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SYNTHESIS OF DIMETHYL ETHER AND ALTERNATIVE FUELS IN THE LIQUID PHASE FROM COAL-DERIVED SYNTHESIS GAS

Topical Report

Task 2.2: Definition of Preferred Catalyst System
Task 2.3: Process Variable Scans on the Preferred Catalyst System
Task 2.4: Life-Test on the Preferred Catalyst System

By
Bharat L. Bhatt

September 1992

Work Performed Under Contract No. AC22-90PC89865

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Air Products and Chemicals, Inc.
Allentown, Pennsylvania

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Contractor

AIR PRODUCTS AND CHEMICALS, INC.
Allentown, PA 18195-1501

Bharat L. Bhatt
September, 1992

Prepared for the United States Department of Energy
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Contents

EXECUTIVE SUMMARY

As part of the DOE-sponsored contract for the Synthesis of Dimethyl Ether (DME) and Alternative Fuels in the Liquid Phase from Coal-Derived Syngas (Contract No. DE-AC22-90PC89865), the single-step, slurry phase DME synthesis process was developed. The development involved screening of catalyst systems, process variable studies, and catalyst life studies in two 300 ml stirred autoclaves.

As a spin-off of the Liquid Phase Methanol (LPMEOH*) process, the new process significantly improves the syngas conversion efficiency of the LPMEOH process. This improvement can be achieved by replacing a portion of methanol catalyst with a dehydration catalyst in the reactor, resulting in the product methanol being converted to DME, thus avoiding the thermodynamic equilibrium constraint of the methanol reaction. Overall, this increases syngas conversion per-pass.

The selectivity and productivity of DME and methanol are affected by the catalyst system employed as well as operating conditions. A preferred catalyst system, consisting of a physical mixture of a methanol catalyst and a gamma alumina, was identified. An improvement of about 50% in methanol equivalent productivity was achieved compared to the LPMEOH process. Results from the process variable study indicate that higher pressure and CO_2 removal benefit the process significantly. Limited life studies performed on the preferred catalyst system suggest somewhat higher than expected deactivation rate for the methanol catalyst.

Several DME/methanol mixtures were measured for their key properties as transportation fuels. With small amounts of DME added, significant improvements in both flash points and Reid Vapor Pressure (RVP) were observed over the corresponding values of methanol alone.

Sedimentation tests were conducted on the catalyst mixtures which indicated acceptable slurry properties of the mixture. The dehydration catalyst preparation was successfully scaled up to produce larger quantifies of material required for a demonstration. The development work described here on DME synthesis at the laboratory scale laid the basis for a demonstration of liquid phase DME technology at DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas.

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* Trademark

INTRODUCTION

Researchers at Air Products demonstrated synthesis of dimethyl ether (DME) from synthesis gas in a slurry-based process in 1986[1]. This new process was investigated as a natural extension of the LPMEOH process technology[2,3] to produce DME in a single reactor with the catalyst slurried in an inert mineral oil. In the reactor, the methanol synthesis, methanol dehydration, and water-gas shift reactions proceed concurrently as follows:

Water-gas shift:	$x\,CO + x\,H_2O \Leftrightarrow x\,CO_2 + x\,H_2$	(1)
Methanol Synthesis:	$y\,CO + 2y\,H_2 \Leftrightarrow y\,CH_3OH$	(2)
Methanol Dehydration:	$2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O$	(3)

Net Reaction: $(x+y)\,CO + (2y-x)\,H_2 \Leftrightarrow CH_3OCH_3 + x\,CO_2 + (y-2)\,CH_3OH + (1-x)\,H_2O$ (4)

where x is moles of CO shifted per mole of DME formed, and y is moles of CO converted to methanol per mole of DME. Combining the reversible reactions simultaneously in a single reactor drives each reaction thermodynamically by removing its inhibiting products as reactants in the subsequent reaction. This synergy offers higher syngas conversion to DME and methanol than otherwise can be attainable by each reaction in a separate vessel, where each reaction proceeds at most to its individual thermodynamic equilibrium limitation. Depending on application, the catalyst loaded into the reactor can be a physical mixture of shift, methanol, and dehydration catalysts or a physical mixture of methanol and dehydration catalysts, or a single catalyst with all three types of activity[1].

Coal-derived synthesis gas, which is usually rich in CO, is ideally suited for conversion to methanol or DME in a slurry reactor, primarily as a result of excellent heat management of the slurry reactor. The benefits of the LPMEOH process have been summarized on a number of occasions[4]. The single-step DME reactor has the additional advantage of enabling the occurrence of the water-gas shift reaction, converting by-product water to H_2, thereby increasing syngas conversion to methanol and ultimately to DME. In addition to the coal-derived gases, other industrial gases containing significant quantities of CO can be used as the fuel for the DME process. An interesting example, where judicious control of the shift reaction leads to significant yields of methanol and DME, makes use of the Basic Oxygen Furnace (BOF) off-gas which typically contains about 60 vol% CO and only 1 vol% H_2. Typical gas compositions from today's O_2-blown gasifiers and BOF off-gas are given in Table 1.

TABLE 1
Examples of Feedstock
(Gas Composition, Mole %)

	H_2	CO	CO_2	Inerts	H_2/CO
O_2-Blown Coal Gasifiers					
Texaco	35	51	13	1	0.69
Shell	30	66	3	1	0.45
BGC-Lurgi	28	57	5	10	0.49
Dow	41	41	16	2	1.00
BOF Off-gas	1	58		25	0.02

Conventional gas-phase processes run each of the three reactions in separate reactors. Recent process advances[5, 6] have attempted to conduct reactions (1) through (3) in a single gas-phase reactor to take advantage of the reaction synergism. However, this benefit can be best realized only if the reaction exotherm is managed. Temperature increases caused by the heat of reaction inhibit the overall conversion and reduce productivity. In addition, deactivation of the copper-based methanol and shift catalysts increases rapidly with increasing temperature. The slurry process allows essentially isothermal operation, minimizing thermally induced catalyst deactivation.

Why is DME interesting? First, synthesis of DME can lead to higher syngas conversion per pass, improving the flexibility of co-producing power and clean liquid fuels in Coal Gasification Combined Cycle (CGCC) power plants[7]. Second, mixtures of DME and methanol may have potential in the clean-burning oxygenated transportation market. On-board generation of DME has already been investigated[8] as a means of improving methanol's cold-start characteristics. Third, and perhaps most important, DME is a well-known intermediate in processes for converting synthesis gas to liquid fuels and chemicals[9, 10]. Apart from being a precursor in Mobil's MTG process, DME offers potential as a chemical building block to mixed ethers, currently attractive as replacement octane blending agents in the U.S. gasoline pool.

