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

Contractor

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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 CO₂ 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 quantities 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.

* 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:

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 H₂ 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

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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 H₂/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 H₂/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 H₂ 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 C₂ and C₃ 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/H₂ 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/H₂ 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 C₂-C₇ 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 H₂ conversion decrease with an increase of the respective component in the feed (see Figure 1). The total syngas (CO + H₂) conversion as well as DME production maximizes at a 50:50 CO:H₂ ratio in the feed. This is consistent with the overall reaction stoichiometry:

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 H₂ lean feed (see Figure 5), while addition of CO₂ 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, CO₂, CH₄, N₂, CH₃OH, C₂H₅OH, and CH₃OCH₃, and the other for H₂. 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 slurring liquid. About 30 grams of total catalyst were used at 20 wt% catalyst loading. The catalyst slurry was reduced in the autoclave using 2% H₂ in N₂ at 100 psig with a temperature ramping.

FIGURE 1

THERMODYNAMIC EQUILIBRIUM ESTIMATIONS

$\text{CO} + \text{H}_2 = \text{C}_2\text{H}_6\text{O} + \text{CH}_4\text{O} + \text{CO}_2 + \text{H}_2\text{O}$ @ 750 PSI/250 C

FIGURE 2

THERMODYNAMIC EQUILIBRIUM ESTIMATIONS

$\text{CO} + \text{H}_2 = \text{C}_2\text{H}_6\text{O} + \text{CH}_4\text{O} + \text{CO}_2 + \text{H}_2\text{O}$ 750 PSI/250 C

FIGURE 3

THERMO. EQU. AT 750 & 1500 PSIG

CO+H2=C2H6+CH4+CO2+H2O @ 250 C

FIGURE 4

THERMO. EQU. AT 250 & 300 DEG C

CO+H2=C2H6+CH4+CO2+H2O @ 750 PSIG

FIGURE 5

THERMO. EQU. WITH 10 % H₂O ADDITION (*)

C₀+H₂=C₂H₆O+CH₄O+C₀H₄O+C₀H₂O+H₂O @750 PSI/250 C

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/OE75-43, F21/OE75-44, and F51/OE75-40, 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% H₂, 13% CO₂, and 1% N₂, was used for catalyst screening.

Initial Experiments

Initial experiments were conducted with a 50:50 methanol to dehydration catalyst ratio. Catalyst F21-OE75-43 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 + H₂) 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/OE75-43 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 be 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.

DME SYNTHESIS WITH DIFFERENT DEHYDRATION CATALYSTS

(TEXACO GAS, 250°C, 5.27 MPa, 1500 SL/KG-HR)

METHANOL CATALYST : F21/OE75-43

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/OE75-43) 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/OE75-43 (81.25%) and Catalyst A (18.75%) while the LPMEOH results were established using 100% F21/OE75-43 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 CO₂. 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/OE75-43) 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.

FIGURE 9

L'PDME SYNTHESIS FROM TEXACO GAS

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

FIGURE 10

LPDME SYNTHESIS FROM TEXACO GAS

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

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**

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FIGURE 13

COMPARISON OF LPDME VS. LPMEOH

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

FIGURE 14

EFFECT OF DIFFERENT DEHYDRATION CATALYSTS

(TEXACO GAS, 250°C, 5.27 MPa)

METHANOL CATALYST : F21/OE75-43

DEHYDRATION CATALYSTS :
 ○ CAT. A
 ● CAT. B
 ▽ CAT. C
 ▼ CAT. E

A. DME PRODUCTIVITY

B. MEOH PRODUCTIVITY

Properties of various dehydration catalysts are summarized in Table 2. Surface areas range from 200 to 250 m²/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 it contains very few impurities. For example, it contains only 0.004% Na₂O and 0.005% Fe₂O₃ compared to 0.03% Na₂O and 0.04% Fe₂O₃ 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

METHANOL CATALYSTS : ○ F21/OE75-43
● F21/OE75-44
▽ F51/OE75-40

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/OE75-43 (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/OE75-43 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)**

Figure 16

Figure 17

EFFECT OF PRESSURE ON DME SYNTHESIS

(SHELL GAS, 250°C)

DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/OE75-43

SPACE VELOCITY : ○ 5000 SL/KG-HR
● 9500 SL/KG-HR

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 H₂ 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% H₂, 13% CO₂, and 1% N₂, 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/OE75-43

SPACE VELOCITY : ○ 4800 SL/KG-HR
 ● 8200 SL/KG-HR
 ▽ 10600 SL/KG-HR

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/OE75-43

REACTOR PRESSURE	○ 2.86 MPa
	● 5.27 MPa
	▽ 7.34 MPa
	▼ 9.74 MPa

After the pressure/space velocity study, the reactor 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 CO₂ Removal

Effect of CO₂ 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% H₂, 16% CO₂, and 2% N₂). Absence of CO₂ 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% H₂ ("stoichiometric gas", Dow gas without CO₂). After about 45 hours on-stream, the feed was changed to Dow gas. DME productivity was almost 90% higher when CO₂ 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 CO₂ 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 CO₂ 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/OE75-43

A. DME PRODUCTIVITY

B. MECH PRODUCTIVITY

Figure 21

EFFECT OF CO₂ ON DME SYNTHESIS

(250° C, 5.27 MPa)

DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/OE75-43

FEED COMPOSITION : ○ 50% CO, 50% H₂ (25-45 HRS ON-STR)

▽ 41% CO, 41% H₂, 16% CO₂, 2% N₂ (70-90 HRS)

● 50% CO, 50% H₂ (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/H₂ PARTIAL PRESSURE ON DME SYNTHESIS (250° C, 7500 SL/KG-HR)

DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/OE75-43

FEED COMPOSITION : ○ 50% CO, 50% H₂ (25-45 HRS ON-STR)
 : ▽ 41% CO, 41% H₂, 16% CO₂, 2% N₂, (70-90 HRS)
 : ● 50% CO, 50% H₂ (100 HRS)

Figure 23

EFFECT OF FEED COMPOSITION ON DME SYNTHESIS

(250° C, 5.27 MPa)

DEHYDRATION CATALYST : CATALYST A

METHANOL CATALYST : F21/OE75-43

FEED COMPOSITION :

- TEXACO GAS-51% CO, 35% H₂, 13% CO₂, 1% N₂
- SHELL GAS-66% CO, 30% H₂, 3% CO₂, 1% N₂
- ▽ DOW GAS-41% CO, 41% H₂, 16% CO₂, 2% N₂
- ▼ 50% CO, 50% H₂
- H₂ RICH-15% CO, 74% H₂, 7% CO₂, 4% N₂

A lower amount of water addition was investigated next. Run No. 10454-77 started with expected productivities but the catalyst performance declined sharply after the water addition was started. The mass balance indicated a significant amount of unaccounted CO_2 in the product, suggesting more water going to the reactor than measured. The run was aborted. When the system was taken apart, we discovered that a significant amount of slurry had left the reactor. A mixture of catalyst slurry and water was found in a trap on the gas-liquid separator return line. We believe there were surges in the water injection system as well as the reactor during the run. The water injection system needed significant modifications to improve the operation of the system. In view of other priorities, no further water injection experiments were conducted in this program.

REACTION MODEL

A simple reaction model was developed to predict trends during the lab studies^[24]. The model was based on the rate expressions for methanol synthesis^[25], methanol dehydration^[8], and water-gas shift^[26] as given in Table 5. For a CSTR, the rates of reactions were computed from the outlet component fugacities. The order of methanol dehydration reaction (N) was assumed to be 1 for simplicity. A computer program was written which would calculate product rates for given rate constants and operating conditions, or alternately back-calculate rate constants at a given condition and product rate.

CATALYST ACTIVITY MAINTENANCE STUDY

Life Run with Texaco Gas

A life run (Run No. 11483-81) was conducted for DME/methanol synthesis with S3-86/Catapal (4.33:1) catalysts using Texaco gas. The operating conditions were 250°C, 750 psig, and 6000 GHSV. The anticipated DME/methanol ratio at these conditions was about 2. Results of the life run are presented in Figures 24 and 25. Initial DME productivity was somewhat higher than expected, but it also showed a sharper initial drop. Over about 620 hours on-stream, DME productivity showed a steady decline. Initially, methanol productivity increased slightly. However, it remained steady most of the run and declined towards the end.

