ 9000 GHSV

FIGURE 11

LPDME SYNTHESIS FROM TEXACO GAS

(MEOH/DEHY CAT MIXES, 250 C, 750 PSI)

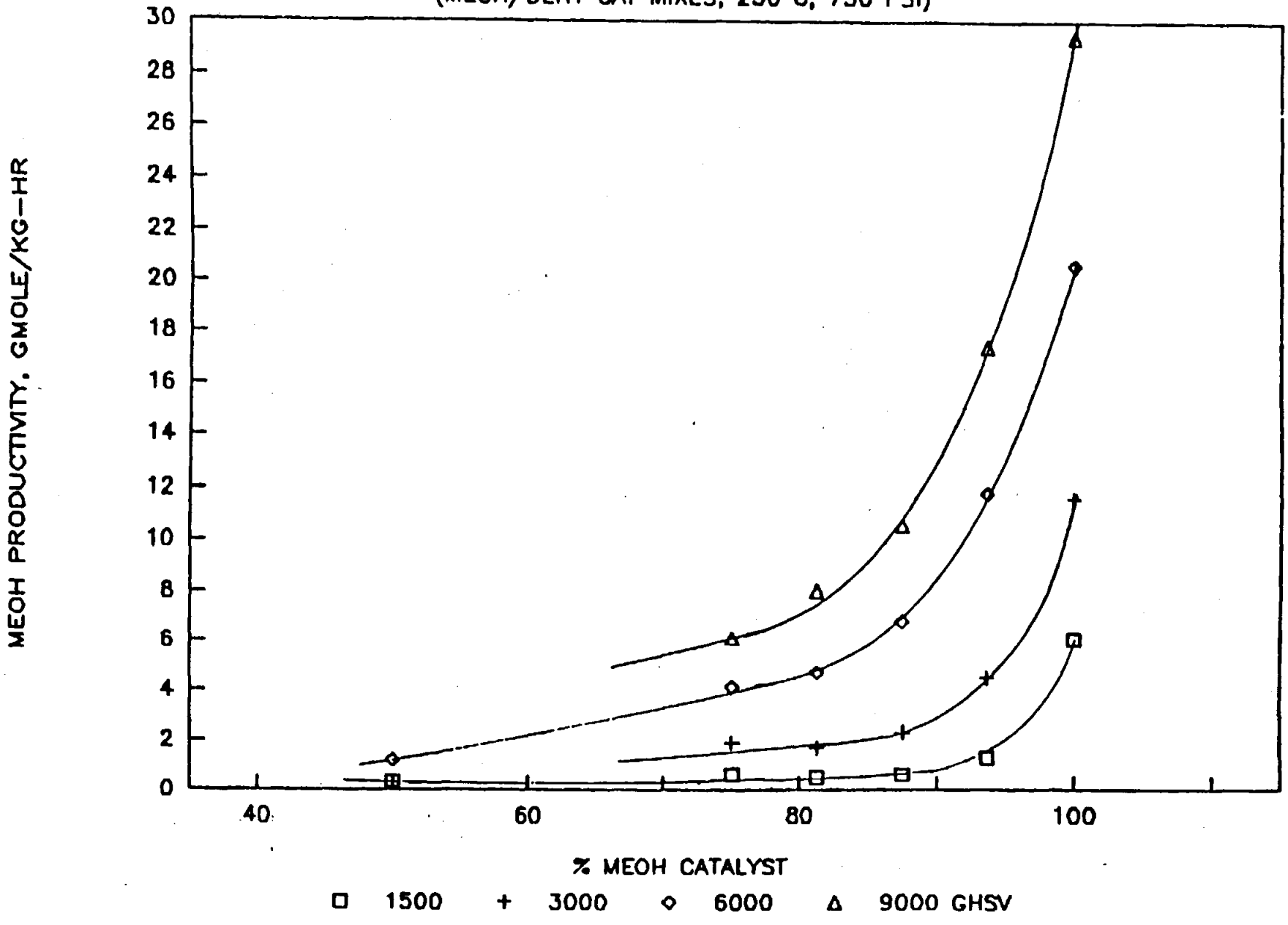


FIGURE 12

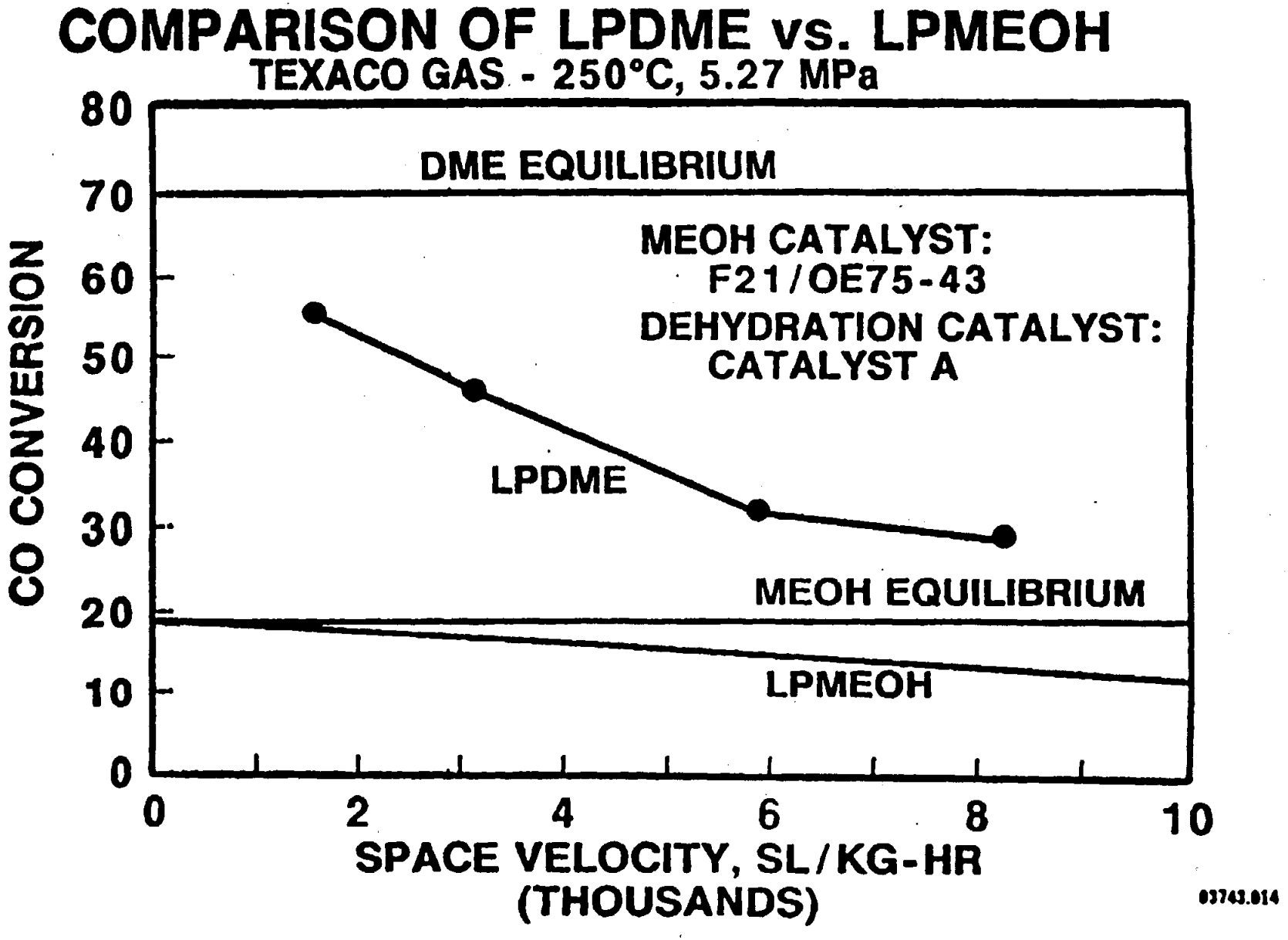
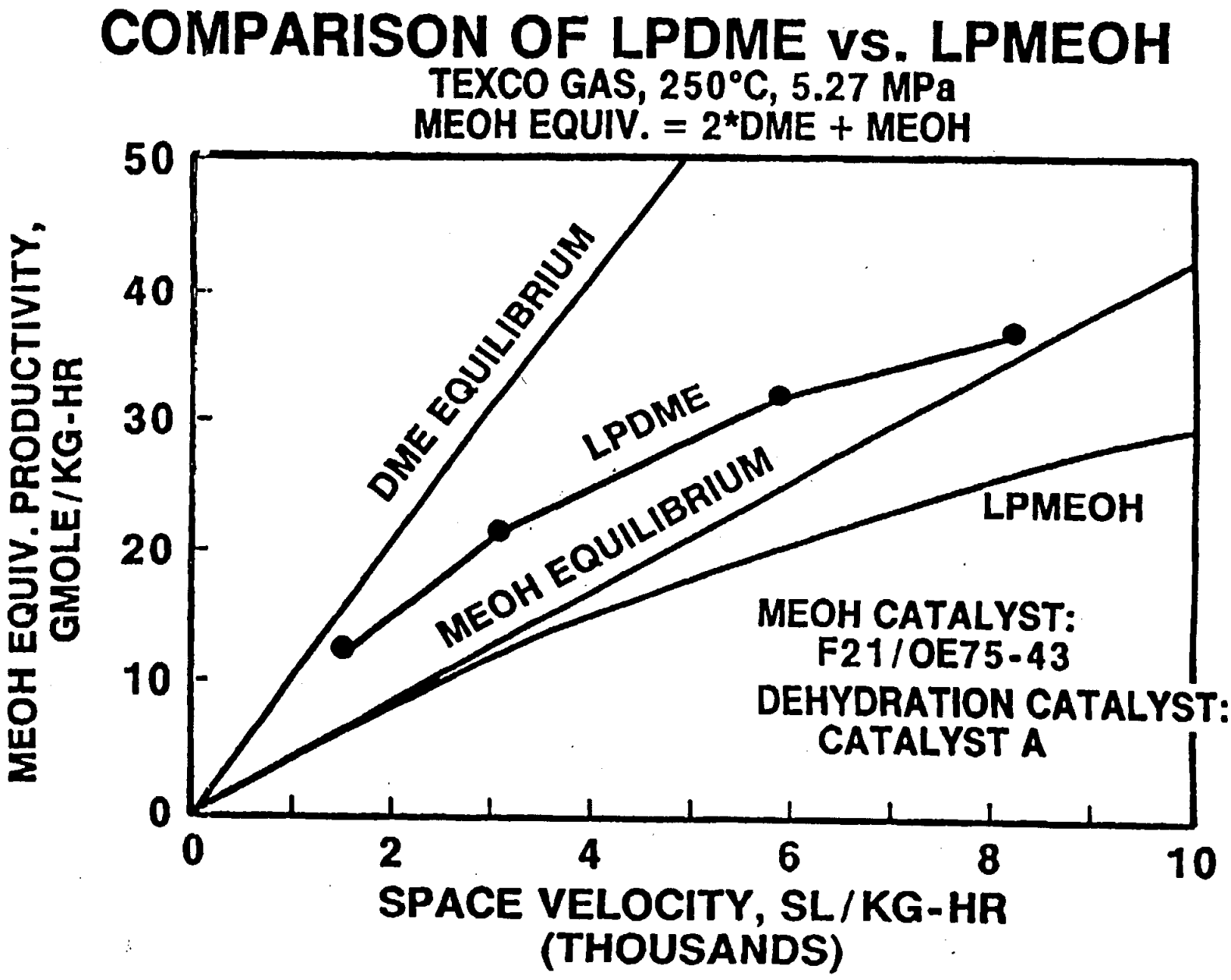