One of the key objectives under the current DOE contract is to develop a technically and economically viable single-step DME process. Early results from this program were included in a paper presented in 1990[11]. Intermediate results were presented at DOE's Indirect Liquefaction Contractors' review meeting[12]. The current report describes the results from the entire program.

OBJECTIVES

The overall objective of the research program was to develop a single-step, slurry phase process for the synthesis of DME/methanol from syngas. The specific objectives were to

- maximize the syngas conversion to DME and methanol, and
- develop the process for various DME/methanol ratios in the product.

SAFETY

The primary hazards associated with the experimental study were toxicity of CO as well as flammability of H_2 and CO. Periodic (every two years) hazards reviews and operational readiness inspections were conducted for the apparatus[13]. The safeguards included use of CO and flammable monitors, ventilation, and automatic shutdown.

ACKNOWLEDGMENTS

The research described here was supported in part under contracts from the U.S. Department of Energy. The author would like to thank Steve Gaul for safe as well as efficient operation of the autoclave systems. In addition, Tom Hsiung provided valuable guidance for the project. Also, Mike Herron's assistance in reaction modeling for data analysis is greatly appreciated.

LITERATURE REVIEW

A literature review was conducted early in the program. A literature search was performed on "DME Synthesis". Chemical Abstracts were searched from 1967 to the present. Some interesting references were found, including patents from Mobil, Shell, and DuPont.

A Mobil patent[14] discloses a new catalyst and process to produce DME (gas phase) from low H_2/CO syngas. The catalyst was a combination of Cu, Zn, and Al. It was made by mixing 50 wt% methanol catalyst (Cu/Zn/Al) powder with 50 wt% dehydration catalyst (gamma alumina) powder and pelleting into a single catalyst. Typical operating conditions were 315°C, 1500 psig, and 4000 GHSV with a feed having an H_2/CO ratio of 1. A fixed bed tubular reactor was used. The catalyst was regenerated using an oxygen-containing gas in the temperature range of 250–540°C for a relatively short time. The catalyst was reduced following regeneration at temperatures ranging from 175–235°C. The cause of deactivation and the reason why oxidative regeneration was used were not discussed. Even though the catalyst showed improved regenerability, the deactivation rate was too high. For example, the syngas conversion dropped from 80–20% in 60 days in spite of 6 regenerations.

A Mobil patent application in South Africa[15] discusses conversion of syngas to DME in detail. Significant deactivation of the methanol catalyst was observed above 288°C in gas phase single-step DME synthesis. The deactivation was believed to be due to coking, catalyst phase change, change in oxidation state, and strong competitive adsorption of CO, especially with H_2 lean feed.

Two DuPont patents[16, 17] claim improved dehydration catalysts with enhanced reaction rate and reduced coking and by-product formation. Aluminotitanate (1% titania on gamma alumina) and aluminosilicate (6% silica on gamma alumina) were used in a tubular gas phase reactor. Methanol was preheated at 270–300°C. The reactor was maintained at about 150 psig and 10,000 GHSV. A maximum temperature of 390–400°C was observed in the bed. Methanol conversion of about 80% was achieved.

A paper from the Indian Institute of Technology, Delhi[18] discusses DME synthesis from methanol using Molecular Sieve 5A. Nitrogen was bubbled through methanol and the mixture was passed through a catalyst bed. The temperature range of 230–310°C produced only DME and water. At higher temperatures (up to 400°), methane as well as C_2 and C_3 hydrocarbons were formed along with carbon deposition on the catalyst. Rate data were correlated for the lower temperature range using a second order rate equation.

A paper from Argentina[19] describes the effect of water addition in methanol feed for formation of hydrocarbons (HC) using an amorphous silica-alumina catalyst. Water addition reduced catalyst activity and selectivity for HC formation as well as coke deposition on catalyst but did not affect methanol dehydration. It is suggested that water interacts with the strong acid sites responsible for HC formation but the weak acid sites are still capable of forming DME. At 370°C, up to 4.5% coke is deposited on the catalyst.

A patent from Shell[6] claims a catalyst comprising of Cu and Zn supported on a gamma alumina for producing DME from syngas. A series of catalysts were tested in a tubular gas phase reactor at 290–300°C, 1700 psig, and 3000 GHSV with syngas containing a CO/H_2 ratio of 1.

Another patent from Shell[20] claims a catalyst system consisting of a physical mixture of two catalysts for DME synthesis from syngas: a Cu/Zn and alkali metal supported on alumina as the methanol catalyst, and tungsten oxide supported on silica-alumina as the dehydration catalyst. A 1:1 CO/H_2 syngas was fed through a fixed bed reactor at 900 psig, 3000 GHSV, and 300°C. The catalysts produced DME selectivity greater than 90% with some methanol, methane, and C_2-C_7 formation. The catalyst mixture was readily regenerated.

A patent from Ethyl[21] claims the production of both DME and methanol from syngas using a rhodium-molybdenum catalyst. A fixed bed or a Berty reactor was used for the tests. The product distribution showed a substantial amount of methane formation (up to 25%).

The literature raised the catalyst deactivation question. Coking is highly likely at higher temperatures (>300°C). Hence operating at higher temperatures may be prohibitive. Also, the selectivity (to DME/methanol) is reduced at higher temperatures with possible formation of a significant amount of methane.

THERMODYNAMICS OF DME SYNTHESIS FROM SYNGAS

Thermodynamic equilibrium yields were estimated for DME synthesis from syngas using a program called EQUIMET, developed by the University of Missouri at Rolla. This program minimizes Gibbs free energy for a given system. Effect of feed composition, pressure, and temperature on equilibrium were determined. The results are summarized in Figures 1–6. Both CO and H_2 conversion decrease with an increase of the respective component in the feed (see Figure 1). The total syngas (CO + H_2) conversion as well as DME production maximizes at a 50:50 CO:H_2 ratio in the feed. This is consistent with the overall reaction stoichiometry:

$$3CO + 3H_2 \leftrightarrow C_2H_6O + CO_2$$

The maximum DME production at 250° and 750 psig is about 15 moles/100 moles of feed (see Figure 2). This corresponds to 90% conversion; requiring a little over 6 moles of feed to produce 1 mole of DME. The effect of pressure on equilibrium yields is illustrated in Figure 3. DME still does not increase significantly when the pressure is increased from 750 psig to 1500 psig. Figure 4 shows the effect of temperature. The maximum DME yield drops to about 12 moles/100 moles of feed when the temperature is increased to 300°C. Addition of water in the feed increases the DME yield for the H_2 lean feed (see Figure 5), while addition of CO_2 in the feed increases the DME yield in a narrow range of CO lean feed (see Figure 6).