Rate constants were estimated using the DME/methanol model described above and are presented as a function of on-stream time in Figure 26. An exponential decay expression was used to correlate the rate constants with on-stream time. The results are summarized in Table 6. Both the methanol and dehydration catalysts showed a decline in activity. However, the methanol catalyst (S3-86) had a much larger decline (4.4%/day) compared to the dehydration catalyst (Catapal, 1.3%/day). Also, while the Catapal appeared to be stabilizing in the second half of the run, the BASF S3-86 seemed to be declining faster. The deactivation rate of the S3-86 catalyst is very high for commercial application. However, the decline rate was not large enough to have an impact on the results from the process variable study, which was typically conducted between 50 and 150 hours on-stream.

After the run, the spent catalyst was analyzed for Fe and Ni to check for metal carbonyl poisoning. Results from atomic adsorption tests indicated about 120 ppm Fe and 35 ppm Ni on the catalyst. This suggests only a small pick-up of Fe and Ni from their initial levels of about 70 ppm and 20 ppm, respectively. Hence, Fe or Ni can be ruled out as possible causes for deactivation.

Table 5

REACTION MODELS

METHANOL SYNTHESIS:

$$r_1 = k_1 f_{CO}^{\frac{1}{3}} f_{H_2}^{\frac{2}{3}} \left(1 - \frac{f_{MEOH}}{K_{eq_1} f_{CO} f_{H_2}^2} \right)$$

METHANOL DEHYDRATION:

$$r_2 = k_2 f_{MEOH}^N \left(1 - \frac{f_{DME} f_{H_2}}{K_{eq_2} f_{MEOH}^2} \right)$$

WATER-GAS SHIFT:

$$r_3 = k_3 f_{CO} f_{H_2O} \left(1 - \frac{f_{CO_2} f_{H_2}}{K_{eq_3} f_{CO} f_{H_2O}} \right)$$

FIGURE 24

DME SYNTHESIS LIFE STUDY

TEXACO GAS, S3-86/CATAPAL = 4.33
250° C, 5.27 MPA, 5700 SL/KG-HR

FIGURE 25

DME SYNTHESIS LIFE STUDY

TEXACO GAS, S3-86/CATAPAL = 4.33
250° C, 5.27 MPA, 5700 SL/KG-HR

FIGURE 26

DME SYNTHESIS LIFE STUDY

TEXACO GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 5700 SL/KG-HR

Table 6

DEACTIVATION RATES DURING DME SYNTHESIS LIFE RUN (RUN NO. 11483-81)

EXPONENTIAL DECAY EXPRESSION FOR RATE CONSTANTS:

$$k = k_0 \cdot \exp (- \alpha \cdot t / 100)$$

where k = rate constant, gmole/hr-kg-atm

k_0 = initial rate constant, gmole/hr-kg-atm

α = deactivation rate, %/day

and, t = on-stream time, days

ON-STREAM TIME, HOURS	METHANOL CATALYST		DEHYDRATION CATALYST	
	BASF S3-86 α , %/DAY		CATAPAL α , %/DAY	
50 - 620	4.4		1.3	
50 - 330	3.3		2.4	
330 - 620	6.3		< 1	

Based on information available from literature, a possible cause of the deactivation is deposition of coke on the S3-86. The spent catalyst was analyzed for graphitic carbon using Raman Spectroscopy. Out of the four spectra of the spent catalyst, two spectra had bands where a peak of graphite was expected. Slurry with fresh catalyst only showed bands for mineral oil. This confirms the presence of some coke on the spent catalyst. Quantification, however, is not possible from this technique. Analysis of a spent catalyst from a previous methanol life run (Run No. 10892-45) also indicated graphitic carbon (four out of five spectra). Therefore, coking as a main cause of deactivation cannot be confirmed.

XRD analysis of the spent catalyst was conducted to measure Cu crystallite size. Results indicate Cu crystallite size grew from 90 Å to about 220 Å, which is somewhat higher than about 150 Å expected for spent LPMEOH catalyst. It should be noted, however, that the temperature control of the reactor during the entire run was excellent (248–252°C). Hydrothermal sintering could, however, occur as higher water concentration exists in the LPDME reactor compared to the LPMEOH reactor.

