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

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ABSTRACT

In December 1989, the United States Department of Energy awarded Air Products and Chemicals, Inc. a contract to investigate the Synthesis of Dimethyl Ether (DME) and Alternative Fuels in the Liquid Phase from Coal-Derived Syngas (Contract # DE-AC22-90PC89865). Key objectives of the program are to develop the technology for the single-step, slurry phase synthesis of DME from coal-derived synthesis gas and to investigate the potential of the slurry phase synthesis of alternative fuels directly from the syngas.

The two objectives are being pursued in parallel in the laboratories. The development of one-step DME synthesis involves screening of catalyst systems, process variable studies (PVS) and catalyst life studies. Two 300 ml autoclaves are used for these experiments. The exploratory work on synthesis of alternative fuels is being conducted in 50 ml micro-autoclaves. Initial areas of emphasis include slurry-phase synthesis of higher alcohols as well as methanol (MeOH) / hydrocarbon mixtures from syngas.

The catalyst screening for the DME synthesis has been completed. Alternative methanol and dehydration catalysts have been evaluated with a "CO-rich" syngas, simulating coal gas from a Texaco gasifier. A preferred catalyst system, consisting of a physical mixture of a methanol catalyst and an alumina, has been identified. An improvement of about 50% in the methanol equivalent (2*DME + MeOH) productivity has been achieved compared to the liquid phase methanol process. Process variables under study include feed composition, pressure, temperature and space velocity. Results to date indicate significant process improvements at higher pressure and with CO_2 removal from syngas. After the PVS, a 30-day life test will be conducted to investigate the aging characteristics of the preferred catalyst system. Following the life study, demonstration of the process is planned next spring at DOE's Alternative Fuel Development Unit in LaPorte, Texas under another program.

The slurry-phase synthesis of higher alcohols using a modified methanol synthesis catalyst has been successfully demonstrated at the laboratory scale. Studies on the one-step synthesis of methanol/hydrocarbon mixtures from syngas are in a preliminary stage.

INTRODUCTION

Synthesis of Dimethyl Ether

Researchers at Air Products demonstrated synthesis of dimethyl ether (DME) from synthesis gas in a slurry-based process in 1986 (Lewnard et al., 1990). This new process was investigated as a natural extension of the liquid phase methanol (LPMEOH[*]) process technology (Espino and Pletzke, 1975; Klosek, J. et al., 1985) to produce DME in a single reactor with the catalyst slurried in an inert mineral oil. In the reactor, the methanol (MeOH) synthesis, methanol dehydration, and water-gas shift reactions proceed concurrently as follows:

$$\text{Water-gas Shift:}\quad x\ CO + x\ H_2O <====> x\ CO_2 + x\ H_2 \tag{1}$$

$$\text{MeOH Synthesis:}\quad y\ CO + 2y\ H_2 <====> y\ CH_3OH \tag{2}$$

$$\text{MeOH Dehydration:}\quad 2\ CH_3OH <====> CH_3OCH_3 + H_2O \tag{3}$$

$$\text{Net Reaction:}\ (x+y)\ CO + (2y-x)\ H_2 <===> CH_3OCH_3 + x\ CO_2 + (y-2)\ CH_3OH + (1-x)\ H_2O \tag{4}$$

where x is the moles of CO which is shifted per mole of DME formed, and y is the 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 (Lewnard et al., 1990).

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 (Studer et al., 1989). 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. 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 coal gasifiers and BOF off-gas are given in Table 1.

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[*] Trademark.

Conventional gas-phase processes run each of the three reactions in separate reactors. Recent process advances (Zahner, 1977; Slaugh, 1983) have attempted to conduct all three reactions, Reactions (1) - (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 the productivity. In addition, the 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? Firstly, 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 (Douglas, 1983; Moore, et al., 1989). Secondly, mixtures of DME and MeOH may have potential in the clean-burning oxygenated transportation market. On-board generation of DME has already been investigated by Karpuk and Cowley (1988) as means of improving methanol's cold-start characteristics. Finally, and perhaps most importantly, DME is a well-known intermediate in processes for converting synthesis gas to liquid fuels and chemicals (Chang, 1983; Shikada et al., 1983). 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 as well as economically viable single-step DME process. Early results from this program were included in a paper presented by Hsiung et al (1990). The current paper describes the progress to-date, and highlights the future plan.

Synthesis of Alternative Oxygenated Fuels

Another major goal of this research program is to investigate the liquid phase synthesis of alternative fuels from coal-derived syngas. Thus far work has been focused in two areas: 1) syngas conversion to mixed alcohols, and 2) one-step syngas conversion to methanol/hydrocarbon mixtures. Mixed alcohols are already known to have good gasoline blending characteristics. Methanol/hydrocarbon mixtures, M85 being an example, are potential stand-alone motor fuels.

The work on mixed alcohols synthesis focuses on conversion of syngas to mixed alcohols over an alkali-promoted Cu-based catalyst suspended in mineral oil:

$$nCO + 2nH_2 \overset{\text{Alk./Cu}}{\Longleftrightarrow} C_nH_{2n+1}OH + (n-1)H_2O.$$

The advantages in slurry phase operation shown in the LPMEOH process, such as effective reaction heat removal, should also apply to the mixed alcohols process. Other advantages, such as improved selectivity to higher alcohols due to the back-mixed nature of the slurry reactor, are also possible.

The concept of one-step conversion of syngas to methanol/hydrocarbon mixtures involves the use of a Cu/ZnO methanol synthesis catalyst together with an acid zeolite such as HZSM-5 in the same slurry reactor. The methanol produced from syngas over the Cu/ZnO catalyst reacts in-situ to DME and then to hydrocarbons over the HZSM-5:

$$CO + 2H_2 \xleftrightarrow{\mathrm{Cu/ZnO}} CH_3OH$$

$$2CH_3OH \xleftrightarrow{\mathrm{HZSM\text{-}5}} CH_3\text{-}O\text{-}CH_3 + H_2O$$

$$nCH_3\text{-}O\text{-}CH_3 \xleftrightarrow{\mathrm{HZSM\text{-}5}} \text{hydrocarbons.}$$

Key issues in developing this process include reaction liquid stability, product reaction rate, and selectivity. Also, since methanol/DME conversion to hydrocarbons generally operates at a higher temperature and lower pressure than methanol synthesis from syngas, the effectiveness of doing both reactions together needs to be investigated.

RESEARCH PROGRAM

Synthesis of Dimethyl Ether

The research program for the synthesis of dimethyl ether is divided in six sub-tasks (see Table 2). Sub-tasks 2.2, 2.3 and 2.4 involve experimental work in laboratory autoclaves. The plans include catalyst screening, process variable scans on the preferred catalyst system and life studies at optimum conditions. Sub-tasks 2.1 and 2.5 consist of process evaluation to set performance targets and detailed process and economic evaluations. Sub-task 2.6 involves planning for demonstration in the LaPorte AFDU.

Catalyst Selection

Commercially available catalysts were used in the study. Three powdered commercial methanol catalysts, designated as F21/0E75-43, F21/0E75-44 and F51/0E75-40, were selected from previous LPMEOH process development work (Hsiung, 1990). Three alumina-based dehydration catalysts, designated as A, B, and C, were selected and tested.

Experiments were conducted in mechanically stirred 300 ml autoclaves. 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 was used at 20 wt% catalyst loading. A stirring speed of about 1200 rpm was used to ensure that mass transfer effects were negligible. Feed gas was pre-blended and delivered into the system from cylinders. 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. Product gas was analyzed by on-line gas chromatography. A schematic of the equipment is shown in Figure 1.

Results for the three alumina-based catalysts evaluated are summarized in Figures 2a and 2b. Figure 2a shows how the DME productivity changes with gas-hourly-space-velocity (GHSV), and Figure 2b shows the methanol productivity versus GHSV. Since the same amount methanol catalyst (F21/0E75-43) was used in these experiments, a catalyst with higher dehydration activity would produce higher DME productivity at the expense of lower methanol productivity. From Figures 2a and 2b, Catalyst A shows the best dehydration activity. The methanol equivalent productivity (2*DME + MeOH) can still be improved, at least theoretically, with an even more active dehydration catalyst since there is unreacted methanol in the reactor effluent.