COMPARISON OF LPDME vs. LPMEOH
TEXACO GAS - 250°C, 5.27 MPa
CO CONVERSION
80
70
60
50
40
30
20
10
0
DME EQUILIBRIUM
MEOH CATALYST:
F21/OE75-43
DEHYDRATION CATALYST:
CATALYST A
LPDME
MEOH EQUILIBRIUM
LPMEOH
0
2
4
6
8
10
SPACE VELOCITY, SL/KG-HR
(THOUSANDS)
03743.014

FIGURE 13



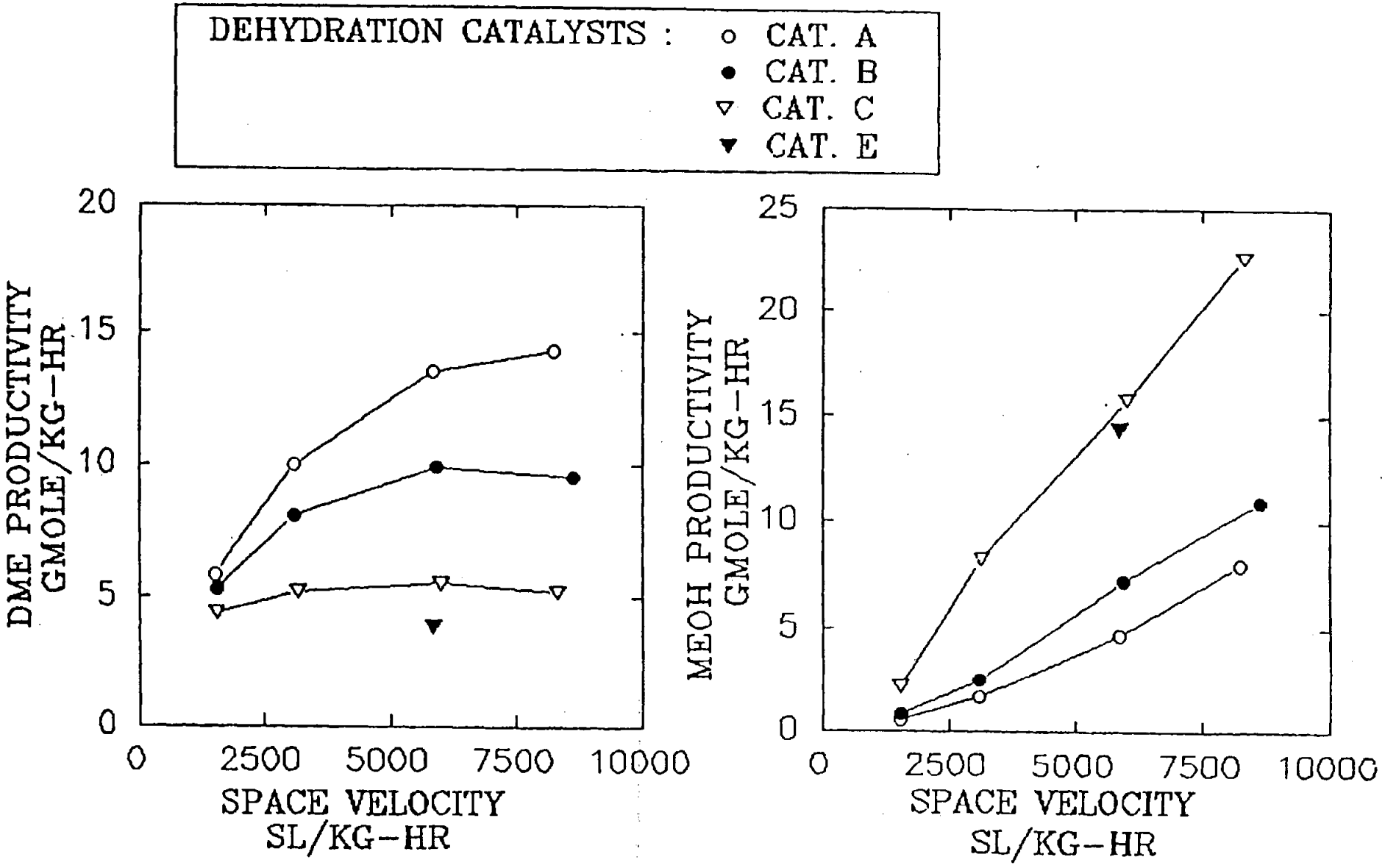
0743.015

FIGURE 14

EFFECT OF DIFFERENT DEHYDRATION CATALYSTS

(TEXACO GAS, 250°C, 5.27 MPA)

METHANOL CATALYST : F21/0E75-43



A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

Properties of various dehydration catalysts are summarized in Table 2. Surface areas range from 200 to 250 m^2/g. Catalyst B has more than twice the pore volume of Catalyst A. Acidity measurements indicate higher acidity (ammonia capacity) for Catalyst C compared to Catalyst A. None of the above properties explain significantly higher activity of Catalyst A compared to the rest of the catalysts. One important feature of Catalyst A is that is contains very few impurities. For example, it contains only 0.004% Na_2O and 0.005% Fe_2O_3 compared to 0.03% Na_2O and 0.04% Fe_2O_3 in Catalyst E. It can be speculated that the purest gamma alumina is best suited for methanol dehydration.