Life Run with Shell Gas

A second life run (Run No. 11782-03) was conducted with S3-86/Catapal (4.33:1) catalysts using Shell gas instead of Texaco gas as feed. Operating conditions similar to the Texaco gas life run were used: 250°C, 750 psig, and 6000 GHSV. As indicated above, there was some growth in Cu crystallite size during the life run with Texaco gas. Texaco gas contains high amounts of CO₂, which reduces the extent of the water-gas shift. Thus, a significant amount of water (as much as 2%) is present in the reactor using Texaco gas as a feed. Shell gas, on the other hand, contains less CO₂, less H₂, and more CO, which helps the shift reaction go much further. Hence, water concentration in the reactor with Shell gas is lower. If the deactivation is indeed due to hydrothermal sintering, the catalyst should be much more stable with Shell gas.

DME/methanol productivities as well as effluent concentrations during the life run are presented in Figures 27 and 28. Initial productivities were close to expected. However, over 500 hours on-stream, DME productivity showed a steady decline. Methanol productivity was steady earlier, but declined later in the run.

Rate constants were estimated using the DME/methanol reaction model and are presented as a function of on-stream time in Figure 29. An exponential decay expression was used to correlate the rate constants with on-stream time. The results are compared with the Texaco gas life run in Table 7. The deactivation rates were very similar for both runs. The methanol catalyst (S3-86) had a much larger decline rate compared to the dehydration catalyst.

The spent catalyst was analyzed for Cu crystallite size as well as Fe, Ni, Cl⁻, S, and graphitic C. The results are compared with those from earlier life runs with Texaco gas in Table 8. The Cu crystallite size growth was similar during both runs. This indicates that hydrothermal sintering may not be the main cause of deactivation since water concentration in the reactor during the Shell gas run was much lower than during the Texaco gas run. The chemical analysis of the spent catalysts does not show any significant poisoning of the catalyst. Raman Spectroscopy analysis did not detect the presence of any graphitic carbon. Therefore, coking as the main cause of deactivation cannot be confirmed.

FIGURE 27

DME SYNTHESIS LIFE STUDY

SHELL GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 6000 SL/KG-HR

FIGURE 28

DME SYNTHESIS LIFE STUDY

SHELL GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 6000 SL/KG-HR

FIGURE 29

DME SYNTHESIS LIFE STUDY

SHELL GAS, S3-86/CATAPAL = 4.33
250°C, 5.27 MPA, 6000 SL/KG-HR

Table 7

DEACTIVATION RATES DURING DME SYNTHESIS LIFE RUNS

EXPONENTIAL DECAY EXPRESSION FOR RATE CONSTANTS:

$$k = k_0 \cdot \exp (- \alpha \cdot t / 100)$$

where k = rate constant, gmole/hr-kg-atm

k_0 = initial rate constant, gmole/hr-kg-atm

α = deactivation rate, %/day

and, t = on-stream time, days

FEED GAS	RUN NO.	ON-STREAM TIME, HOURS	MEOH CATALYST BASF S3-86 α , %/DAY	DEHY. CATALYST CATAPAL α , %/DAY
TEXACO	11483-81	50-620	4.4	1.3
SHELL	11782-03	50-500	4.8	< 1

TABLE 8 Analysis of Catalyst Samples				
Analysis	Method	Fresh Catalyst	Spent Catalyst Texaco Gas Run (Run No. 11483-81)	Spent Catalyst Shell Gas Run (Run No. 11782-03)
Cu Cryst. Size	XRD	90Å	220Å	225Å
Fe	Atom. Ads.	70 ppm	120 ppm	40 ppm
Ni	Atom. Ads.	220 ppm	35 ppm	75 ppm
Cl ⁻	Atom. Ads.	<150 ppm	<150 ppm	<150 ppm
S	Atom. Ads.	<50 ppm	<50 ppm	<50 ppm
Graphitic C	Raman Spect.	No	Yes	No

A life run for methanol synthesis with DME injection is recommended to see if DME produces by-products that are detrimental to catalyst stability. Also, life runs at conditions which would inhibit coking are suggested. For example, operating at a lower temperature (240°C) or higher space velocity (9000 GHSV) could improve stability. Catalyst systems with lower alumina proportions may have better catalyst life as lower DME and H₂O concentrations will exist in the reactor. Additional DME life studies are suggested for future programs.