EXPERIMENTAL TECHNIQUES

Experiments were conducted in mechanically stirred 300 ml autoclaves. The details of the two units are given in a hazards review[13]. A schematic of the equipment is shown in Figure 7. A stirring speed of about 1200 rpm was used to ensure that mass transfer effects were negligible. The feed gas was pre-blended and delivered into the system from cylinders. The product gas was analyzed by on-line gas chromatography. Two Thermal Conductivity Detectors (TCDs) were used: one for CO, CO_2, CH_4, N_2, CH_3OH, C_2H_5OH, and CH_3OCH_3, and the other for H_2. The analytical system was described by Byerley[22] (see Appendix I).

The catalyst was a physical mixture of a methanol and a dehydration catalyst. Drakeol-10, a white mineral oil from Penreco, was the slurrying liquid. About 30 grams of total catalyst were used at 20 wt% catalyst loading. The catalyst slurry was reduced in the autoclave using 2% H_2 in N_2 at 100 psig with a temperature ramping.

FIGURE 1

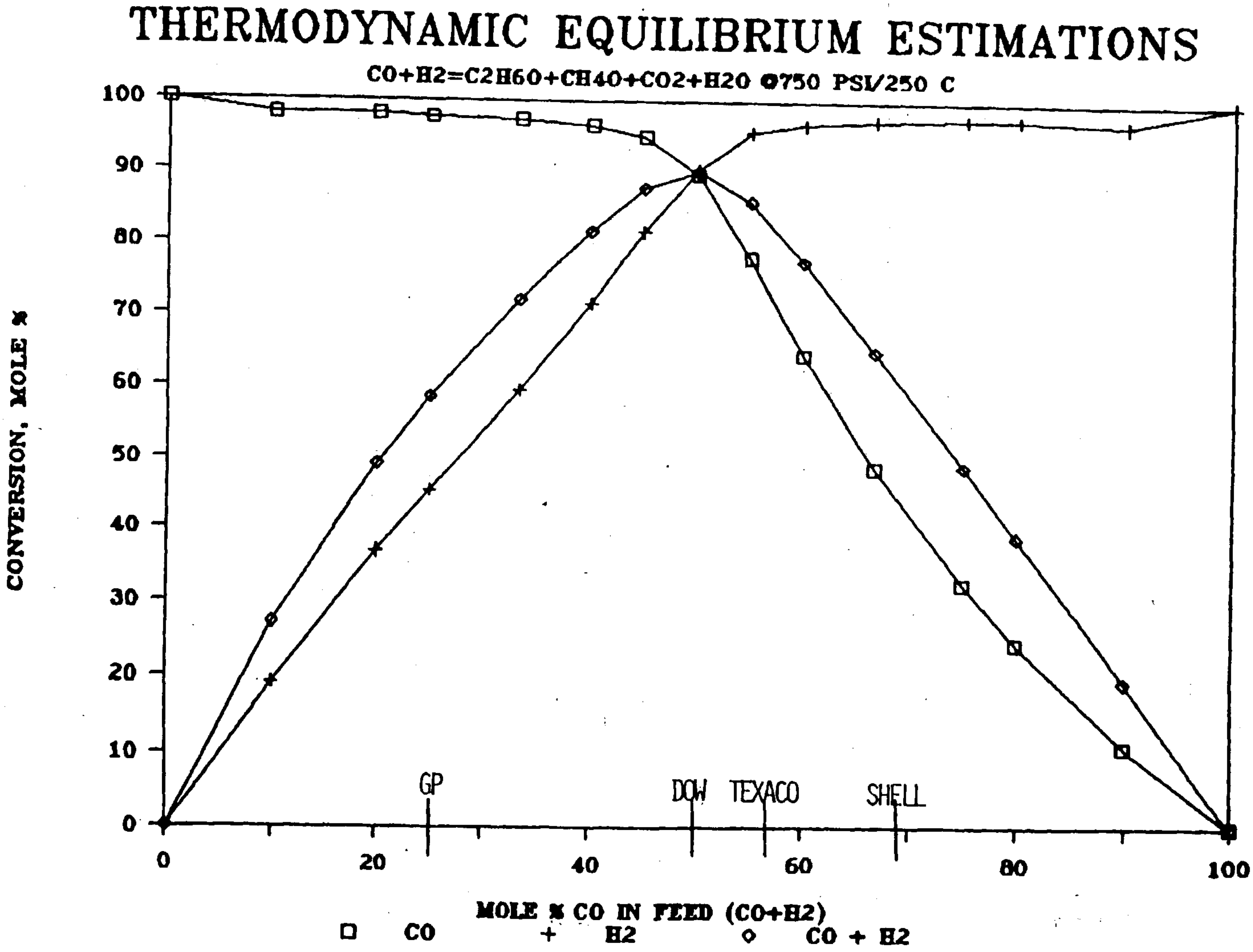
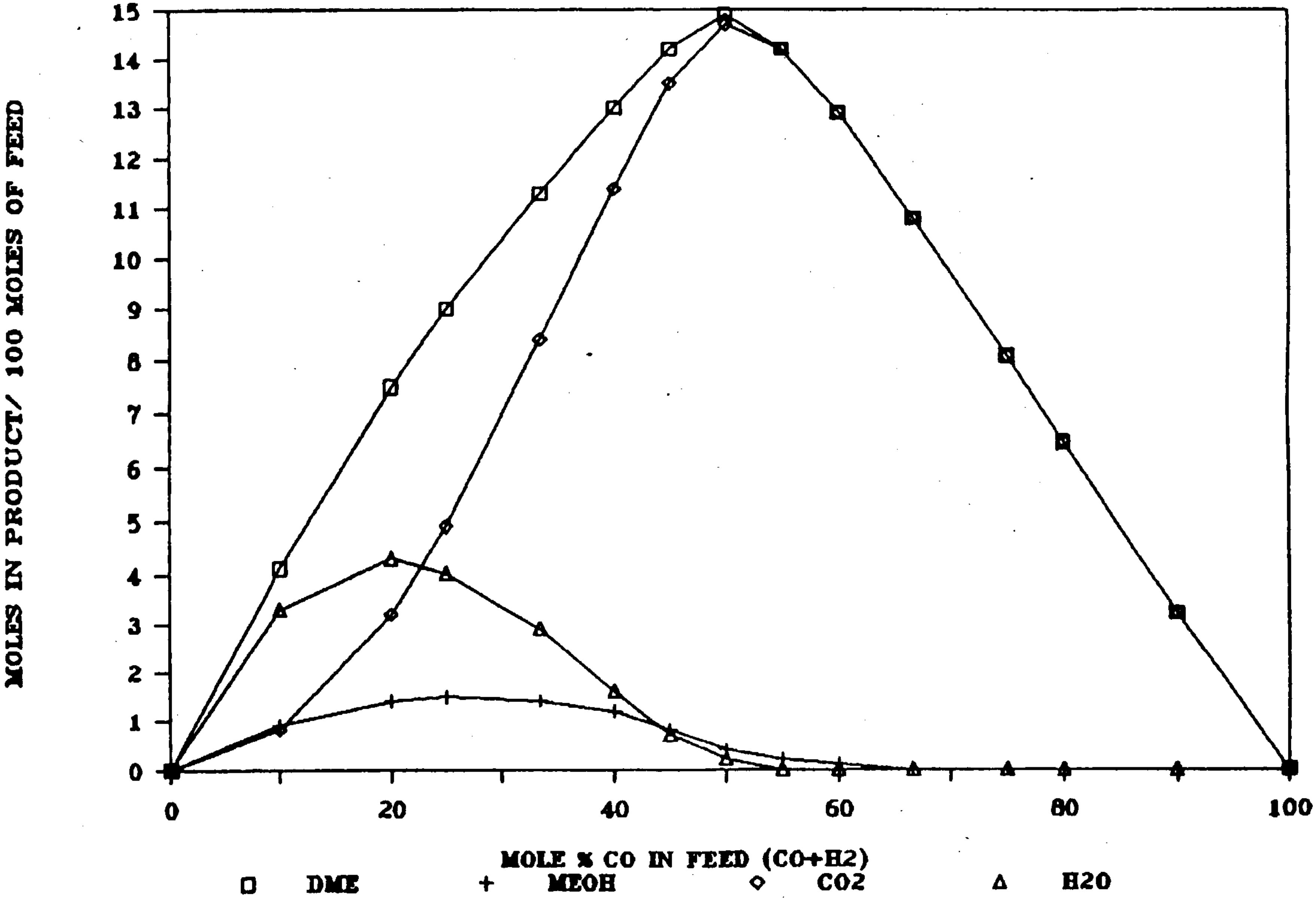