The methanol catalyst also affects the product distribution. A catalyst with a higher methanol activity should produce more methanol, and hence DME, if other conditions are held constant. Figure 3 compares the results for three commercial methanol catalysts. The same amount of Catalyst A was used in these experiments. 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 3, Catalyst F21/0E75-43 produced more than double the amount of DME/MeOH product. However, when used 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.

Comparison of Liquid Phase DME (LPDME) with LPMEOH Process

The results of LPDME are compared with LPMEOH results in Figures 4 and 5. For LPDME, the catalyst was a mixture of F21/0E75-43 and Catalyst A. The LPMEOH results were established using 100% F21/0E75-43 catalyst. Figure 4 presents the CO conversion as a function of GHSV. 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 CO 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 is plotted as a function of GHSV in Figure 5 and compared with the results from the LPMEOH process. 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.

Process Variable Study

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

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. After about 2 days on syngas to stabilize the catalyst activity, the pressure was varied in the range of about 5-10 MPa (750-1400 psig) at 250°C. Results from these tests at both 5000 and 9500 sl/kg-hr (GHSV) are plotted in Figure 6. 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.

After the pressure study, reactor temperature was increased from 250 to 260°C at 5.27 MPa (750 psig) and 9500 GHSV. Increasing the temperature from 250 to 260°C, increased the DME productivity while decreasing the methanol productivity (see Figure 7). 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. Coking of catalyst with formation of methane has been indicated in the literature for the dehydration reaction at temperatures greater than 310°C (Garg and Gupta, 1985; Comelli and Figoli, 1987). Bell and Chang (1981) 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 enough reaction rates without significant coking.

Effect of CO_2 removal was studied with the same catalyst system (another batch) using 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 water-gas shift to go forward, reacting 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 (Dow gas without CO_2). After about 45 hours on-stream, the feed was changed to Dow gas. The DME productivity was almost 90% higher when CO_2 was absent from the Dow gas (see Figure 8). The methanol productivity was about the same. After about 90 hours on-stream, the feed was changed back to the Dow gas without CO_2 to check for any deactivation. The DME productivity was about 20% lower than the initial productivity with the same gas. The drop is more than expected, and may be caused by slurry loss during feed change in addition to some catalyst deactivation. The 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%.

Additional tests were conducted at higher pressure during this run to check the dilution effect of CO_2. 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 9). Thus, the dilution effect of CO_2 is minimum. There was some increase in methanol productivity, which would be expected. It is interesting to note that the methanol productivities obtained from Dow gas as well as Dow gas without CO_2 are much higher than obtained from Texaco or Shell gas. This indicates that the catalyst system is not optimized for the former gases and lacks dehydration activity. Dow gas with or without CO_2 has a more balanced H_2/CO ratio and hence produces higher amount of methanol. Since, the methanol synthesis reaction is the pressure sensitive reaction, increasing pressure produces more methanol but the DME productivity does not increase.

Fuel Tests on DME/MeOH Mixtures

Three DME/MeOH mixtures were measured for their fuel properties. These mixtures were prepared with nominal DME concentrations of 1, 2 and 4 mole%. Southwest Research Institute (SwRI) was contracted to perform the measurement of flash point, Reid Vapor Pressure (RVP) and Octane Number. Results from these tests are compared with those from MeOH produced at

DOE's Alternative Fuels Development Unit (AFDU) at LaPorte and M85 (85 vol% MeOH in gasoline) in Table 3. With small amounts of DME added, significant improvements in both flash point and RVP were observed over MeOH. With a flash point of 7^{o}C and RVP of 6.4 psi, MeOH alone has a cold-start problem in winter conditions. Adding DME into MeOH brings those properties close to those of M85, an acceptable automobile fuel. The results indicate an average octane # of about 101 for the mixtures compared to 99 for LaPorte methanol and 97 for M85. These results are encouraging and more tests with DME/MeOH mixtures will be worthwhile.

Future Plans

Additional work under the process variable study will involve investigating the effect of water addition to hydrogen lean gas such as Shell gas. As mentioned earlier, the in-situ water gas shift would produce additional hydrogen and improve the MeOH and DME productivity. Also, we plan to briefly study DME synthesis with hydrogen-rich gas. Following the completion of the process variable study, a life test will be conducted for 500 to 1000 hours on-stream to estimate catalyst deactivation rates.

Demonstration Plans for DME Synthesis at the LaPorte AFDU

The next logical step in the development of slurry-phase DME synthesis technology is a demonstration at DOE's LaPorte Alternative Fuels Development Unit (AFDU). The AFDU is equipped with a 22.5" ID, 29 ft tall reactor. This facility has been used to successfully demonstrate slurry-phase methanol (MeOH) synthesis under previous DOE contracts. Production rates as high as 12 tons/day of MeOH were attained, limited only by the capacity of the feed compression equipment.

In addition to demonstrating the feasibility of mixed MeOH-DME synthesis in a single-stage, slurry reactor, the AFDU run will also verify that conclusions drawn in the laboratory are valid for intermediate and large-scale reactors. While bench-scale reactors are essential in demonstrating reaction feasibility and intrinsic kinetics, they cannot address many of the scale-up issues. Back-mixing in the reactor and mass transfer limitations, for example, are critical factors in commercial designs and cannot be adequately investigated in the lab. It is anticipated that data obtained from the AFDU will demonstrate the magnitude and importance of these two phenomena.

The initial demonstration at the AFDU will be of relatively short duration - only the most strategic process variables will be evaluated. The AFDU will be operated in such a manner as to simulate once-through flow of a predetermined coal gasifier-derived syngas. Different proportions of MeOH and DME catalysts will be evaluated. The first run will be 100% MeOH catalyst to establish the base-line catalyst activity. For each co-catalyst proportion, data will taken over a range of space velocities and superficial gas velocities.

AFDU Modifications

The existing LaPorte plant will require some modification to facilitate the DME demonstration. A simplified flowsheet of the as-modified plant is presented in Figure 10. The components which make the simulated syngas (H2, CO, and CO_2) are blended together, compressed, and combined with recycle gas. The combined stream is preheated in the heat exchanger (21.10) and introduced to the bottom of the slurry reactor (27.10). For DME synthesis, the typical reactor conditions are 250^oC and 5.27 MPa (750 psig). Within the reactor, catalyst is suspended in a white mineral oil. The upward movement of the synthesis gas is sufficient to agitate the slurry and form a homogenous, three-phase system. The MeOH, DME, and Shift reaction steps are all exothermic. The heat of reaction is initially absorbed by the slurry oil (which maintains excellent temperature control) and ultimately transferred to the utility-oil cooling loop through a tube bundle which is internal to the reactor.

The reactor effluent, which contains MeOH, DME, water, CO_2 and unreacted syngas, first passes through a cyclone separator (to remove entrained slurry), then is cooled in a heat exchanger (21.10) and directed to a separator (27.14). Within the separator, condensed oil is removed as a liquid and returned to the reactor. The vapor from the separator is processed in the MeOH Recovery section which consists of a cooling water exchanger and a number of phase-separators. MeOH and water (and some dissolved DME) are withdrawn at ambient pressure and temperature and sent to storage.

When this facility was set-up to demonstrate LPMEOH technology, the resultant gas from the MeOH Recovery section was recycled to the front-end (after a small fraction of flow was purged to remove inerts such as nitrogen). For the purpose of DME technology demonstration, further processing of the reactor effluent is required. The additional needs of the process are two fold: first, the CO_2 which is produced in the reactor must be removed to avoid its undesirable build-up in the synthesis loop and second, some quantity of DME needs to be recovered for the purpose of subsequent analysis. Within the DME & CO_2 Recovery section, DME and CO_2 are partially condensed from the vapor stream exiting the MeOH Recovery section. Imported refrigeration is utilized to affect the separation. The resultant vapor is recycled to the front-end as in the case of LPMEOH. The condensed DME/CO_2 stream is then partially vaporized to separate the bulk of the CO_2 from the DME. The CO_2-rich stream is sent to the flare, the DME-rich stream is directed to storage at ambient temperature and somewhat elevated pressure.

Future Directions

A new DOE contract, which is currently under negotiation, intends to make further modifications to the AFDU to provide deeper levels of CO_2 removal and allow for purification of reaction products. These modifications, which are scheduled to be completed by late summer in 1992, should allow greater flexibility to demonstrate a wider variety of syngas compositions as well as intermediate product recycle.