SEDIMENTATION TESTS FOR DEHYDRATION CATALYST

Sedimentation tests were conducted for Catapal gamma alumina, BASF S3-86, and their mixtures. The purpose of these tests was to compare slurry properties of the dehydration catalyst to that of the methanol catalyst. The sedimentation tests show a collective effect of particle properties such as size, density, shape and orientation, and interference from neighboring particles. Fluid viscosity and density also affect the sedimentation rate. Fast settling rate and tighter packing are preferred slurry properties. Smaller packing volume is also desirable from a volumetric productivity point of view, since it allows loading of more catalyst (weight basis) into a fixed reactor volume.

The tests were conducted with 19 grams of catalyst and 77.85 grams of Drakeol-10 oil in a 100 ml graduated glass cylinder. The separation line between the concentrated and the dilute phase was noted visually. Results of these tests are summarized in Table 9 and Figure 30. As expected from the density and particle size difference, the alumina has a slower settling rate and looser packing than the methanol catalyst. However, the difference is not large. The 80/20 mixture, which is considered optimum for DME synthesis, is only slightly different than the methanol catalyst. Also, the two catalysts did not separate into two visible layers. Hence, the slurry property of the mixture is quite acceptable.

TABLE 9 Sedimentation Test for Methanol and Dehydration Catalysts in Drakeol-10 Oil (19 gms of catalyst in 77.85 gms of oil)				
BASF S3-86 Catapal	100% 0%	80% 20%	50% 50%	0% 100%
Time, Min	Volume of Slurry, ml			
0	98	98	99	99
15	56	68	70	79
30	37	45	48	55
45	32	37	41	49
60	30	34	36	44
75	29	32	34	40
90	28	31	32	37
105	28	30	31	35
120	27	29	30	33
960	27	28	29	32

CATALYST PREPARATION FOR LAPORTE DME RUN

LaRoche Chemicals was contracted to heat treat about 2,000 lbs of Catapal alumina for use as a dehydration catalyst at LaPorte. A 200 lb trial batch was prepared by LaRoche. The surface area (SA) for this lot was about 200 m²/g as compared to Air Products' laboratory prepared Catapal with a SA of about 225 m²/g. Temperatures in the LaRoche pilot plant were greater than 550°C, in contrast to the lab heat treatment at 500°C. However, the temperatures required in the two units to produce similar products were not expected to be the same.

The LaRoche heat-treated Catapal was activity tested in the 300 cc autoclave (Run No. 11483-94). The tests were conducted with Texaco gas at 250°C, 750 psig, and 6000–9000 GHSV. BASF S3-86 was used as the methanol catalyst with S3-86/Catapal ratio of 4.33. DME and methanol productivities from these two tests are compared with those from lab prepared Catapal catalysts in Figure 31. Two lab prepared catalysts are presented in the figure: Catapal heat treated at a typical temperature of 500°C (SA=225 m²/g) and Catapal heat treated at 550°C (SA=200 m²/g). The performance of the pilot scale preparation (Batch A) of Catapal appears to be about the same as both the lab prepared Catapal catalysts.

Loss on Ignition (LOI) tests were conducted on the pilot scale (Batch A) and the lab prepared aluminas. Results from these tests are summarized in Table 10. The pilot plant prepared alumina had significantly higher weight loss from ambient to 300°C (physical water). However, both the catalysts showed about 1% weight loss from 300 to 500°C (chemical water). The higher physical water in the pilot batch was probably due to readsorption of water during cooling and packing. This was not a concern since this water would be removed in the reactor which is typically at 250°C. The chemical water content, however, must be kept at a minimum (around 1%) as it remains in the alumina at reaction temperatures.