TABLE 2
Properties of Various Dehydration Catalysts

Catalyst	Catalyst #	BET Surface Area, m^2/g	Total Pore Vol, cc/g	Avg. Pore dia, Å	Acidity Capacity Gain in NH_3, wt%	Acidity Strength NH_3 Peak temp, °C
Catapal Gamma Lab-500	Catalyst A 136J144-1 (500)	223	0.41	94		
Catapal Gamma Lab-550	Catalyst A 136J144-1 (550)	197	0.41	100		
LaRoche Eta-alumina	Catalyst C 294J1-33X2	253	0.56	108	4.8	95
Harshaw Gamma Alumina Pellets	Catalyst B AL-3996R	219	0.90	144		
Catapal Gamma Alumina Pellets	Catalyst A 136J148-1C				3.7	94

Evaluation of Methanol Catalysts

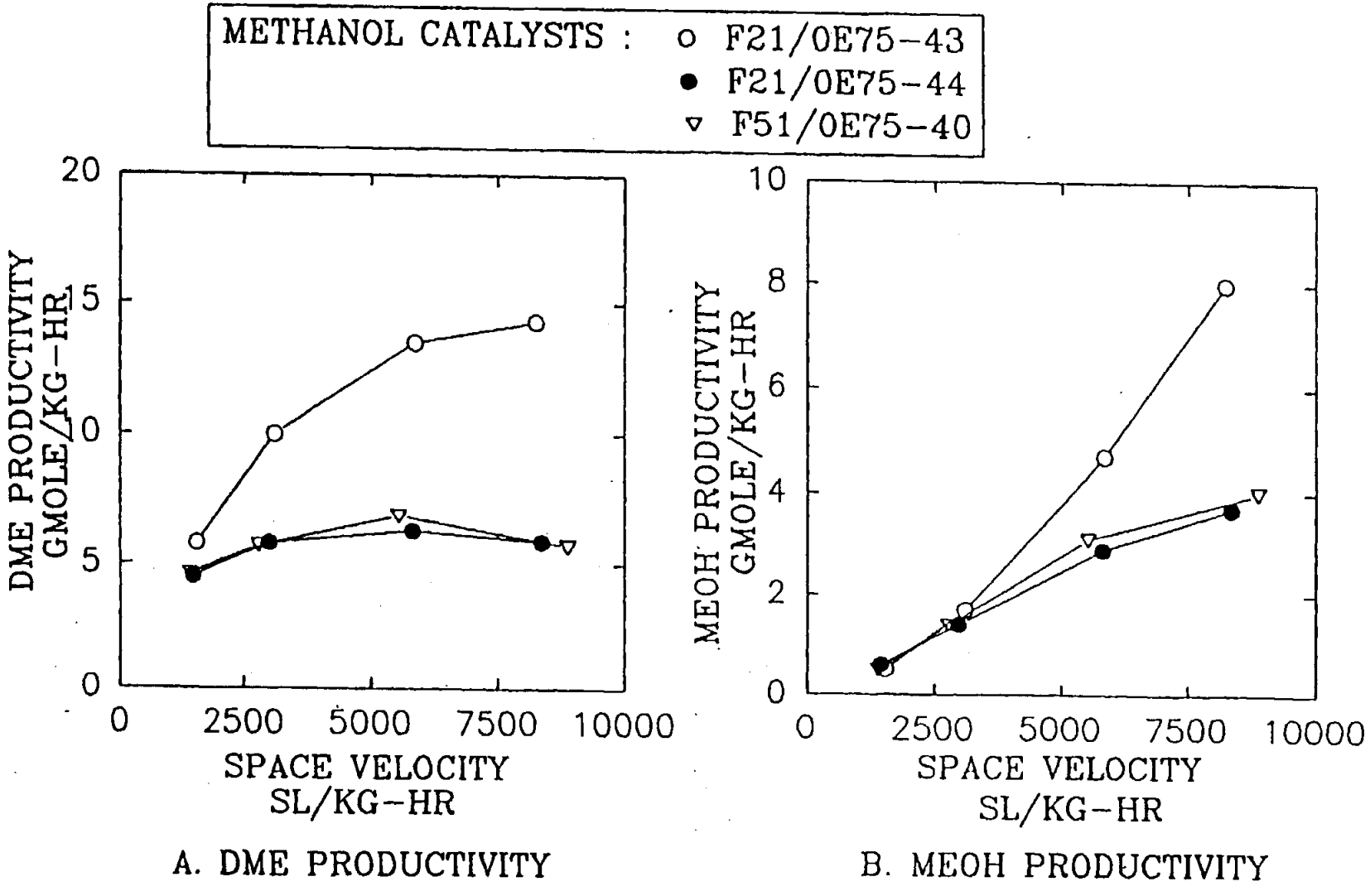
Activity of the methanol catalyst also affects product distribution. A catalyst with a higher methanol activity should produce more methanol, and hence DME, if other conditions are held constant. Two alternate commercial methanol catalysts, F21/0E75-44 (Run No. 10454-40) and F51/0E75-40 (Run No. 10454-51) were tested and compared with Catalyst F21/0E75-43. Catalyst A was used as the dehydration component at 18.75%. Figure 15 compares the results for three commercial methanol catalysts. Catalyst F21/0E75-43 produced both more DME and more methanol than the other two catalysts. This result is not unexpected, since Catalyst F21/0E75-43 is also a more active methanol catalyst. However, the difference in DME and methanol productivity is surprising. As shown in Figure 15, Catalyst F21/0E75-43 produced more than double the amount of DME/methanol product. However, when used for methanol synthesis alone, Catalyst F21/0E75-43 is only up to 10% more active than the other two catalysts. Presumably, by reacting methanol away, the new DME process can truly challenge the activity of a methanol catalyst.

FIGURE 15

EFFECT OF DIFFERENT METHANOL CATALYSTS

(TEXACO GAS, 250° C, 5.27 MPA)

DEHYDRATION CATALYST : CATALYST A



A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

Addition of Shift Catalyst

An experiment (Run No. 11483-39) was conducted to enhance the water-gas shift reaction in the reactor. Ten percent of the F21/0E75-43 (BASF S3-86)-Catalyst A (Catapal) optimum mixture was replaced with BASF K3-110 shift catalyst. The ratio of the three catalysts used was: BASF S3-86/ Catapal/BASF K3-110=73.1/16.9/10. Results of this run are compared with those from the S3-86/ Catapal=81.25/18.75 run in Figure 16. H_2O concentrations in the effluent, estimated based on reaction chemistry and mass balance, reduced with use of the shift catalyst. However, DME productivity also lowered while methanol productivity increased. This can be partly explained to be due to reduction of methanol as well as dehydration catalyst quantity. However, the difference in two DME productivities is too large and may be partly due to deactivation. Thus, the idea of replacing part of the optimum methanol/dehydration catalyst mixture with shift catalyst was not successful in this single experiment.

PROCESS VARIABLE STUDY

Pressure, temperature, space velocity, and feed composition were varied during this study. A catalyst system consisting of 81.25% F21/0E75-43 as methanol catalyst and 18.75% Catalyst A as the dehydration catalyst was used for these experiments.

Shell Gas

A pre-mixed gas simulating coal gas from a Shell gasifier, with a composition of 66% CO, 30% H_2, 3% CO_2, and 1% N_2, was used to study the effect of pressure, temperature, and space velocity. Run No. 10454-43 started with expected DME productivity, but the catalyst deactivated relatively quickly. It was suspected that operating at lower space velocity (1500 GHSV) during nights and weekends might have caused deactivation due to coking. In addition, there was a temperature control problem around 190 hours on-stream, reaching a high temperature of about 295°C in the reactor. This appeared to accelerate the deactivation. The unit was shut down at this point. XRD analysis of spent catalyst did not indicate significant crystallite size growth of Cu (150Å). Analysis of the sample by atomic adsorption spectroscopy showed no Fe or Ni pickup (58 ppm Fe, 38 ppm Ni). Thus, significant hydrothermal sintering or chemical poisoning was not detected.

Another run (Run No. 11483-48) was started using a new batch of the catalyst mix with Shell gas. The syngas flow was kept at 6000 GHSV continuously through weekdays and weeknights. At the weekend, the syngas flow was stopped, the reactor purged and sealed with reduction gas (2% H_2 in N_2) at 250°C and 750 psig. The catalyst appeared to be stable through about 80 hours of operation with syngas. Due to lack of sufficient syngas supply, the run was terminated.

Run No. 11483-52 was started up with a new batch of catalyst mix and Shell gas. After about 2 days on syngas to stabilize the catalyst activity, the pressure was varied in the range of 750–1400 psig (5–10 MPa) at 250°C. Results from these tests at both 5000 and 9500 sl/kg-hr (GHSV) are plotted in Figure 17. A substantial increase in DME productivity was observed with increasing pressure at both space velocities. Increased pressure also resulted in a large increase in methanol productivity at 9500 GHSV. An increase in pressure increases the methanol formation rate, which in turn promotes an increase in DME production.