Synthesis of Alternative Oxygenated Fuels

Liquid Phase Syngas Conversion to Mixed Alcohols

The liquid phase synthesis of mixed alcohols was investigated using two catalysts: a commercial Cu/ZnO methanol synthesis catalyst and the same catalyst promoted with cesium. The Cs-promoted catalyst was used because the literature shows that the C_{2+} alcohol selectivity of a Cu-based methanol synthesis catalyst increases when doped with an alkali such as cesium (Nunan et al., 1989). The Cs-promoted catalyst was prepared by impregnation of the Cu/ZnO catalyst with an aqueous solution of cesium formate using a procedure similar to that of Nunan et al (1989). The target Cs-loading was 1.3 wt%, shown by later elemental analysis to be 1.1 wt%. A key issue addressed was the impact of the high CO_2 level in the coal-derived syngas on the effectiveness of the alkali-promoted Cu catalyst. The slurrying liquid used was Penreco Drakeol-10 mineral oil, the same liquid used in the LPMEOH process. It is noteworthy that this oil is stable in the presence of these catalysts at 300°C; no breakdown products were observed at 300°C in N_2 flow.

The experiments were conducted in 50 ml stirred micro-autoclave reactors operating in a continuous flow mode without recycle. The catalysts were activated in-situ by gradually raising the temperature to 240°C in a flow of 4% syngas in N_2. The syngas feed was simulated Texaco gasifier gas, which has a nominal composition of 51% CO, 35% H_2, 13% CO_2, and 1% N_2. The reaction conditions were 300°C and 7.0 MPa (1000 psig), conditions shown by pressure and temperature scans to be effective for the production of higher alcohols. Reaction products were analyzed on-line by gas chromatographs equipped with thermal conductivity (TCD) and flame ionization (FID) detectors.

Figure 11 shows the effect of gas-hourly space velocity (GHSV) on the alcohol production rate for each catalyst. Catalyst composition has little influence on the methanol rate, which increases linearly with GHSV. In fact, the product methanol concentration is relatively invariant with GHSV, suggesting that the methanol synthesis reaction is close to equilibrium across this range of GHSV. The Cs-promoted catalyst produces C_2-C_5 alcohols at a much higher rate than the unpromoted catalyst. For example, at a space velocity of 5,000 sl/kg-hr, the Cs-promotion results in about 50% greater C_2-C_5 alcohols production rate.

Figure 12 shows the alcohol product distribution obtained at 5,000 GHSV for each catalyst. As can be seen, Cs-promotion results in a higher selectivity to higher alcohols, particularly 1-propanol, isobutanol, and 2-methyl-1-butanol. The Cs-promoted catalyst, before and after 120 hr on syngas feed, was analyzed for Cs content. No measurable loss of Cs was observed.

One-Step Syngas Conversion to Methanol/Hydrocarbon Mixtures

Studies on the one-step synthesis of methanol/hydrocarbon mixtures from syngas are in a preliminary stage. Results will reported when we are further in to the studies.

Future Plans

Commercial as well as new higher alcohols catalysts will evaluated in the slurry reactor. Also, work will continue on the one-step conversion of syngas to methanol/hydrocarbon mixtures.

CONCLUSIONS

Synthesis of Dimethyl Ether

The new one-step DME process significantly improves the syngas conversion efficiency of the LPMEOH process. This improvement can be achieved by replacing a portion of methanol catalyst with 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 catalyst system employed as well as operating conditions. In this study, three alternative methanol catalysts and as many dehydration catalysts were investigated. A preferred catalyst system, consisting of a physical mixture of a methanol catalyst and an alumina, was identified. An improvement of about 50% in the methanol equivalent productivity was achieved compared to the liquid phase methanol process. With commercially existing methanol and dehydration catalysts, improvement in methanol activity has the greatest potential to further enhance the process performance.

A process variable study is underway with the preferred catalyst system. Results to date indicate that higher pressure and CO_2 removal benefit the process. Water injection studies with H_2-lean feed are planned. Following the completion of the process variable study, a life test will be conducted to estimate catalyst deactivation rates. Although the methanol catalyst has been proven to be stable in the LPMEOH reactor, its stability still needs to be studied in the presence of the DME catalyst.

The development work described here on DME synthesis at laboratory scale has laid a basis for an early demonstration of liquid phase DME technology in DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas.

Synthesis of Alternative Oxygenated Fuels

The slurry phase synthesis of C_2+ alcohols from high-CO_2, coal-derived syngas using an alkali-promoted methanol catalyst has been successfully demonstrated. Mineral oil has been shown to be a suitable reaction liquid based on its stability at high temperature.

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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 OFFGAS	1	58	16	25	0.02

TABLE 2

SYNTHESIS OF DIMETHYL ETHER (TASK 2)

OBJECTIVE: TO DEVELOP A SINGLE-STEP, SLURRY PHASE PROCESS FOR SYNTHESIS OF DME/MEOH FROM SYNGAS

SUBTASKS:

2.1 PROCESS EVALUATION PERFORMANCE TARGETS
2.2 DEFINITION OF PREFERRED CATALYST SYSTEM
2.3 PROCESS VARIABLE SCANS ON THE PREFERRED CATALYST SYSTEM
2.4 LIFE-TEST ON THE PREFERRED CATALYST SYSTEM
2.5 DETAILED PROCESS AND ECONOMIC EVALUATIONS
2.6 PLAN FOR DEMONSTRATING LPDME IN THE LAPORTE AFDU

TABLE 3

SwRI Test Results on DME/MeOH Mixtures

Blend	DME, mol % nominal	DME, wt% Gravimetric	Flash Pt. degree C	RVP, psi @ 37.8 C	Octane # RON	Octane # MON
1	1	1.52	-15	5.85	118.5	86.4
2	2	3.02	-25	8.40	120+	86.2
3	4	5.94	-40	12.60	113.0	84.5
LaPorte MeOH	NA	NA	7	6.4	111.1	87.0
M85	NA	NA	-65	10.3	108.8	85.6