FIGURE 30

SEDIMENTATION TEST FOR METHANOL AND
DEHYDRATION CATALYSTS IN DRAKEOL-10
(19 GMS OF CATALYST IN 77.85 GMS OF OIL)

FIGURE 31

SCALE-UP OF ALUMINA PREPARATION FOR DME SYNTHESIS
(METHANOL CATALYST : S3-86 (81%), TEXACO GAS, 250°C, 750 PSIG)

ALUMINA (19%) :
 ▲ PILOT SCALE PREP OF CATAPAL (BATCH "C", NEW PDU)
 ▲ PILOT SCALE PREP OF CATAPAL (BATCH "A", OLD PDU)
 □ LAB SCALE PREP OF CATAPAL. (500°C)
 ■ LAB SCALE PREP OF CATAPAL. (550°C)

TABLE 10 Loss on Ignition (LOI) Test Results for Catapal Samples			
Catalyst	Lab Heat Treated Catapal	Old Pilot Plant Heat Treated Catapal Batch A	New Pilot Plant Heat Treated Catapal Batch C (Double Heat Treat)
Weight Loss from Ambient to 300°C	0.4%	3.8%	1.2%
Weight Loss from 300 to 500°C	1.2%	1.1%	1.7%

While work continued with LaRoche to get higher SA alumina with low water content, LaRoche switched to a new pilot unit and had difficulties in producing the same quality material as the old pilot unit. The old pilot unit was no longer available. After several trials, LaRoche was able to bring the LOI down to a reasonable level. The LOI from 300 to 500°C for the alumina (Batch C), which was heat treated twice in the new pilot unit, was about 1.7% compared to 1.2% for the heat treated Catapal (see Table 10). The surface area for this batch was about 250 m²/g, which was our target level. The activity test (Run No. 11728-18) of this batch indicated significantly less DME and more methanol productivities than the lab prepared as well as the old pilot unit (PDU) prepared aluminas (see Figure 31). This indicated lower than expected activity for Batch C. Considering slightly higher than expected LOI and SA along with lower activity, it appeared that the heat treatment was incomplete.

LaRoche modified the new PDU to allow lower alumina feed rate, resulting in higher heat treatment temperature. However, an activity test on a sample from this batch (Batch D) did not show any improvements over Batch C. Also, the LOI and SA were slightly higher than expected indicating that the heat treatment was still incomplete.

At that point, LaRoche indicated that they could not make any further improvements in the heat treatment. Their new PDU was a direct fired heat treater while the old PDU was an indirect fired rotary kiln. They referred us to Vista Chemicals, which frequently gets Catapal heat treated at Discovery Chemicals on a toll basis. Discovery Chemicals has an indirect fired rotary kiln. Contacts with Vista Chemicals revealed that they have a commercial heat treated gamma alumina powder catalyst, Catapal-G. However, the SA of Catapal-G is lower than our lab prepared alumina (150 vs. 225 m²/g).

Since we were close to the start up of the DME demonstration at LaPorte, no further work was conducted on the scale-up. It was decided to use alumina from Batch A at LaPorte, which had acceptable properties and enough alumina available for the LaPorte operations (200 lbs).

EFFECT OF REDUCTION PROCEDURE ON DME SYNTHESIS

During the DME R&D work, the methanol catalyst was always activated using dilute hydrogen (2% H_2 in N_2) for simplicity. The methanol catalyst was loaded along with the dehydration catalyst and then the activation was carried out in the reactor.

The run plan at LaPorte involved first a methanol run, followed by two DME runs. Reduction using dilute syngas (2.1% CO , 1.4% H_2 , and 0.5% CO_2 in N_2) has been proven for the LPMEOH process and is preferred operationally in the AFDU at LaPorte. So, the "routine" methanol catalyst (100%) activation using dilute syngas was planned for the first run. However, in case of problems with alumina addition, the fall back plan called for reducing the mixture of the two catalysts for the second run. Therefore, it was important to check if the dilute syngas reduction was equivalent to dilute hydrogen reduction for DME synthesis.

A test (Run No. 11782-25) was conducted with dilute syngas reduction in the 300 cc autoclave. A mixture of BASF S3-86 catalyst and LaRoche prepared Catapal (Batch A) was used for this test with a ratio of about 4.33. The activity of the catalyst mixture was checked using Texaco gas at 250°C, 750 psig, and 6000 GHSV. DME and methanol productivities from this run are compared with earlier results from hydrogen reduction (Run No. 11483-21) in Figure 32. DME productivity was about 20% lower when the dilute syngas was used for activation. This was a surprising result. Therefore, the system was thoroughly checked for the potential presence of metal carbonyls, specifically $Fe(CO)_5$ and $Ni(CO)_4$. The carbonyl levels were found to be insignificant. The dilute syngas run was repeated (Run No. 11782-28). The results reproduced well with the earlier experiment. A hydrogen reduction run (Run No. 11782-31) then followed these two runs. The hydrogen reduction results also reproduced. Therefore, the difference between the two activation procedures is believed to be real.