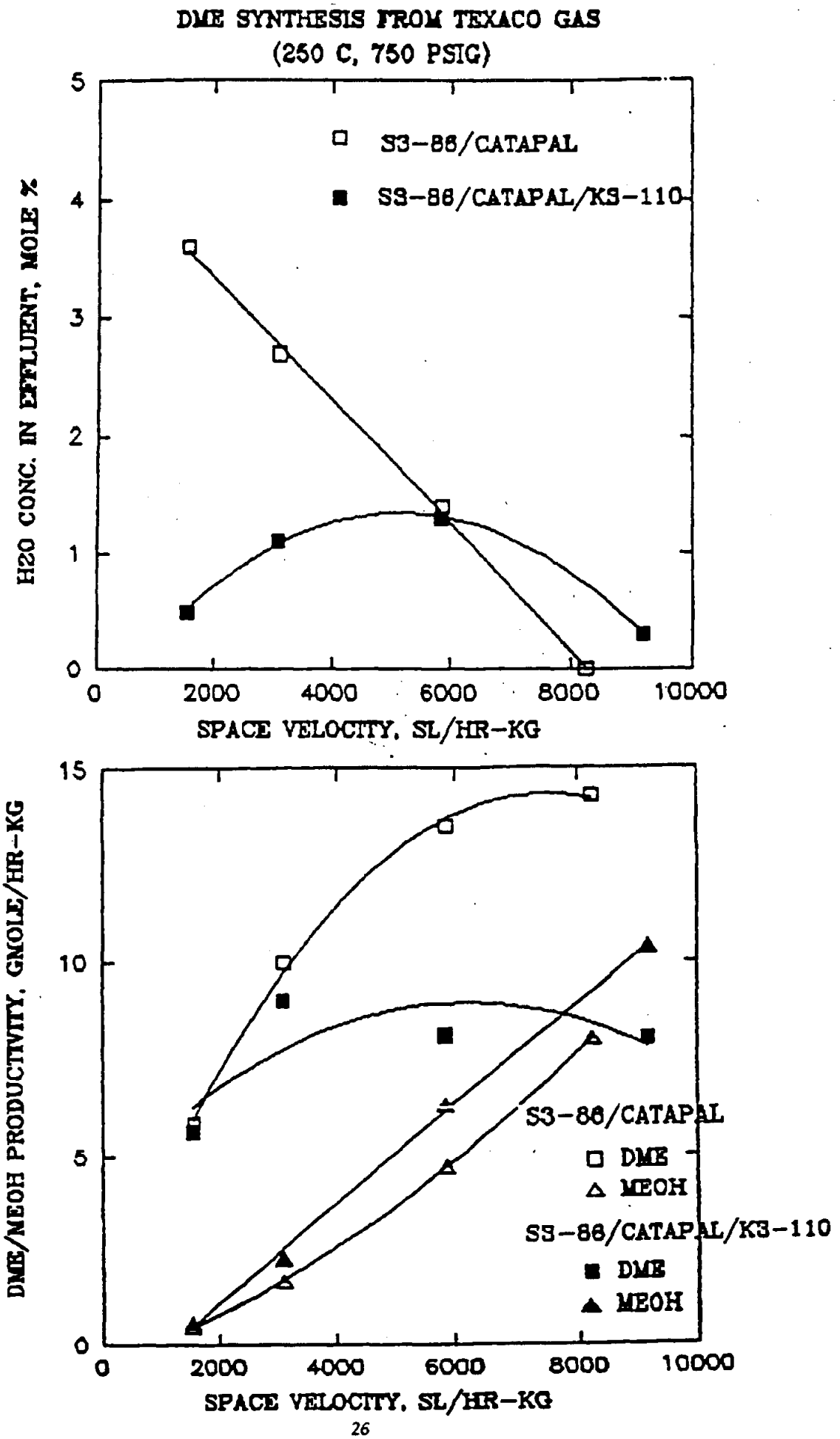

DME SYNTHESIS FROM TEXACO GAS
(250 C, 750 PSIG)
H2O CONC. IN EFFLUENT, MOLE %
SPACE VELOCITY, SL/HR-KG
S3-86/CATAPAL
S3-86/CATAPAL/K3-110
DME/MEOH PRODUCTIVITY, GMOLE/HR-KG
SPACE VELOCITY, SL/HR-KG
S3-86/CATAPAL
DME
MEOH
S3-86/CATAPAL/K3-110
DME
MEOH

Figure 16

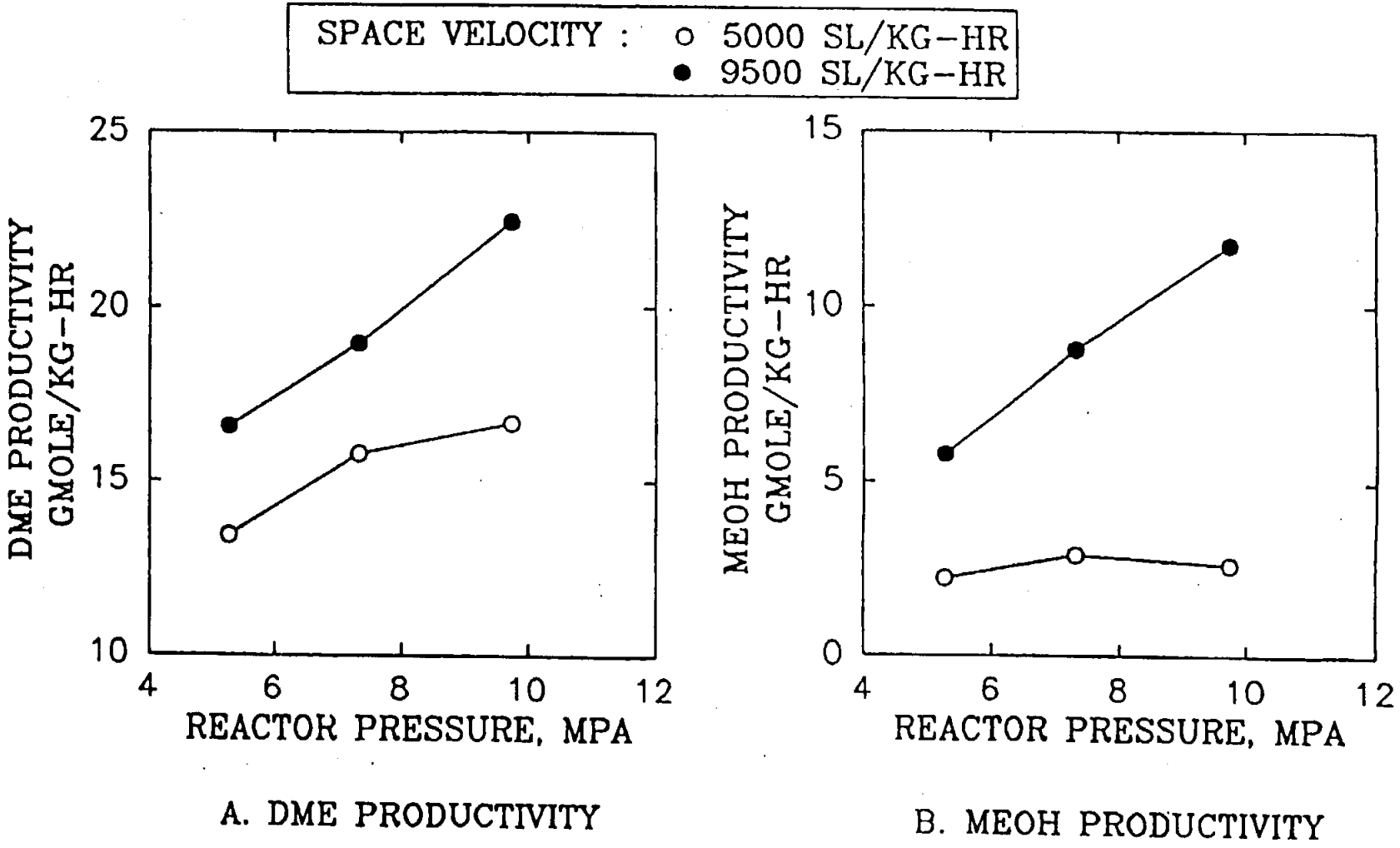
Figure 17

EFFECT OF PRESSURE ON DME SYNTHESIS

(SHELL GAS, 250° C)

DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/0E75-43



A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

After the pressure study, the reactor temperature was increased from 250 to 260°C at 750 psig (5.27 MPa) and 9500 GHSV. This resulted in higher DME productivity and lower methanol productivity (see Table 3). This indicates that the dehydration rate increased more than the methanol formation rate. Thus, the activation energy for the dehydration reaction is probably higher than the methanol formation reaction. After that test, the unit was kept under reduction gas purge at 260°C over the weekend, and then the temperature was further increased. The results at 270 and 280°C (Table 3) indicated deactivation over the weekend. The deactivation was confirmed by repeating an earlier test.

TABLE 3
Effect of Temperature on DME Synthesis at 750 psig and 9000 GHSV

On-Stream Time Hours	Temperature °C	Methanol Prod. gmole/kg-hr	DME Prod. gmole/kg-hr	Methanol Equiv. Prod. gmole/kg-hr
73.5	250	5.8	16.6	39.1
84.5	260	4.6	20.0	44.5
← Under Reduction Purge at 260°C over a weekend →				
91.0	270	2.0	14.9	31.7
95.8	280	1.8	16.6	35.0

Coking of catalyst with formation of methane has been indicated in the literature for the dehydration reaction at temperatures greater than 310°C[18,19]. Bell and Chang[15] observed significant deactivation of the methanol catalyst above 288°C in gas phase single-step DME synthesis. They believed the deactivation was due to coking, catalyst phase change, change in oxidation state, and strong competitive adsorption of CO, especially with H_2 lean feed. Hence, it is important to maintain a lower temperature (around 250°C) to minimize coking. The liquid phase reactor offers excellent temperature control to achieve high reaction rates without significant coking.