THERMODYNAMIC EQUILIBRIUM ESTIMATIONS
CO+H2=C2H6O+CH4O+CO2+H2O @750 PSI/250 C
CONVERSION, MOLE %
100
90
80
70
60
50
40
30
20
10
0
GP
DOW
TEXACO
SHELL
0
20
40
60
80
100
MOLE % CO IN FEED (CO+H2)
□ CO
+ H2
◇ CO + H2

FIGURE 2



THERMODYNAMIC EQUILIBRIUM ESTIMATIONS

CO+H2=C2H6O+CH4O+CO2+H2O @750 PSI/250 C

FIGURE 3

THERMO. EQU. AT 750 & 1500 PSIG

CO+H2=C2H6O+CH4O+CO2+H2O @250 C

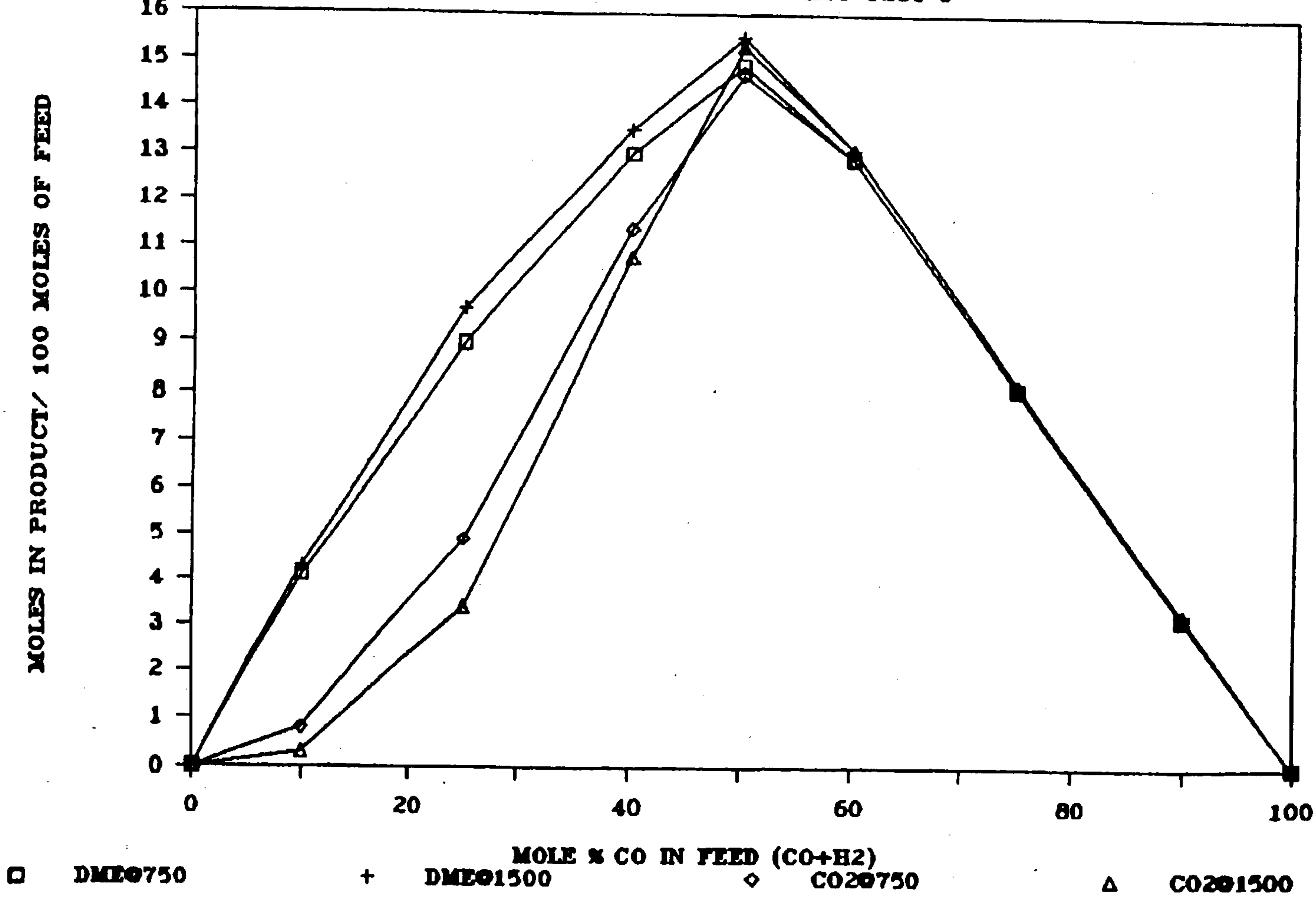


FIGURE 4

THERMO. EQU. AT 250 & 300 DEG C

CO+H2=C2H6O+CH4O+CO2+H2O @750 PSIG

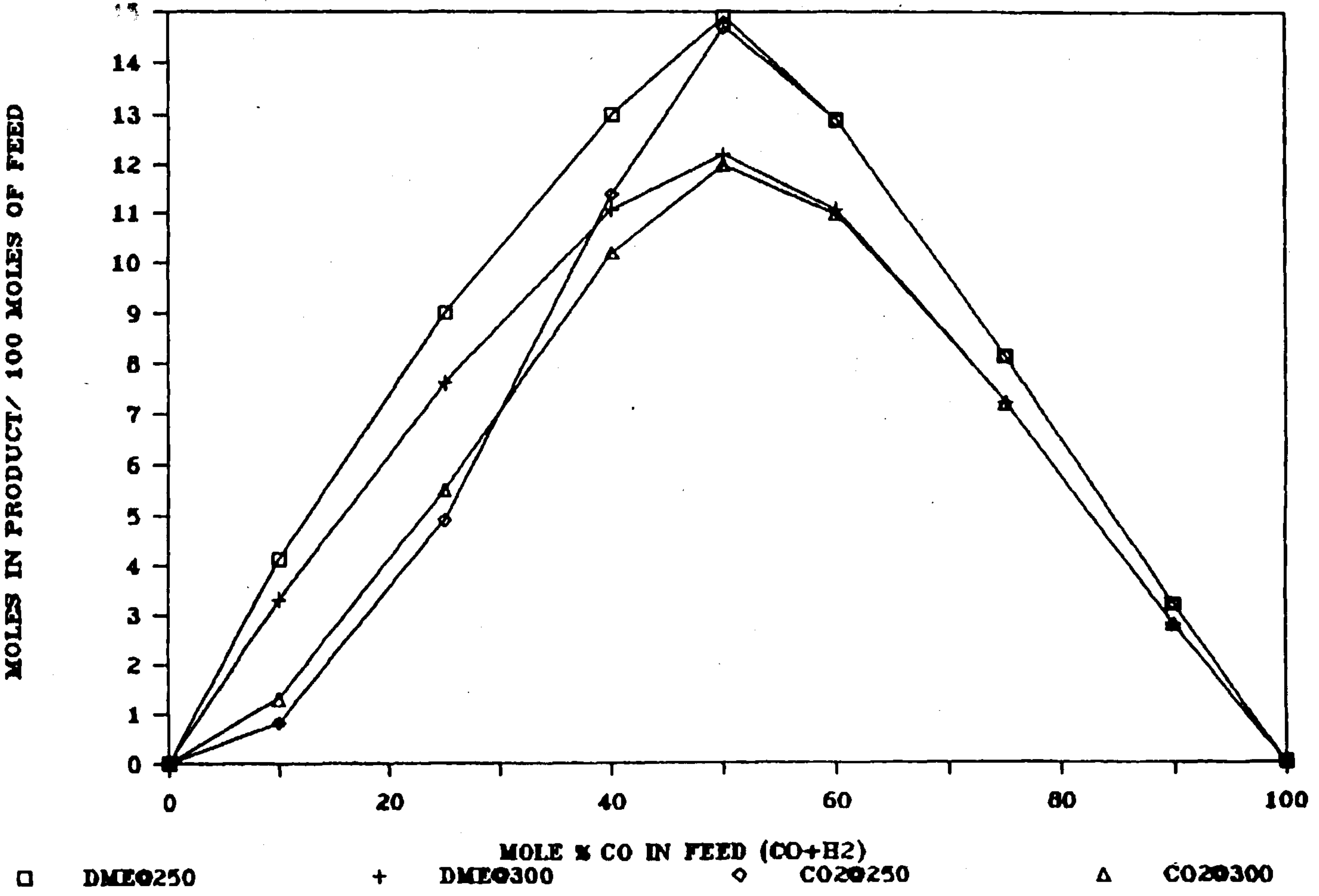


FIGURE 5

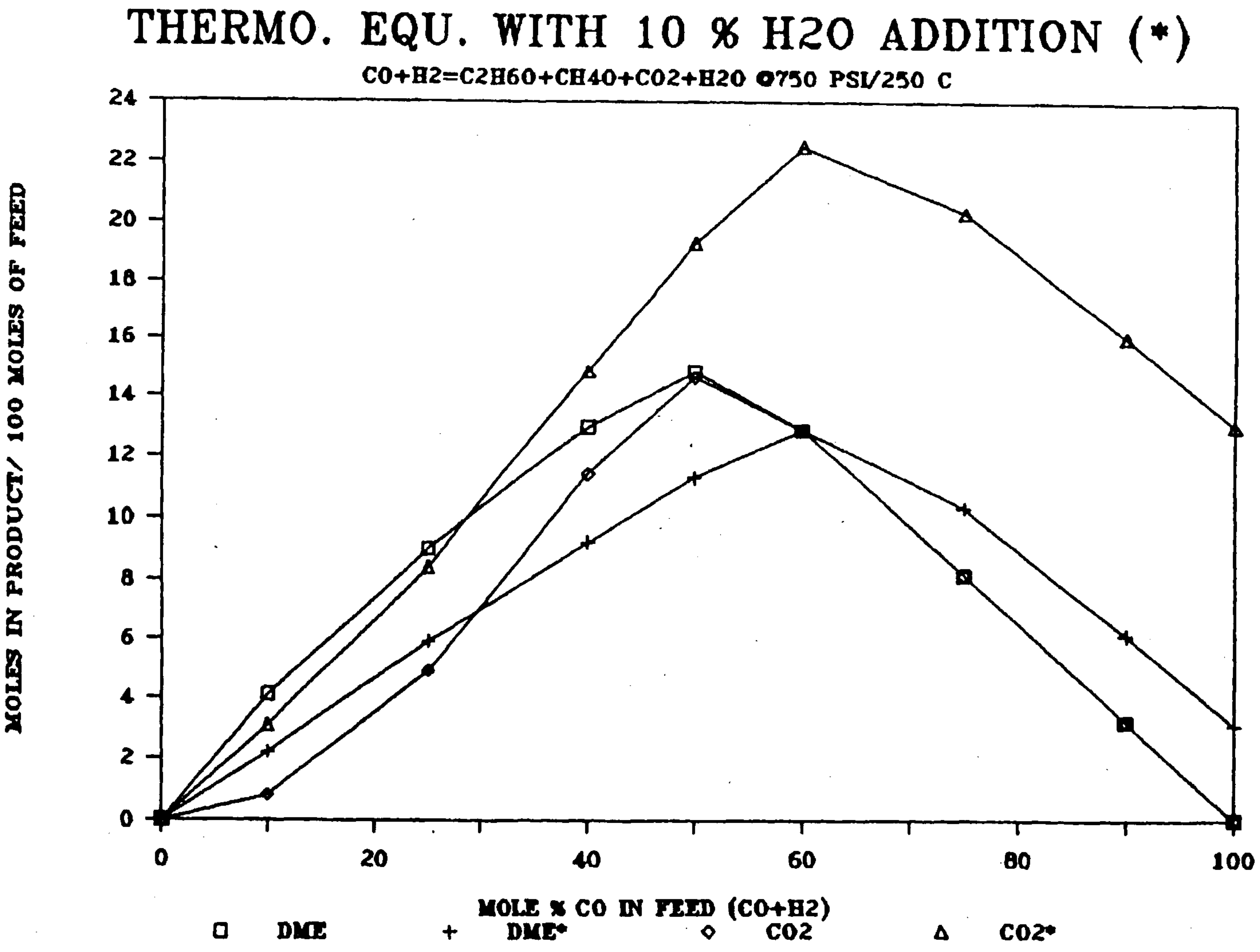

THERMO. EQU. WITH 10 % H2O ADDITION (*)
CO+H2=C2H6O+CH4O+CO2+H2O @750 PSI/250 C