URE 1

SCHEMATIC OF REACTOR SYSTEM

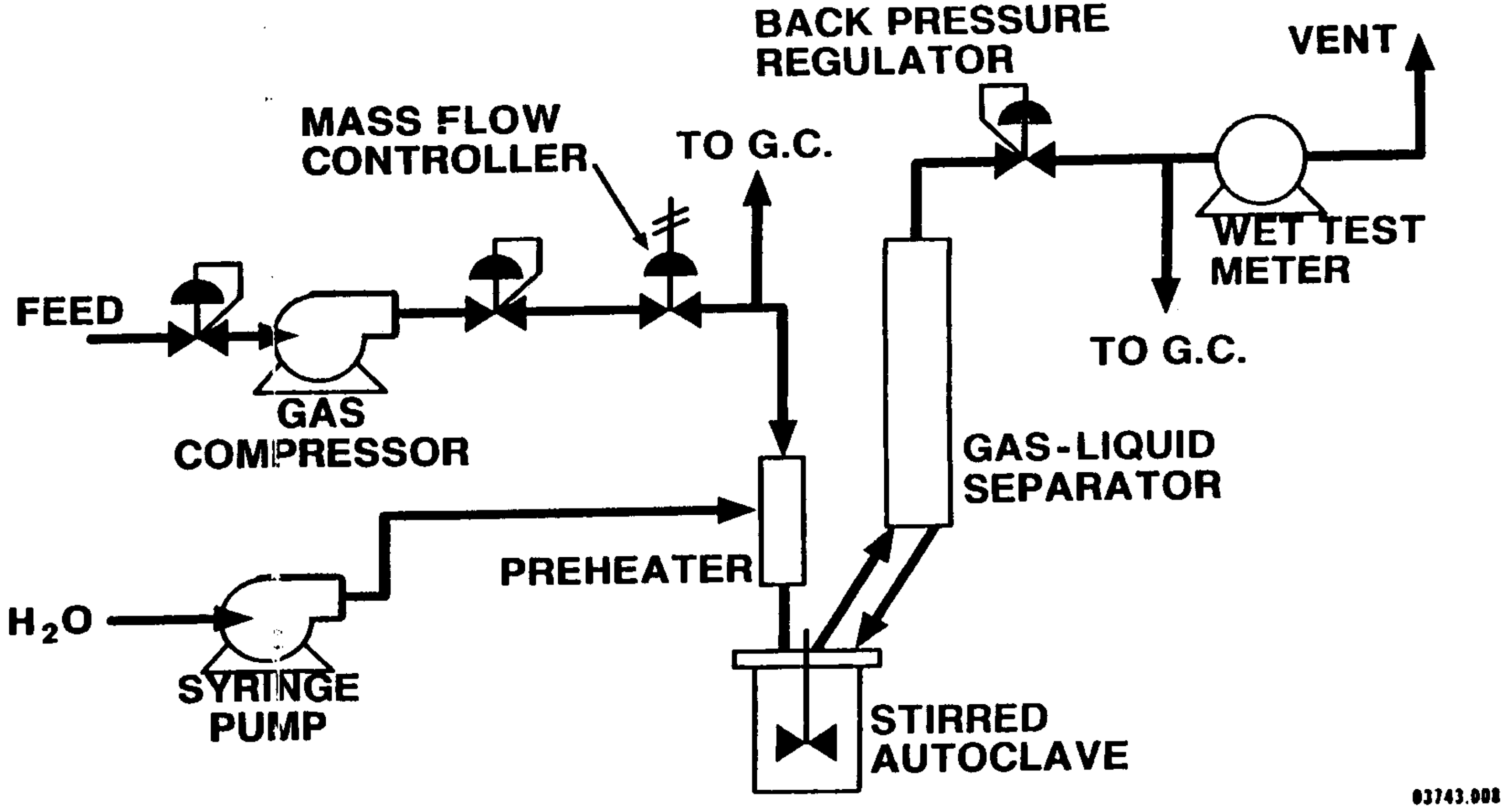
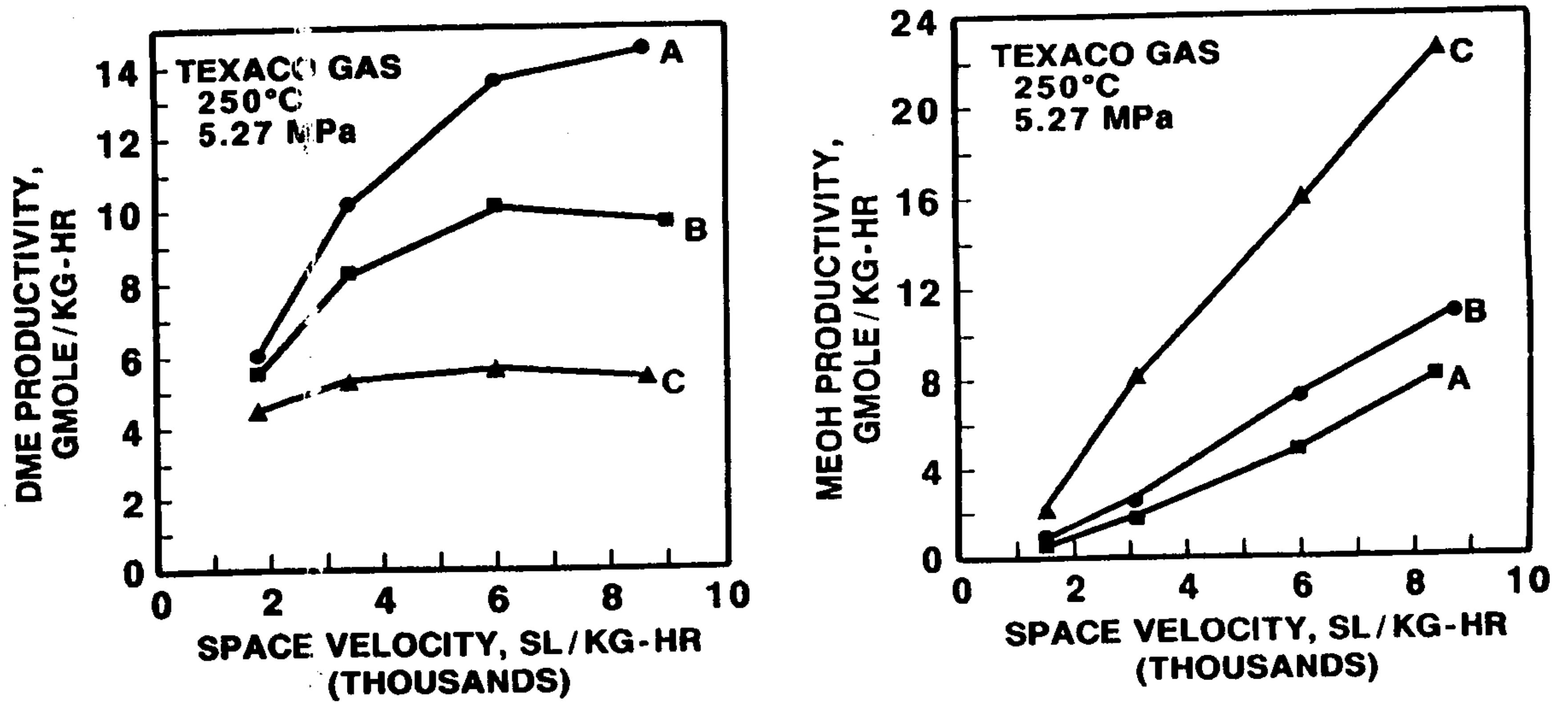


FIGURE 2

EFFECT OF DIFFERENT DEHYDRATION CATALYSTS

METHANOL CATALYST: F21/OE75-43



A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

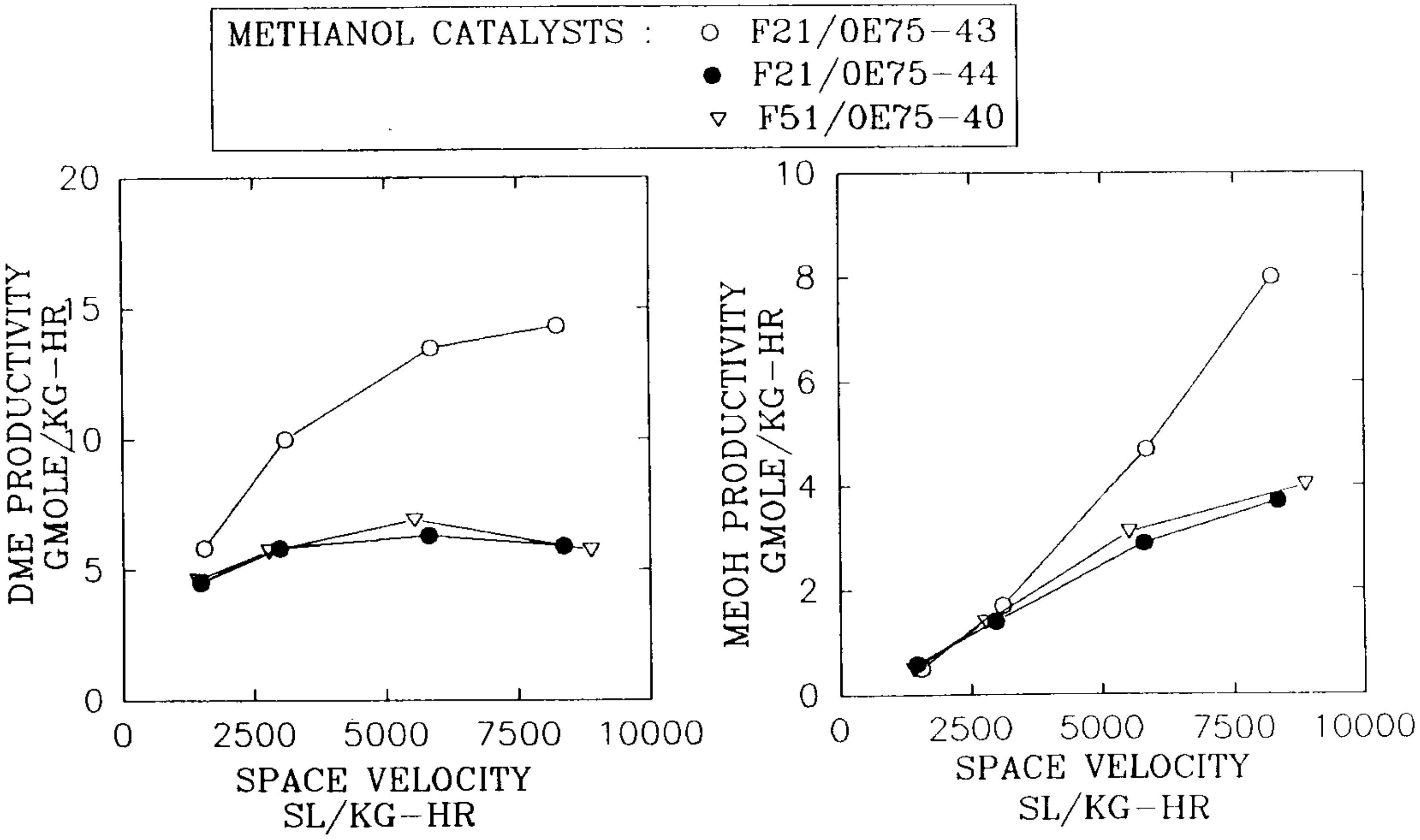
03743.008

FIGURE 3

EFFECT OF DIFFERENT METHANOL CATALYSTS

(TEXACO GAS, 250° C, 5.27 MPA)