Texaco Gas

A syngas simulating coal gas from a Texaco gasifier with a composition of 51% CO, 35% H_2, 13% CO_2, and 1% N_2, was also evaluated at different operating conditions (Run No. 10454-61). The initial productivities were about 10–15% lower than expected. Holding the reactor under reduction gas purge at 250°C over a weekend after reduction may be the reason for the lower activity. It was decided to conduct future reactor holds at 200°C. The run was repeated with a fresh batch of catalyst (Run No. 11483-72). The initial productivities during this run were close to the expected amounts from the screening experiments.

The first set of experiments evaluated the catalyst system at space velocities ranging from 4000–11,000 GHSV and pressure ranging from 400–1400 psig (2–10 MPa). Results are summarized in Figures 18 and 19. DME productivity almost doubled when the pressure was increased from 400 psig to 1400 psig and methanol productivity increased 4–5 times in the same pressure range. Increase in pressure increases methanol formation rate, which in turn triggers the increase in DME production. High methanol productivities at higher pressures and space velocities indicate the catalyst system can be optimized for those conditions with higher proportions of dehydration catalyst.

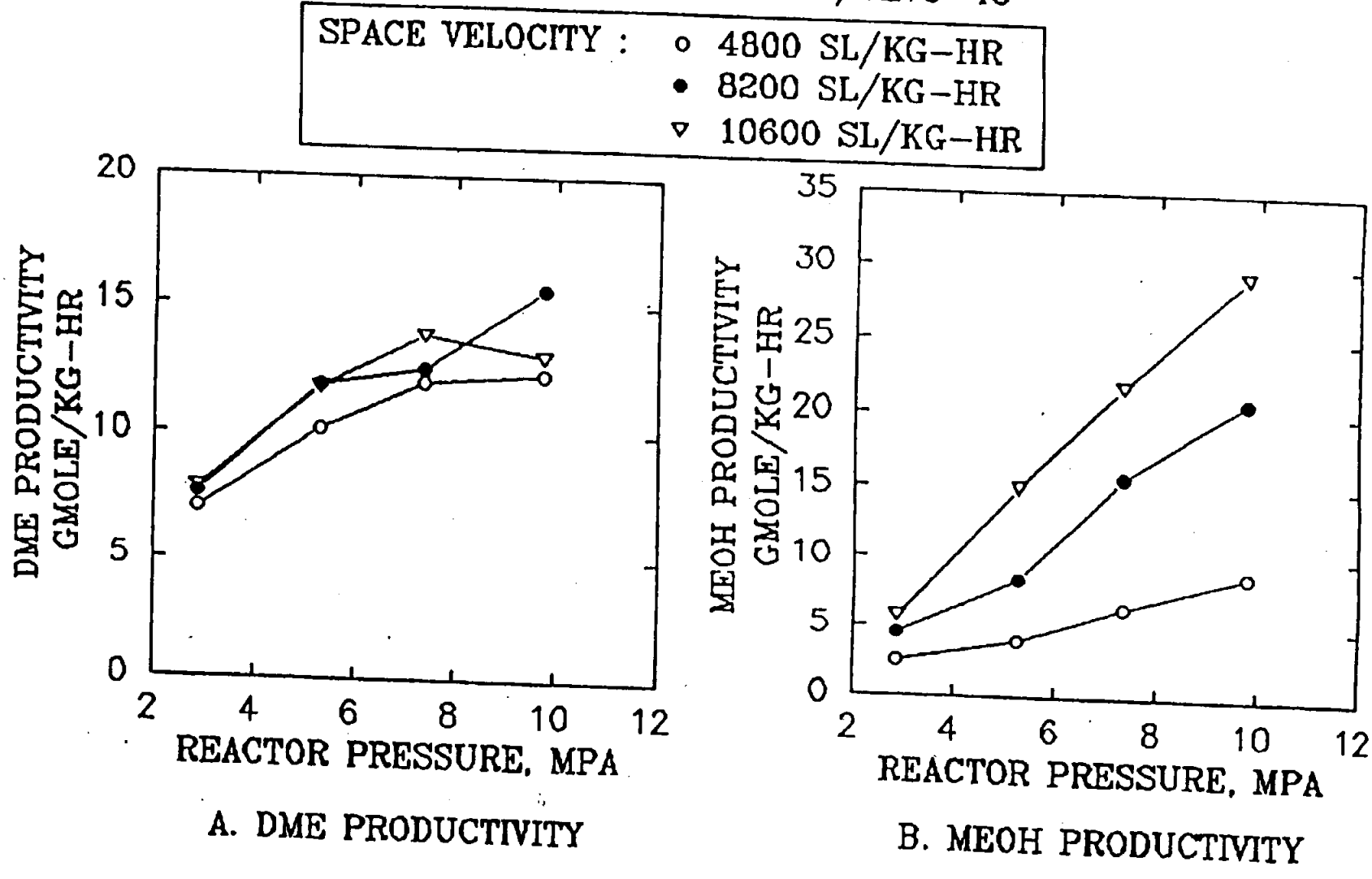
Figure 18

EFFECT OF PRESSURE ON DME SYNTHESIS

(TEXACO GAS, 250° C)

DEHYDRATION CATALYST : CATALYST A

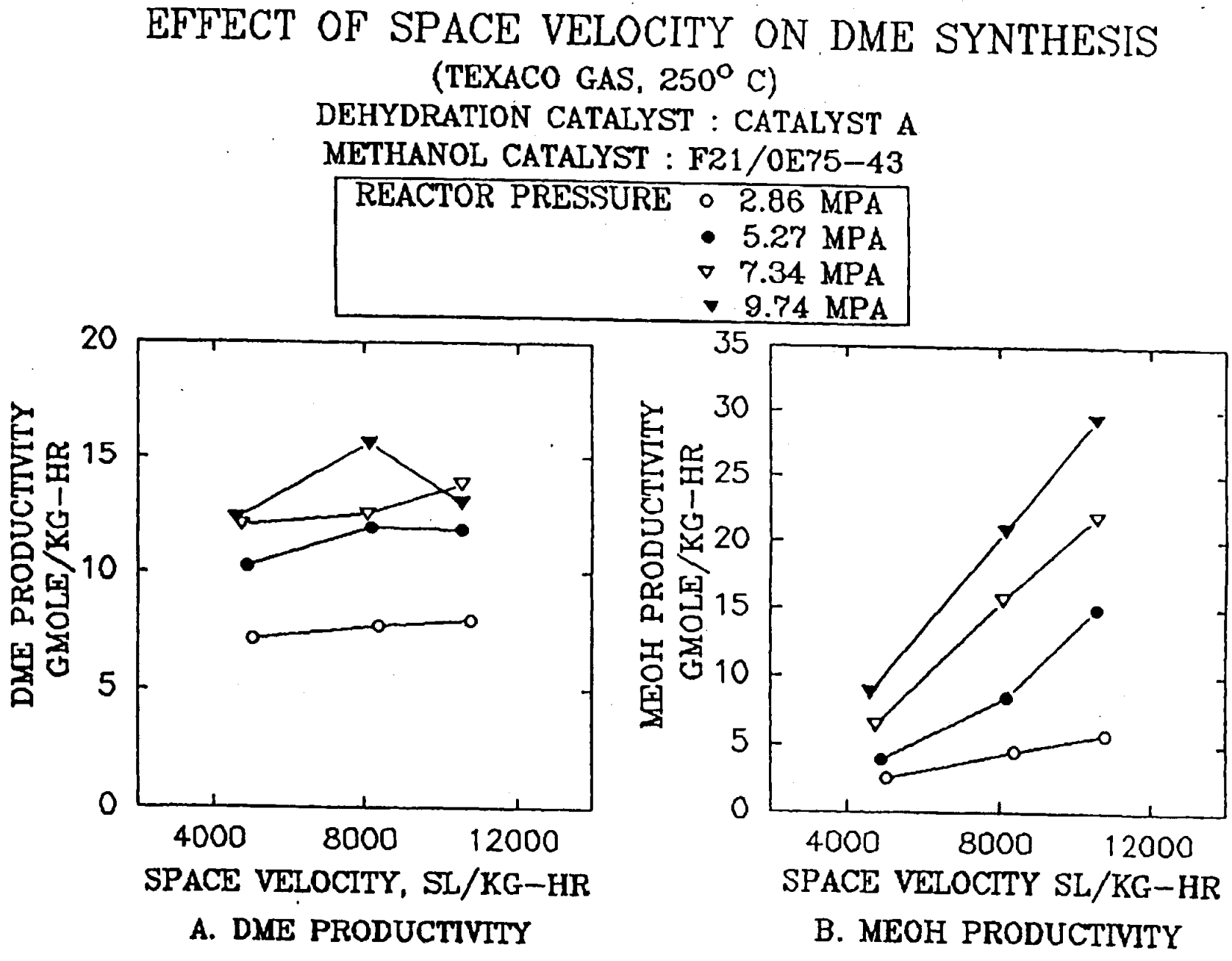
METHANOL CATALYST : F21/0E75-43



A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

Figure 19


EFFECT OF SPACE VELOCITY ON DME SYNTHESIS
(TEXACO GAS, 250° C)
DEHYDRATION CATALYST : CATALYST A
METHANOL CATALYST : F21/0E75-43
REACTOR PRESSURE
2.86 MPA
5.27 MPA
7.34 MPA
9.74 MPA
DME PRODUCTIVITY GMOLE/KG-HR
0
5
10
15
20
4000
8000
12000
SPACE VELOCITY, SL/KG-HR
A. DME PRODUCTIVITY
MEOH PRODUCTIVITY GMOLE/KG-HR
0
5
10
15
20
25
30
35
4000
8000
12000
SPACE VELOCITY SL/KG-HR
B. MEOH PRODUCTIVITY