MOLES IN PRODUCT/ 100 MOLES OF FEED
0
2
4
6
8
10
12
14
16
18
20
22
24
0
20
40
60
80
100
MOLE % CO IN FEED (CO+H2)
□ DME
+ DME*
◇ CO2
△ CO2*

FIGURE 6

THERMO. EQU. WITH 10 % CO2 ADDITION (*)

CO+H2=C2H6O+CH4O+CO2+H2O @750 PSI/250 C

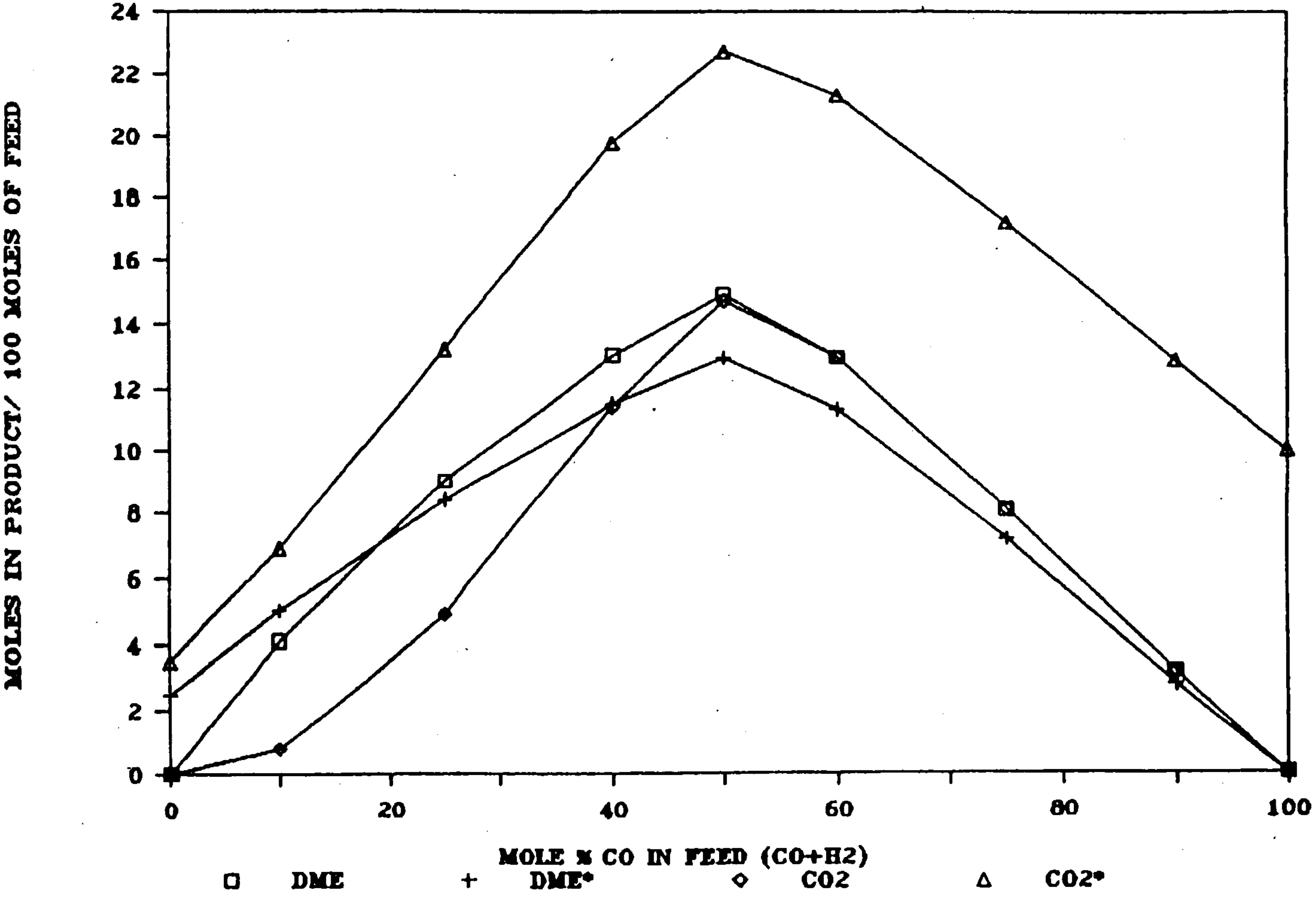
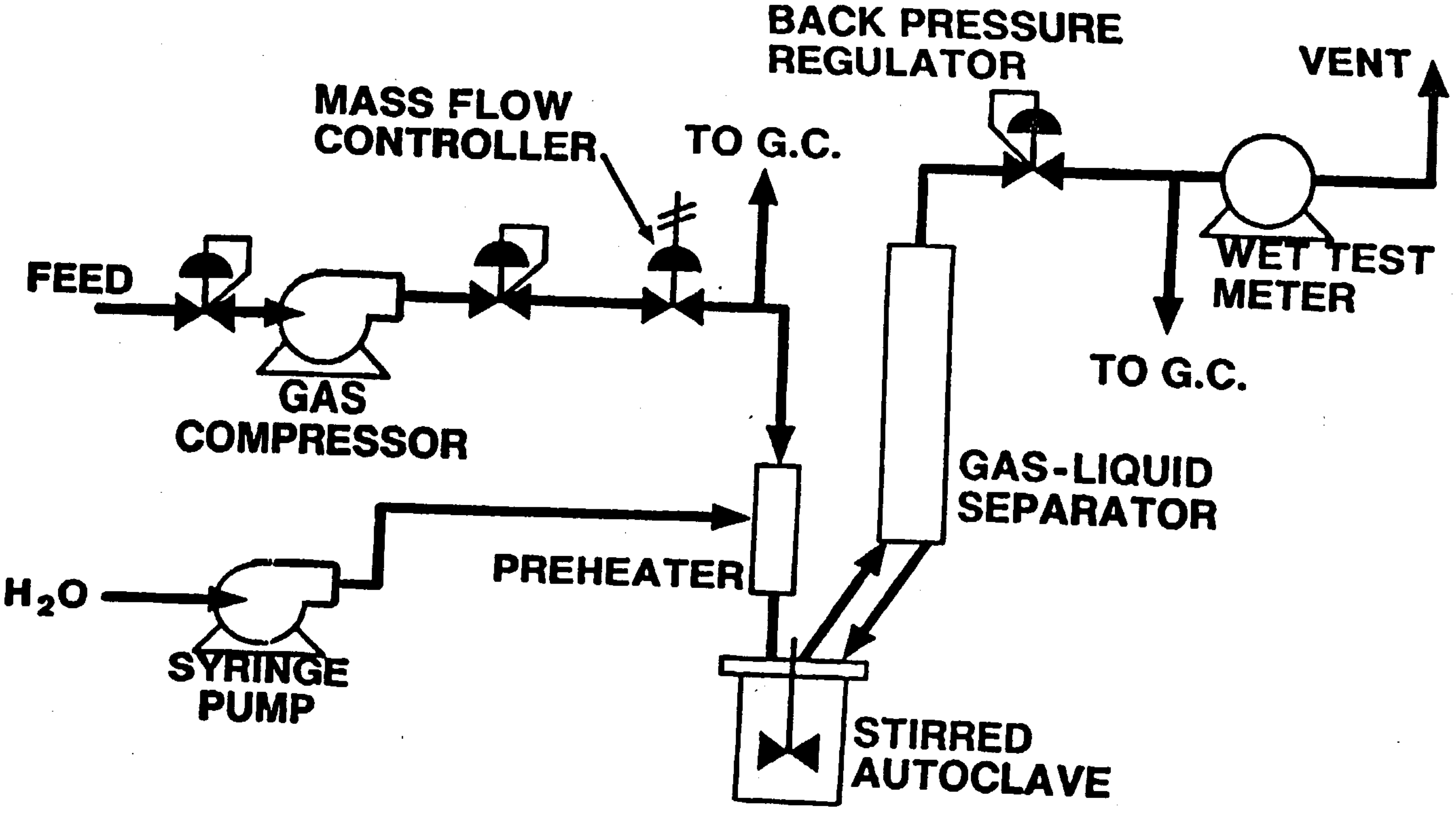