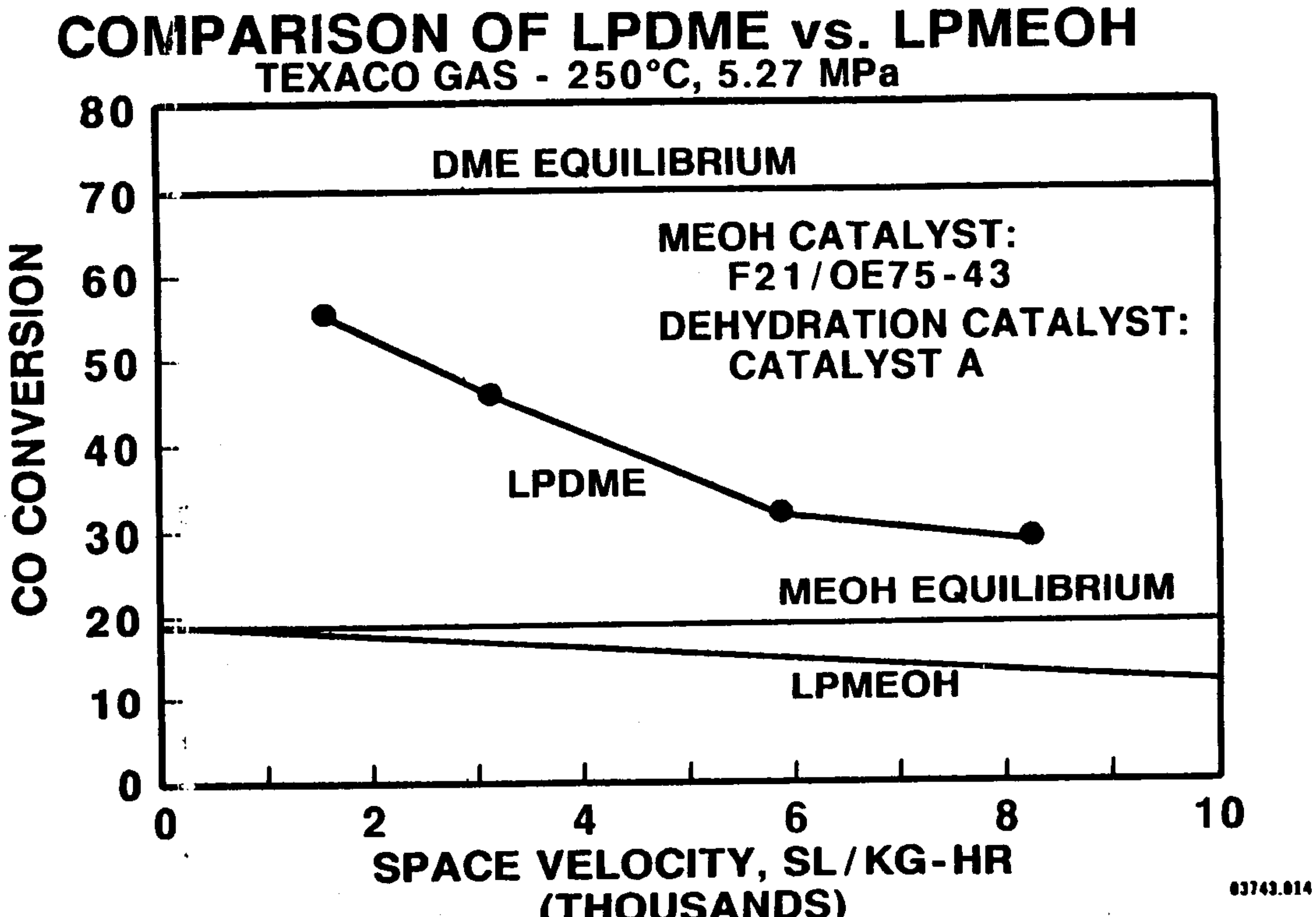
DEHYDRATION CATALYST : CATALYST A



A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

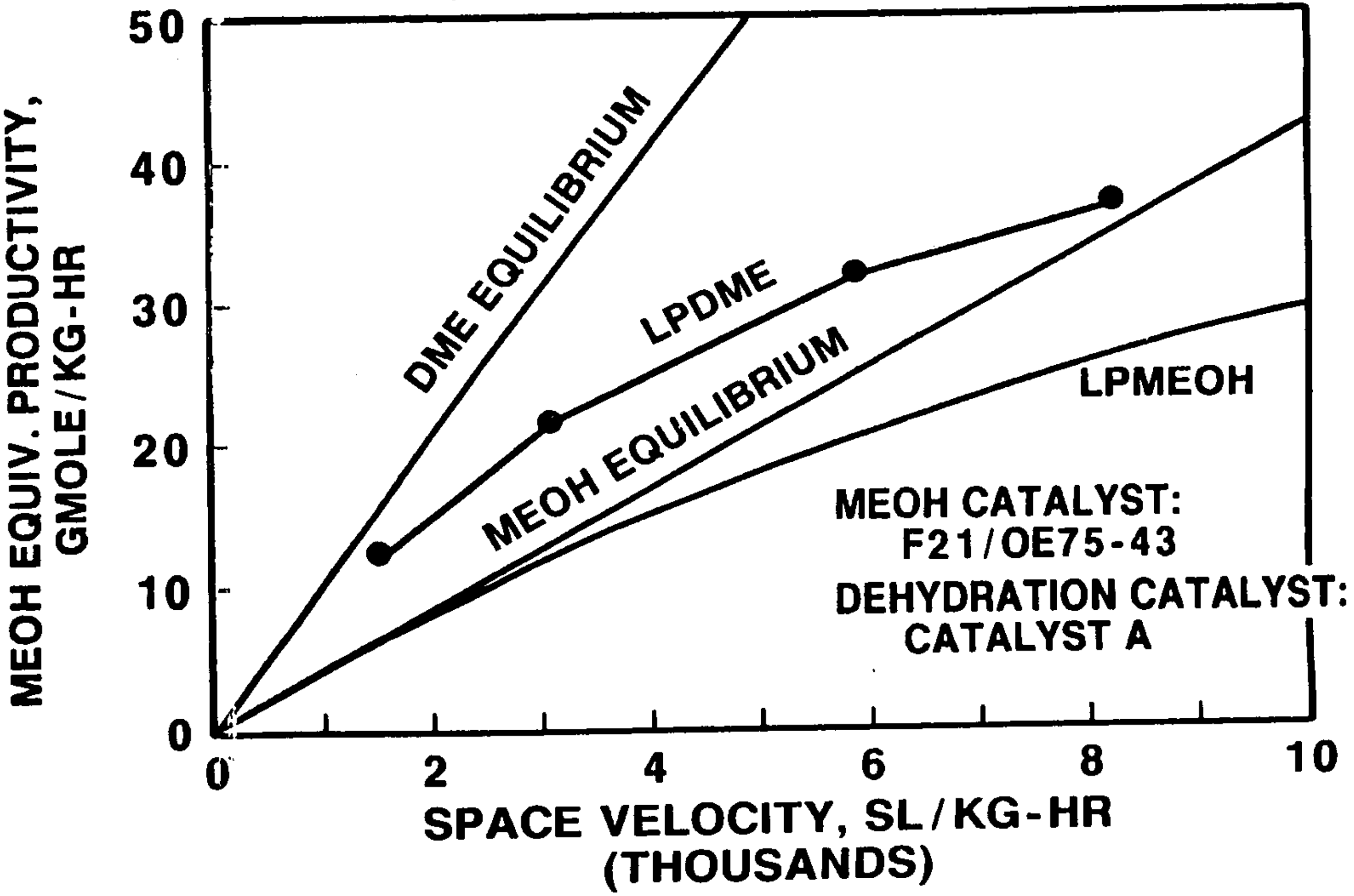
FIGURE 4


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

URE 5

COMPARISON OF LPDME vs. LPMEOH