After the pressure/space velocity study, the redactor temperature was varied in the range of 250–280°C at 750 psig and 8100 GHSV. The results from this study are presented in Figure 20. DME productivity went through a maximum at 270°C. This suggests that at higher temperatures DME undergoes significant further reaction. Perhaps these reactions form coke precursors. Methanol productivity decreased with increasing temperature indicating dehydration reaction is more sensitive to temperature change than methanol formation.

During the process variable study, the run at 750 psig, 8200 GHSV, and 250°C was repeated several times to check for any deactivation. Results from these runs are compared in Table 4. The catalyst system appeared to be reasonably stable during the process variable study. DME productivity declined slightly while methanol productivity increased.

TABLE 4
Catalyst Stability During Process Variable Study
(Results @ 250°C, 750 psig, 8200 sl/hr-kg)

	Initial Activity	Activity Before Pr/GHSV Study	Activity Before Temp. Study	Activity After Temp. Study
Run No.	11483-72A	11483-72C	11483-72N	11483-72Q
On-Stream Time, Hrs.	24	55	139.5	163.75
Methanol Prod. gmole/hr-kg	8.3	8.4	10.7	10.8
DME Prod. gmole/hr-kg	11.9	11.9	11.4	11.4

Effect of CO_2 Removal

Effect of CO_2 removal was studied with the same catalyst system (another batch, Run No. 11483-60) using a feed gas simulating coal gas from a Dow gasifier (41% CO, 41% H_2, 16% CO_2, and 2% N_2). Absence of CO_2 in the feed would allow the water-gas shift to go forward, reacting product water away. This in turn would increase the dehydration reaction rate producing more DME. The run was started up with a feed consisting of 50% CO and 50% H_2 ("stoichiometric gas", Dow gas without CO_2). After about 45 hours on-stream, the feed was changed to Dow gas. DME productivity was almost 90% higher when CO_2 was absent from the Dow gas (see Figure 21). Methanol productivity was about the same. After about 90 hours on-stream, the feed was changed back to Dow gas without CO_2 to check for any deactivation. DME productivity was about 20% lower than initial productivity. The drop was more than expected, and may have been caused by slurry loss during feed change in addition to some catalyst deactivation. Productivity, however, was still about 50% higher than that obtained earlier with Dow gas. After accounting for the activity loss, it is estimated that CO_2 removal from Dow gas increases DME productivity by about 55–60%.

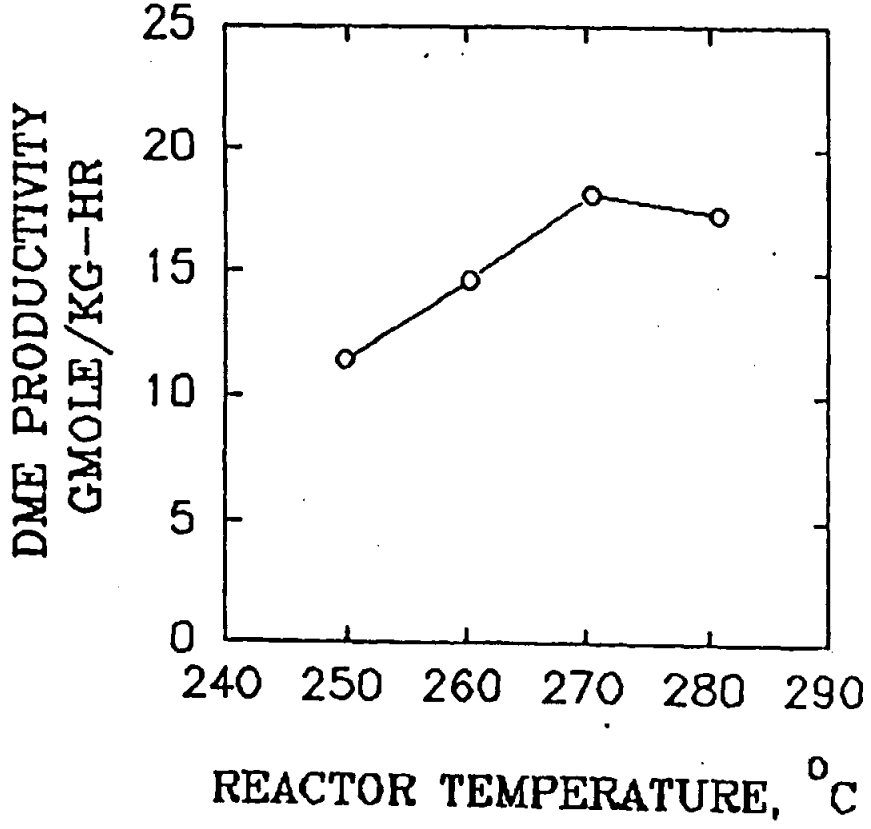
Figure 20

EFFECT OF TEMPERATURE ON DME SYNTHESIS

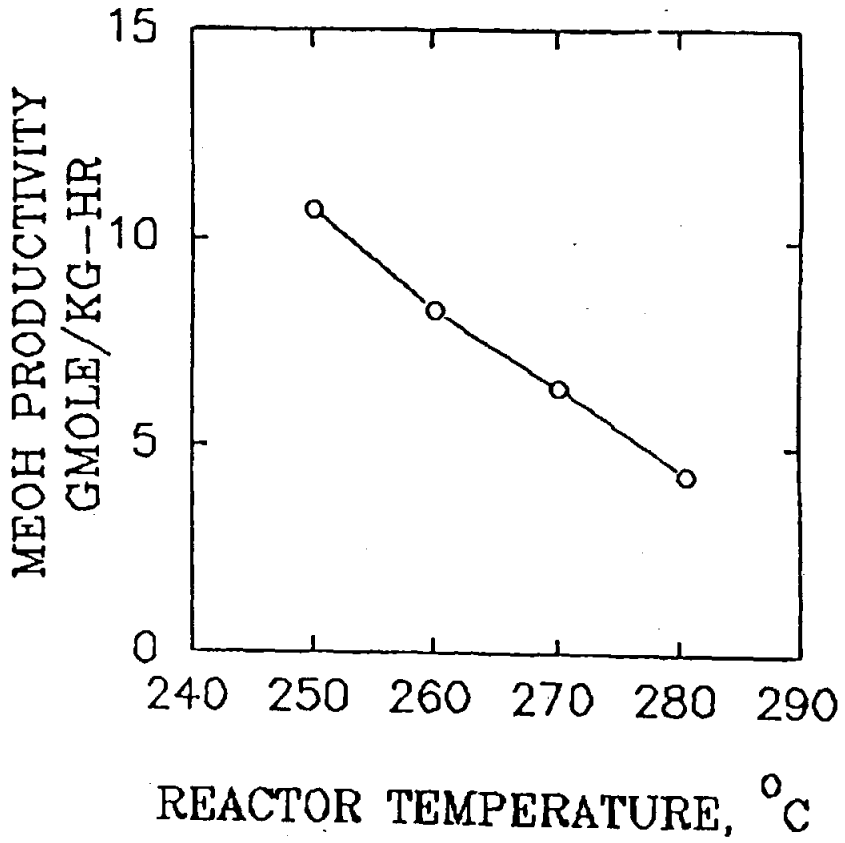
(TEXACO GAS, 5.27 MPA, 8100 SL/KG-HR)

DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/0E75-43



A. DME PRODUCTIVITY



B. MEOH PRODUCTIVITY

Figure 21

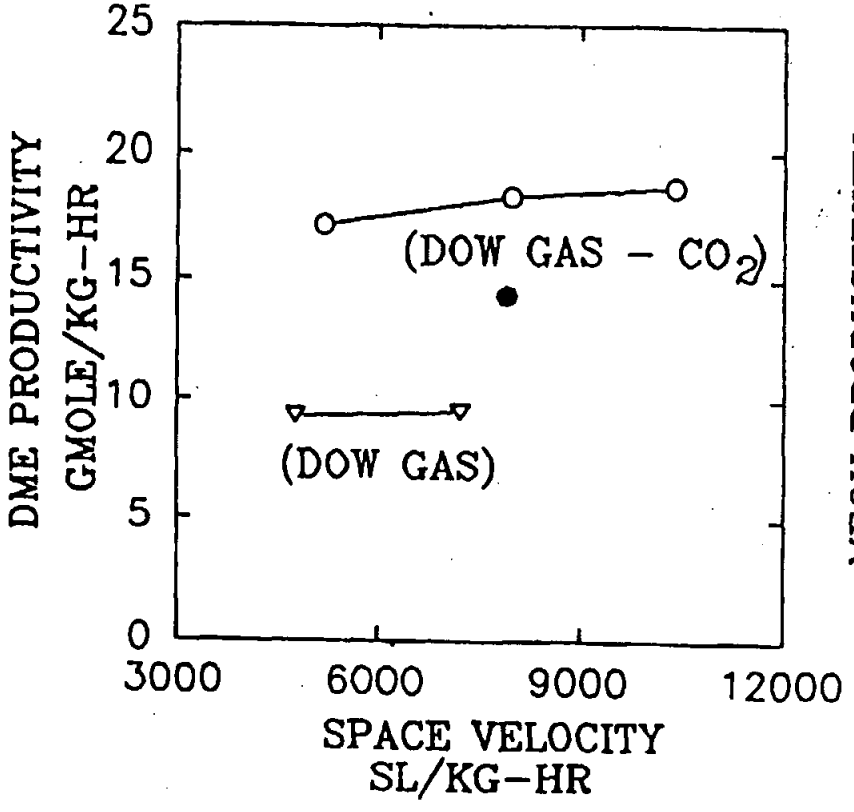
EFFECT OF CO2 ON DME SYNTHESIS

(250° C, 5.27 MPA)

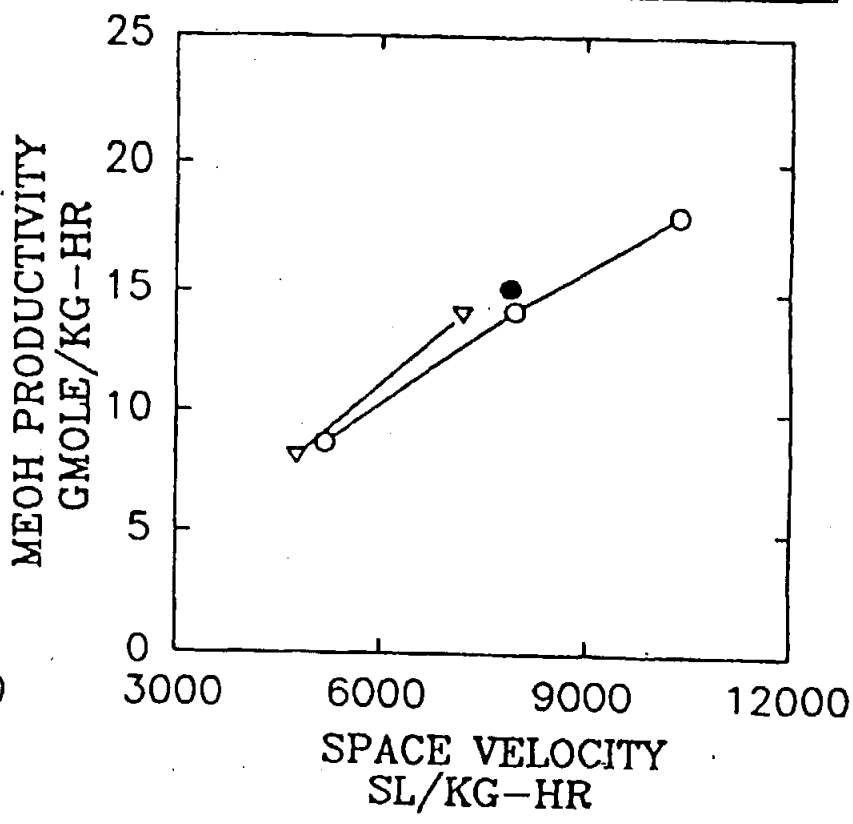
DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/0E75-43

FEED COMPOSITION :
- ○ 50% CO, 50% H_2 (25-45 HRS ON-STR)
- ▽ 41% CO, 41% H_2, 16% CO_2, 2% N_2 (70-90 HRS)
- ● 50% CO, 50% H_2 (100 HRS)



A. DME PRODUCTIVITY



B. MEOH PRODUCTIVITY

The productivity difference observed in Run No. 11483-60 could be attributed to dilution due to the presence of CO_2. Additional tests were conducted at higher pressure during this run to check the dilution effect. Higher pressure would increase the partial pressure of CO and H_2 in Dow gas. Results at higher pressure indicate no improvement in DME productivity (see Figure 22). Thus, the dilution effect of CO_2 is minimum.

Effect of Feed Composition

In addition to the feed gases tested above, a H_2-rich gas (74% H_2, 15% CO, 7% CO_2, and 4% N_2) was evaluated to study DME synthesis with a CO-lean gas (Run No. 11483-67). Tests were conducted at various space velocities at 250°C and 750 psig. The results from the H_2-rich gas are compared with those from Texaco gas, Shell gas, Dow gas, and "Stoichiometric" gas (50% CO, 50% H_2) in Figure 23. Texaco and Shell gas have similar DME and methanol productivities. Shell gas has a lower H_2/CO ratio than Texaco gas (0.45 vs. 0.69) which could reduce DME/methanol productivities. However, the Shell gas also has lower CO_2 (3% vs. 13%), which would improve productivities. The two effects appear to balance each other. Although the catalyst system (ratio) was optimized for Texaco gas, it appears to be close to the optimum for Shell gas, as indicated by low methanol productivity and high DME productivity.

Dow gas yielded lower DME productivity in spite of having a higher H_2/CO ratio (1.0). However, it produced a large quantity of methanol suggesting that the catalyst system was not optimum for Dow gas. DME productivity could be improved by using a larger proportion of dehydration catalyst. The "stoichiometric" gas produced the largest amount of DME and a substantial amount of methanol. Besides having a H_2/CO ratio of 1, this gas contained no CO_2. Higher proportions of the dehydration catalyst will further improve the overall productivity from this gas.

The H_2-rich gas made a lot of methanol but very little DME. It appears that a very high amount of H_2 in the feed is favorable for methanol synthesis but inhibits the water-gas shift reaction. This in turn slows down DME formation. A higher proportion of the dehydration catalyst will help improve the overall productivity somewhat.

From the above results as well as some previous results, it can be concluded that the "best" feed for methanol synthesis is not necessarily the "best" feed for DME synthesis. For example, the optimum H_2/CO ratio in the feed for DME synthesis is about 1 compared to 2 for methanol synthesis. Unlike methanol synthesis, DME synthesis does not need any CO_2 in the feed and actually favors feed without CO_2.

Effect of Water Addition

Run No. 10454-73 was conducted to investigate the effect of water addition to a H_2 and CO_2 lean gas similar to Shell gas. The methanol catalyst has good water-gas shift activity and hence adding water could increase the H_2/CO ratio. The run was started without any water addition at 250°C, 750 psig, and 4800 sl/hr-kg. After checking out the initial productivities, two levels of water addition were studied: 8.6% and 19.9%. A minimum of about 18% water addition to Shell gas is needed to get its H_2/CO ratio to 1. DME productivity dropped significantly with only a minor increase in methanol productivity when water was injected into the feed. Looking at the CO, H_2, and CO_2 concentrations, it appeared that the water-gas shift was occurring, but at the expense of methanol and DME synthesis. A run without water addition at the end of the study showed only partial recovery in catalytic activity. The catalyst may have deactivated due to excessive water on the catalyst.