FIGURE 7

SCHEMATIC OF REACTOR SYSTEM



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RESULTS AND DISCUSSION

CATALYST SCREENING

As described in the statement of work, only commercially available catalysts were studied. Three powdered commercial methanol catalysts, BASF S3-86, BASF S3-85, and ICI 51-2C, designated as F21/0E75-43, F21/0E75-44, and F51/0E75-40, were selected from previous LPMEOH process development work[23]. Five alumina-based dehydration catalysts, Catapal gamma-alumina, Harshaw gamma-alumina, LaRoche eta-alumina, Davison silica-alumina, and LaRoche gamma-alumina, designated as A, B, C, D, and E, respectively, were selected and tested. Gamma-aluminas were emphasized since literature suggested a preference towards them. Gas simulating coal gas from a Texaco gasifier, with a composition of 51% CO, 35% H_2, 13% CO_2, and 1% N_2, was used for catalyst screening.

Initial Experiments

Initial experiments were conducted with a 50:50 methanol to dehydration catalyst ratio. Catalyst F21-0E75-43 was used as a methanol catalyst since that is the preferred catalyst for LPMEOH. Catalyst D (Run No. 10892-74) and Catalyst A (Run No. 10892-88) were tested as dehydration components. The run with Catalyst D was conducted to duplicate an earlier run performed at Air Products[1]. The initial reactor conditions were 250°C, 750 psig, and 1500 sl/kg-hr. After 43 hours on-stream, the syngas (CO + H_2) conversion was about the same as observed earlier[1] (46–48%). However, the DME/methanol ratio was much higher than before.

Also, the catalyst appeared to be deactivating significantly with time on-stream as shown in Figure 8. In addition to methanol and DME productivities, Figure 8 shows methanol equivalent productivity, which is defined as 2 times DME productivity plus methanol productivity. This definition is based on stoichiometry as well as the heat of combustion; a mole of DME is produced from 2 moles of methanol and has about twice the heat of combustion of methanol. A possible explanation was that silica in Catalyst D (a silica-alumina catalyst) poisoned the methanol catalyst. Therefore, Catalyst A (gamma-alumina without silica) was tested next. Results indicated higher syngas conversion (54%) and also, the catalyst appeared to be stable through about 100 hours on-stream (see Figure 8). The conversions far exceeded the methanol alone equilibrium conversion of 34% at 1500 sl/kg-hr, 250°C, and 750 psig. Presumably, the consumption of methanol to produce DME alleviates the equilibrium limitation. There was very little methanol in the effluent suggesting that the methanol catalyst was the controlling factor.

Catalyst Ratio Study

Since the results with the 50:50 F21/0E75-43 and Catalyst A system appeared encouraging, further experiments were conducted using these two catalysts in different proportions. A higher proportion of methanol catalyst (75%) was tested next (Run No. 10892-95), since methanol catalyst was found to rate controlling at 50% proportion. A higher proportion of methanol catalyst resulted in an increase in DME productivity (5.3 vs. 4.7 gmole/kg-hr) as well as methanol productivity (0.5 vs. 0.3 gmole/kg-hr). However, the methanol productivity was still small, indicating that the system was still deficient in methanol activity. Hence, an even higher proportion of methanol catalyst would be beneficial.