TEXCO GAS, 250°C, 5.27 MPa
MEOH EQUIV. = 2*DME + MEOH



03743.015

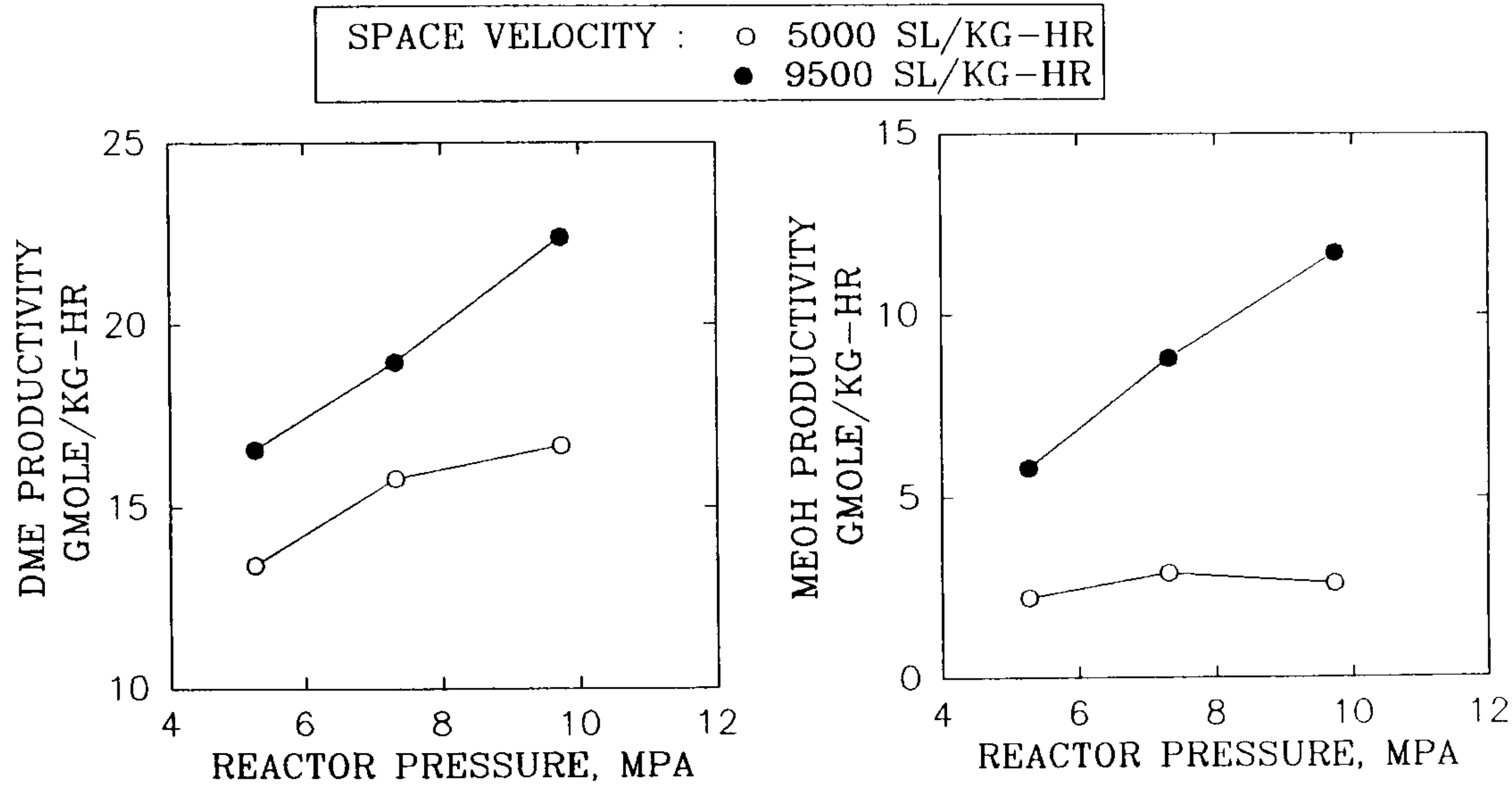
FIGURE 6

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

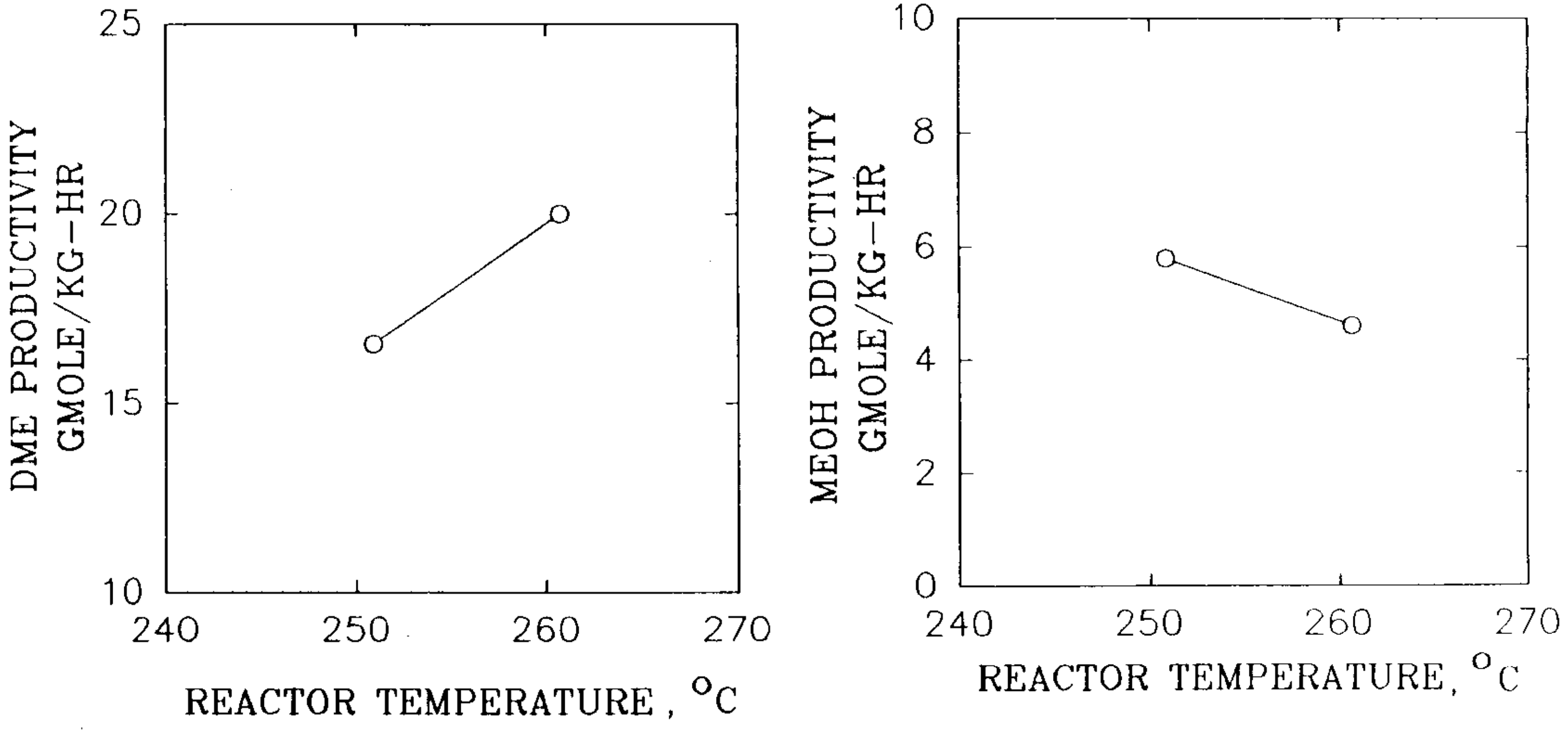
I 'RE 7

EFFECT OF TEMPERATURE ON DME SYNTHESIS

(SHELL GAS, 5.27 MPA, 9500 SL/KG-HR)

DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/0E75-43

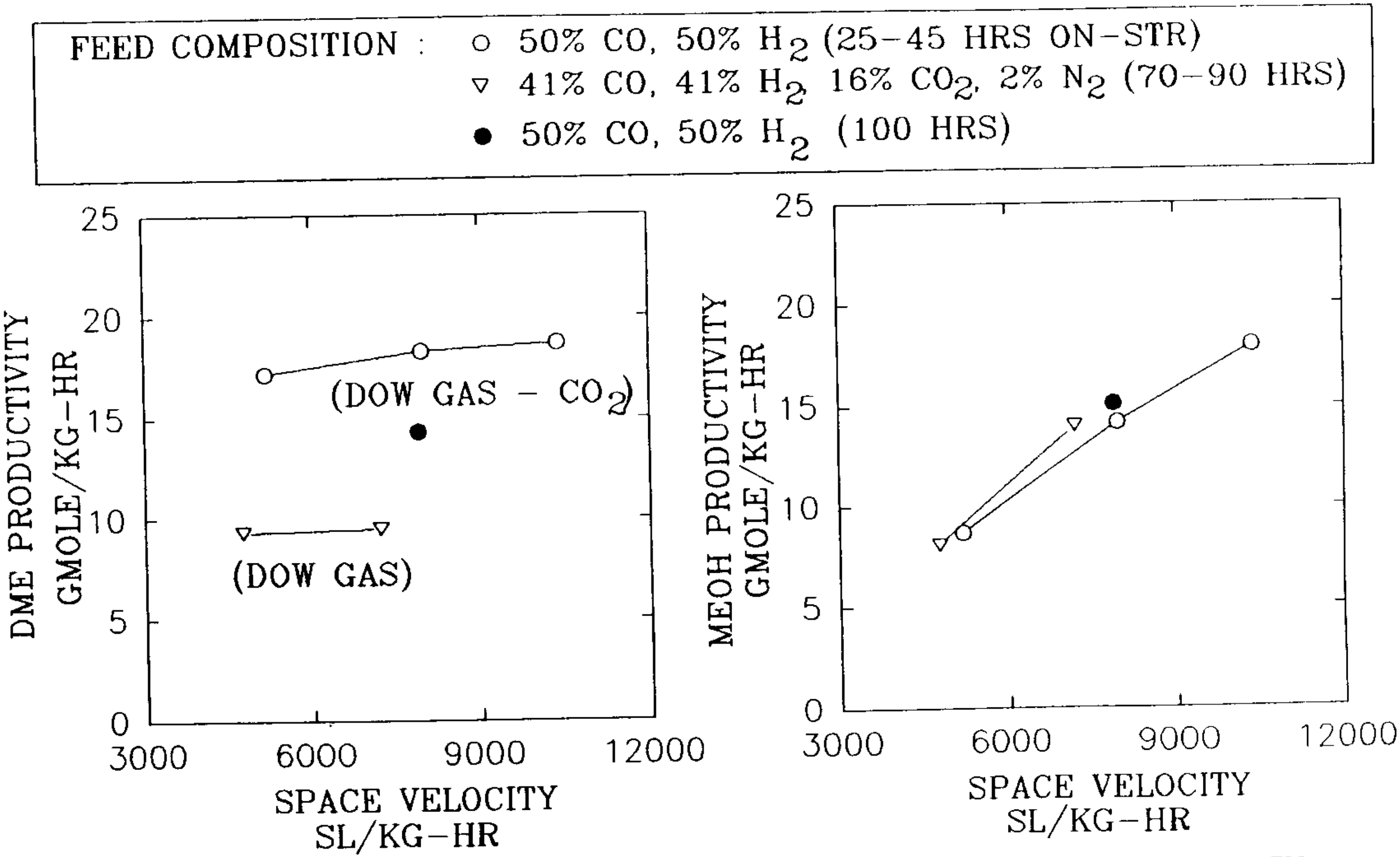


A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

FIGURE 8

EFFECT OF CO2 ON DME SYNTHESIS
(250° C, 5.27 MPA)
DEHYDRATION CATALYST : CATALYST A
METHANOL CATALYST : F21/0E75-43



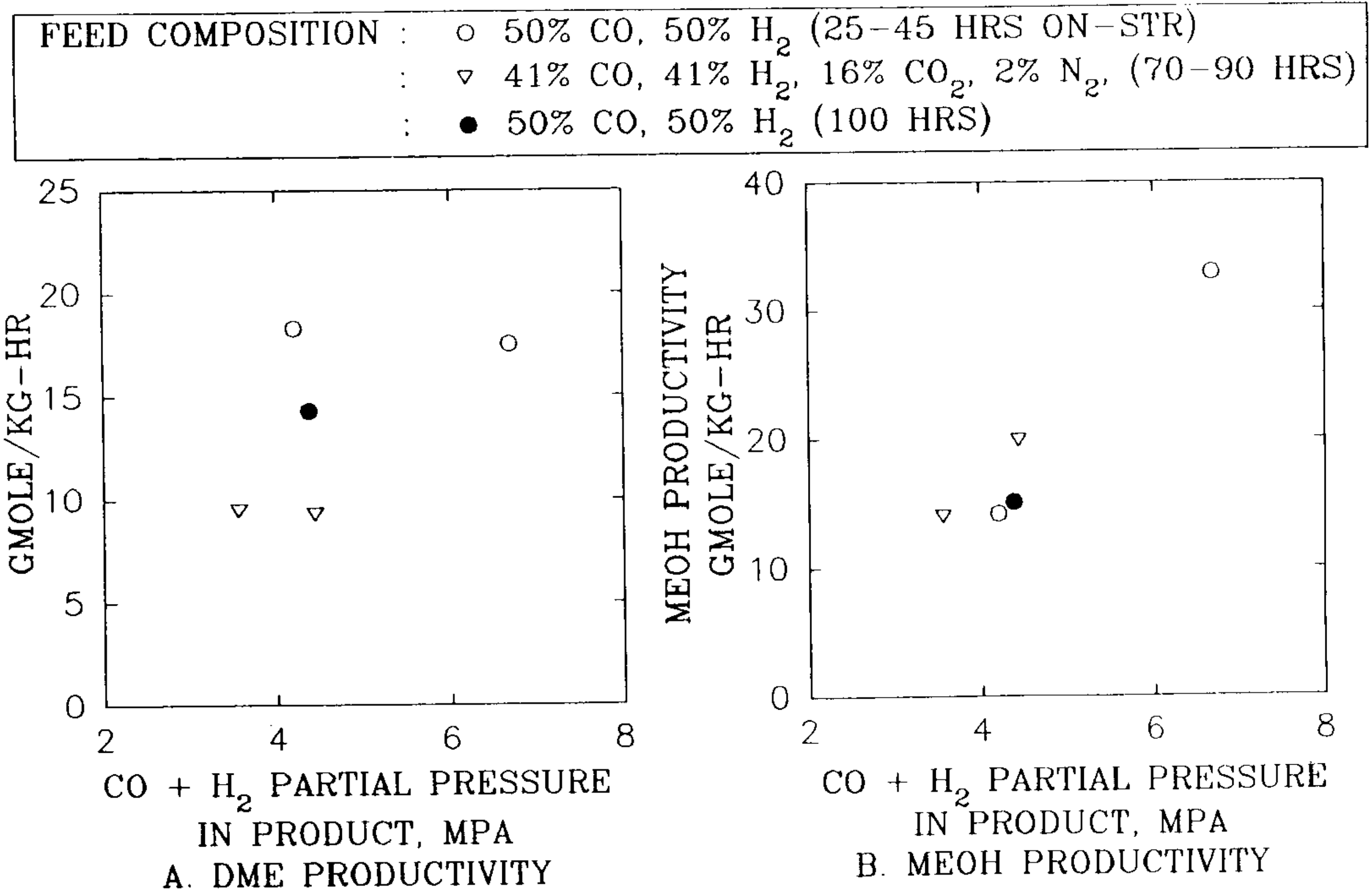
A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