Figure 22

EFFECT OF CO/H_2 PARTIAL PRESSURE ON DME SYNTHESIS

(250^0 C, 7500 SL/KG-HR)

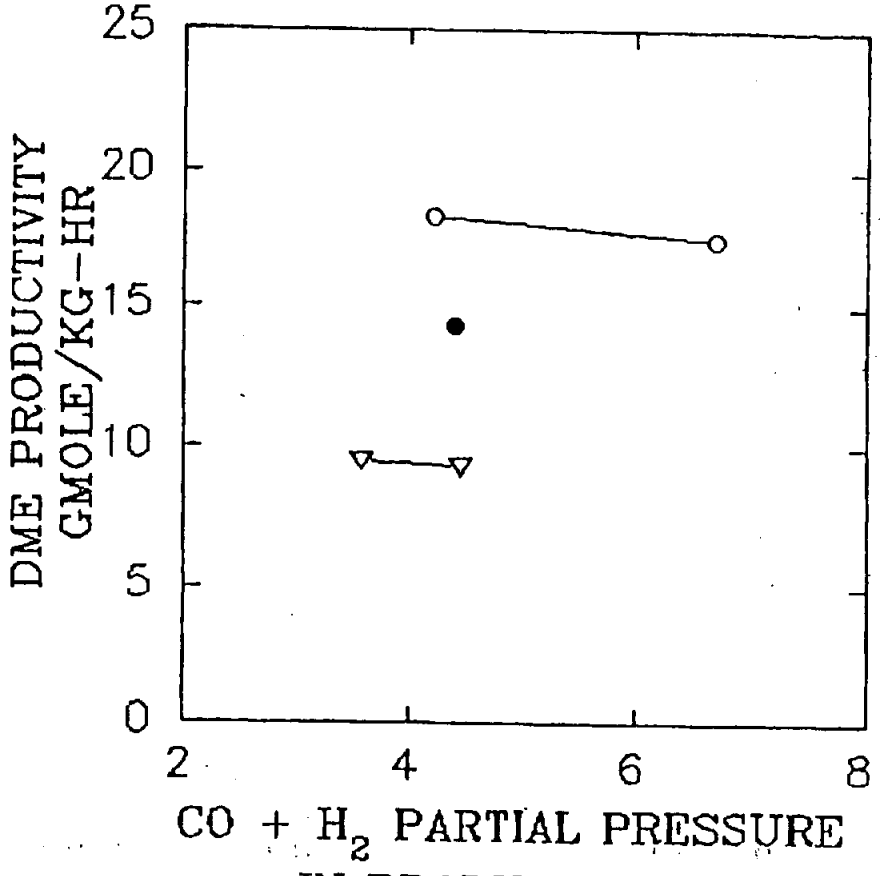
DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/0E75-43

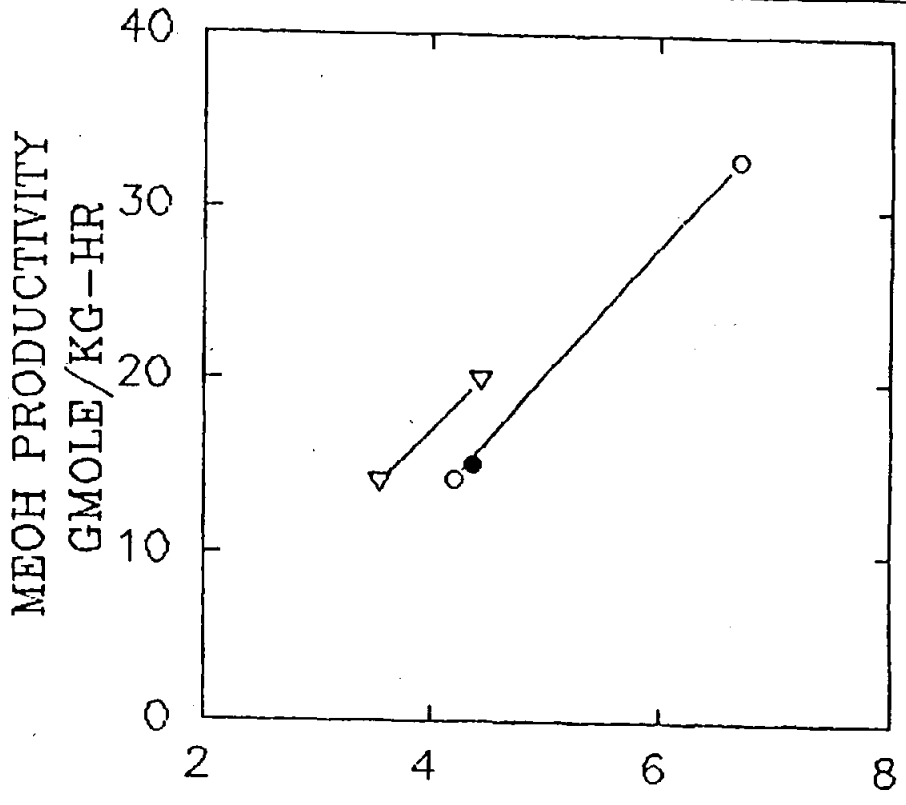
FEED COMPOSITION : ○ 50% CO, 50% H_2 (25-45 HRS ON-STR)

: ▽ 41% CO, 41% H_2, 16% CO_2, 2% N_2, (70-90 HRS)

: ● 50% CO, 50% H_2 (100 HRS)



A. DME PRODUCTIVITY



B. MEOH PRODUCTIVITY

Figure 23

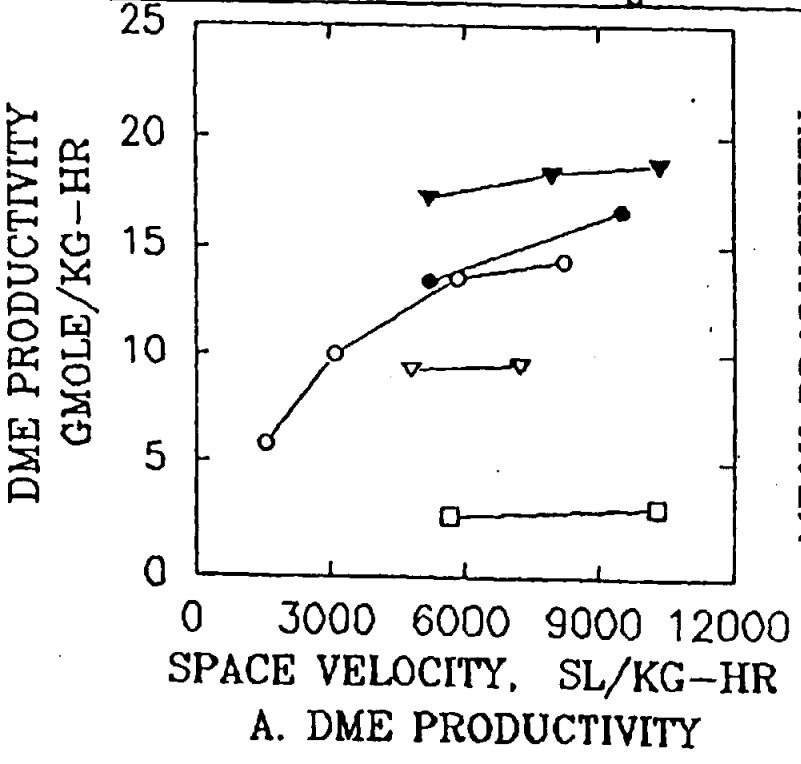
EFFECT OF FEED COMPOSITION ON DME SYNTHESIS

(250° C, 5.27 MPA)

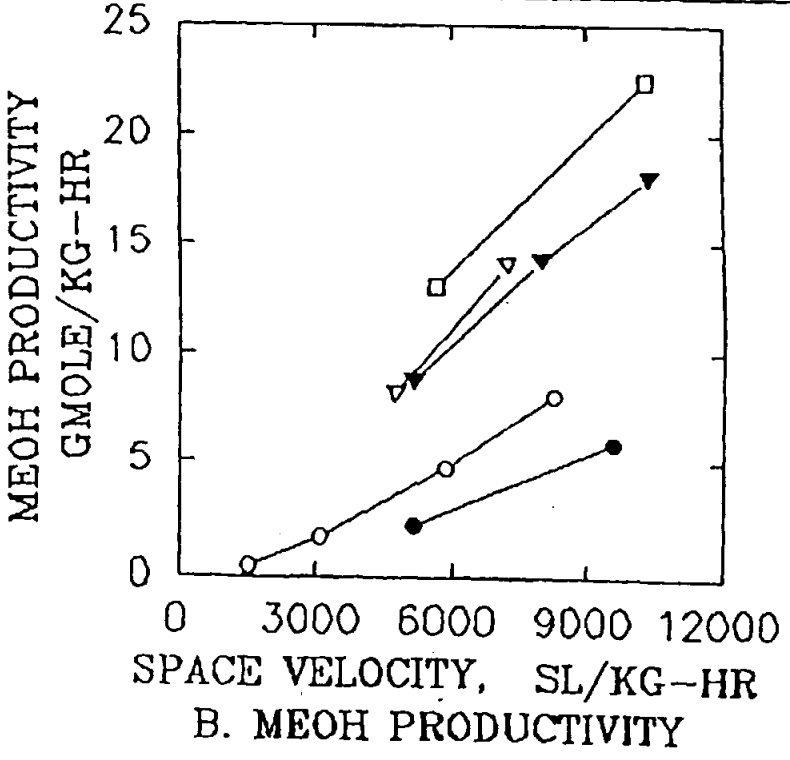
DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/0E75-43

FEED COMPOSITION :
- ○ TEXACO GAS-51% CO, 35% H_2, 13% CO_2, 1% N_2
- ● SHELL GAS-66% CO, 30% H_2, 3% CO_2, 1% N_2
- ▽ DOW GAS-41% CO, 41% H_2, 16% CO_2, 2% N_2
- ▼ 50% CO, 50% H_2
- □ H_2 RICH-15% CO, 74% H_2, 7% CO_2, 4% N_2



A. DME PRODUCTIVITY



B. MEOH PRODUCTIVITY