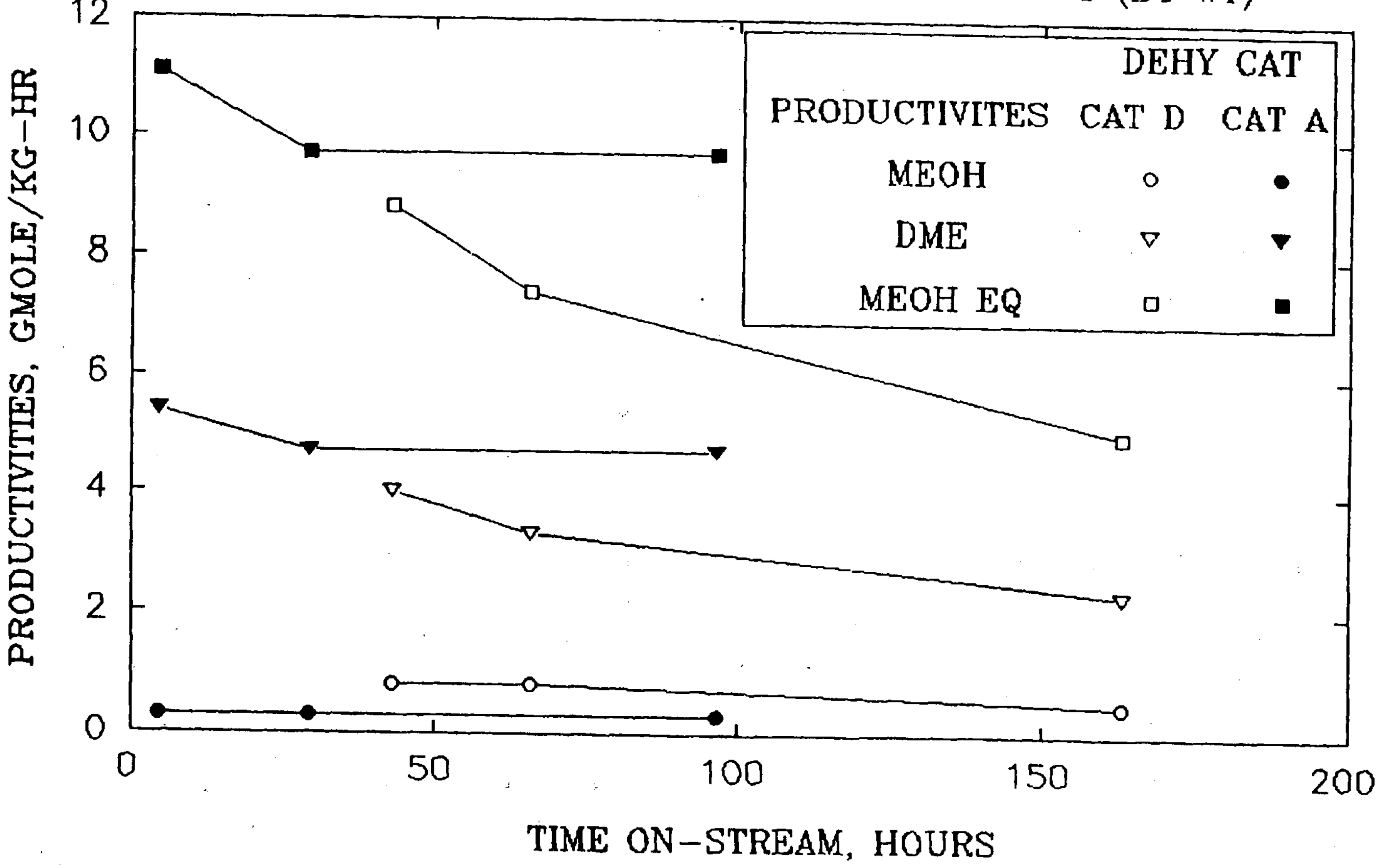
FIGURE 8

DME SYNTHESIS WITH DIFFERENT DEHYDRATION CATALYSTS

(TEXACO GAS, 250^{0}C, 5.27 MPA, 1500 SL/KG-HR)

METHANOL CATALYST : F21/0E75-43

METHANOL/DEHYDRATION CATALYST RATIO = 1 (BY WT)



Three runs (Run Nos. 11483-08, 11483-16, and 11483-21) were conducted with the methanol catalyst (F21/0E75-43) proportion ranging between 75 and 100%. The balance was dehydration Catalyst A. The tests were conducted at 250°C and 750 psig in the range of 1500–9000 sl/kg-hr space velocity. Results from these runs along with those from earlier runs at lower methanol catalyst proportion are compared in Figures 9–11. Methanol equivalent productivity is plotted as a function of % methanol catalyst in Figure 9. It appears that the maximum methanol equivalent productivity is obtained at about 81% methanol catalyst. This is true for the entire range of space velocity studied. The data at 75% is an average of the earlier run (Run No. 10892-95) and a repeat run (Run No. 11483-34). This run was repeated because the productivity dropped sharply at 75% methanol catalyst, showing some discontinuity. Also, we did not have high space velocity data at the composition. The repeat run confirmed the earlier data.

DME productivity is plotted in Figure 10. It also shows the maximum at 81% methanol catalyst. Methanol productivity is plotted in Figure 11. It remains low up to 81% methanol catalyst and then increases sharply at higher proportions. It seems that at methanol catalyst proportions higher than 81%, the lack of dehydration activity due to lower amounts of alumina starts controlling the overall reaction rate.

Comparison of Liquid Phase DME (LPDME) with the LPMEOH Process

It is worthwhile to compare the results of LPDME with existing LPMEOH results. For LPDME, the catalyst was a mixture of F21/0E75-43 (81.25%) and Catalyst A (18.75%) while the LPMEOH results were established using 100% F21/0E75-43 catalyst. Figure 12 shows the CO conversion as a function of space velocity. The CO conversion in LPDME is 1 to 2 times greater than that in LPMEOH and much higher than the equilibrium conversion achievable by the methanol reaction alone.

In LPDME, a significant portion of the CFO converted (theoretically, as high as 1/3) ends up as CO_2. Therefore, it is important to compare the productivity towards useful products. Methanol equivalent productivity from the two processes is plotted as a function of space velocity in Figure 13. LPDME produces about 50% more useful products than the LPMEOH process. The big gap between DME equilibrium and the DME performance curve indicates that there is still room for improvement.

Evaluation of Dehydration Catalysts

Alternate dehydration catalysts were screened at the proportion of 81.25% methanol catalyst (F21/0E75-43) and 18.75% dehydration catalyst. Catalysts B, C, and E were tested in Run Nos. 11483-30, 11483-26, and 11483-92, respectively. Results from these tests are compared with those from Catalyst A in Figure 14. DME and methanol productivity are plotted as a function of GHSV. Since the same methanol catalyst was used at the same proportion in these experiments, a catalyst with higher dehydration activity would produce higher DME productivity at the expense of lower methanol productivity. From Figure 14, it is clear that Catalyst A has the best dehydration activity and Catalyst B is second in activity. Catalysts C and E have poor dehydration activity as indicated by relatively low DME productivity and high methanol productivity. The methanol equivalent productivity produced by Catalyst A can still be improved, at least theoretically, with an even more active dehydration catalyst since there is some unreacted methanol in the reactor effluent.