URE 9

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



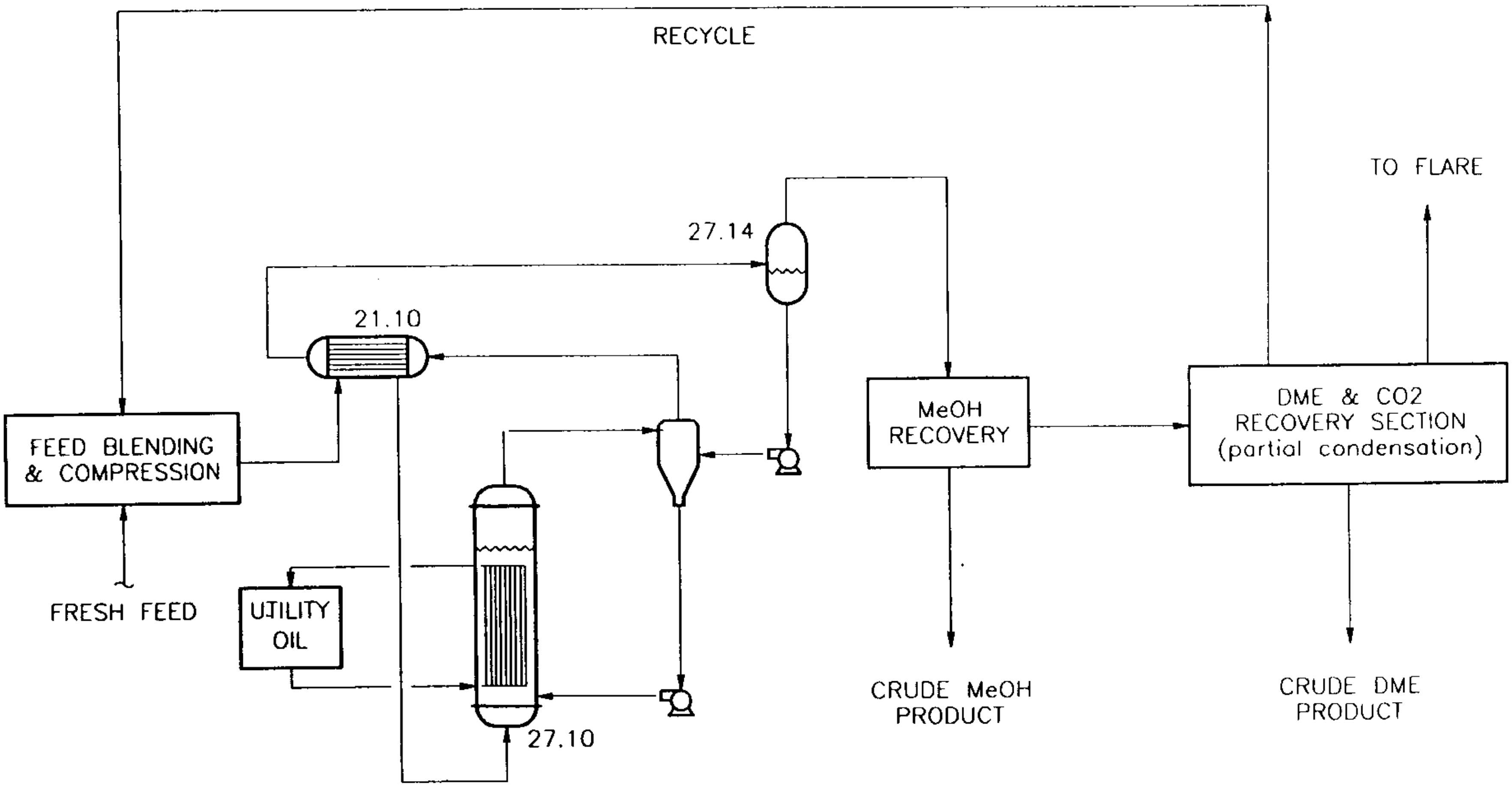
A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

FIGURE 10

LaPORTE ALTERNATIVE FUELS DEVELOPMENT UNIT

MODIFIED FOR MARCH 91 DME RUN



I JRE 11

Alcohol Production Rate vs. GHSV

Reaction Conditions: 300°C, 7.0 MPa, Texaco Gas

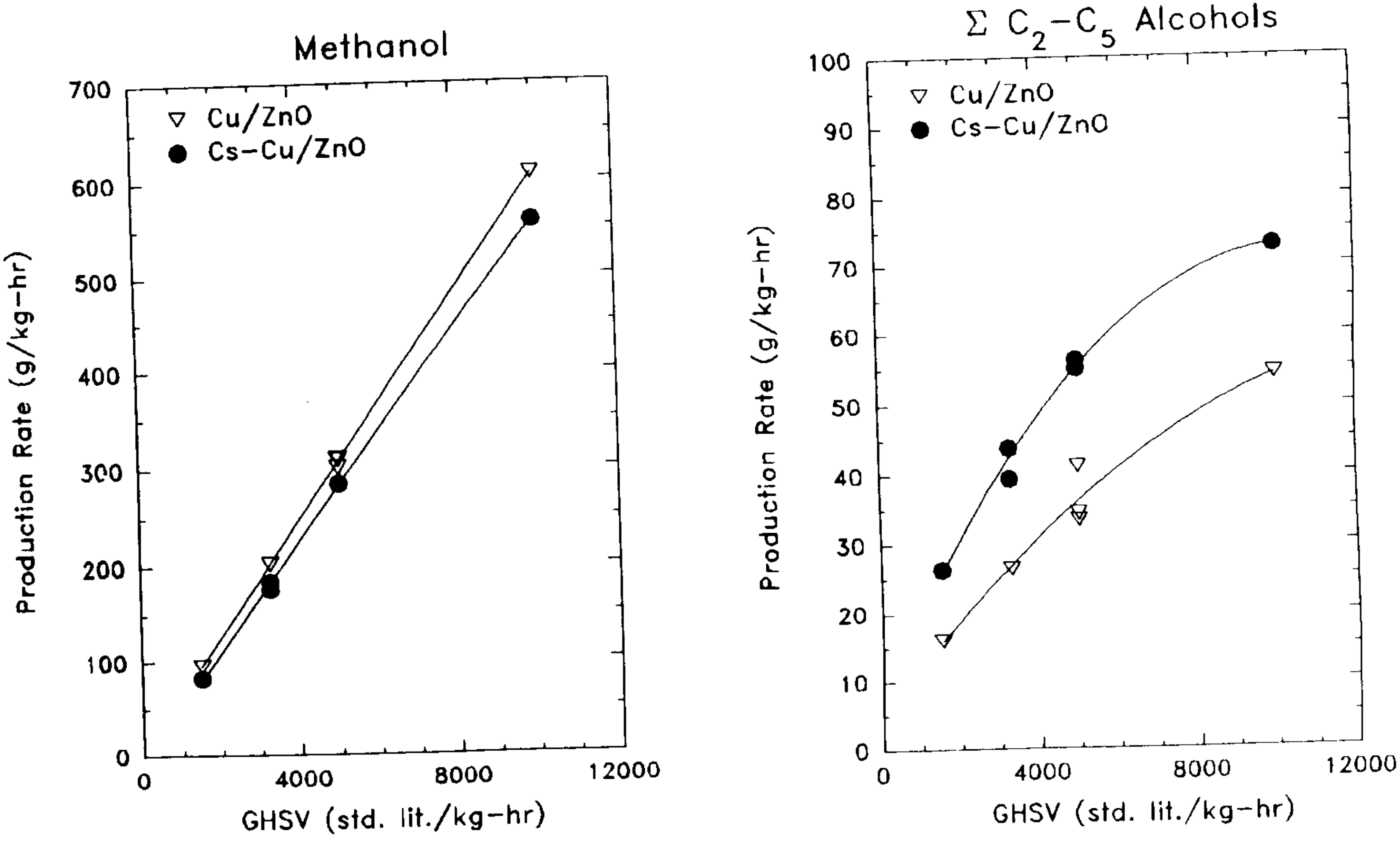


FIGURE 12

Product Alcohol Selectivity

Reaction Conditions: 300°C, 7.0 MPa 5,000 GHSV, Texaco Gas