One possible reason could be that the water released from alumina interferes with the dilute syngas reduction. The dilute syngas reduction starts at a lower temperature than dilute hydrogen reduction. Therefore, we decided to dry the alumina before syngas reduction. The drying was conducted in the reactor at 120°C to simulate the limitations at LaPorte. The results from this run (Run No. 11782-33) indicate some improvement in activity. However, a significant difference remained between the two reductions. Perhaps the lack of complete drying at 120°C is important. A run with completely dry alumina would be worthwhile to confirm the water effect. With the LaPorte operation coming up, it was recommended that hydrogen reduction be used for catalyst mixture if we operated under the fall back plan.

Cu/ZnO CRYSTALLITE SIZE GROWTH DURING DME SYNTHESIS

Cu/ZnO crystallite sizes were measured for various spent methanol catalysts from the DME studies. The results are summarized in Table 11 along with other important parameters such as on-stream time, feed gas, and reduction gas. For comparison, results from LPMEOH runs (10454-37, 84) using 100% BASF S3-86 are included. The LPDME results include screening runs (11483-21, 16, and 10454-56), process variable runs (11483-72, 10454-43), life runs (11483-81, 11782-03), and reduction runs (11782-25, 28, 31, 33). For the screening as well as process variable DME studies, the Cu and ZnO crystallite sizes of the spent catalyst were close to LPMEOH (130–170 Å and 60–90 Å vs. 150 Å and 90 Å for LPMEOH). DME life studies indicated somewhat higher Cu crystallite

FIGURE 32 EFFECT OF REDUCTION PROCEDURE ON DME SYNTHESIS
(81% BASF S3-86, 19% CATAPAL, 250°C, 750 PSIG)

sizes (220Å). This suggests that over the long term, the product water could be sintering the catalyst. Cu crystallite sizes were also higher (220Å) when dilute syngas was used for reduction. This supports the hypothesis that water from alumina could be sintering the methanol catalyst.

TABLE 11
Cu/ZnO Crystallite Size Growth During DME Synthesis

	Run No.	Catalyst	% Methanol Catalyst	Feed Gas	Reduction Gas	On-Stream Time hrs	Cu Cryst. Size Å	ZnO Cryst. Size Å
LPMEOH	10454-37	S3-86	100	Texaco	Dil. H ₂	85	158	93
LPMEOH	10454-84	S3-86	100	Texaco	Dil. H ₂	200	147	88
LPDME Screening	11483-21	S3-86/Catapal Lab-500	81.25	Texaco	Dil. H ₂	60	130	65
LPDME Screening	11483-16	S3-86/Catapal Lab-500	93.75	Texaco	Dil. H ₂	80	162	82
LPDME Screening	10454-56	S3-86/Catapal Lab-550	81.25	Texaco	Dil. H ₂	50	168	88
LPDME PVS	11483-72	S3-86/Catapal Lab-500	81.25	Texaco	Dil. H ₂	190	171	89
LPDME PVS	10454-43	S3-86/Catapal Lab-500	81.25	Shell	Dil. H ₂	205	150	57
LPDME Life	11483-81	S3-86/Catapal Lab-500	81.25	Texaco	Dil. H ₂	620	220	83
LPDME Life	11782-03	S3-86/Catapal Lab-500	81.25	Shell	Dil. H ₂	500	225	81
LPDME Reduction	11782-25	S3-86/Catapal Batch A	81.25	Texaco	Dil. Syngas	20	210	120
LPDME Reduction	11782-28	S3-86/Catapal Batch A	81.25	Texaco	Dil. Syngas	20	230	140
LPDME Reduction	11782-31	S3-86/Catapal Batch A	81.25	Texaco	Dil. H ₂	20	170	110
LPDME Reduction	11782-33	S3-86/Catapal Batch A	81.25	Texaco	Dil. Syngas After Insitu Drying	20	180	120

FUEL TESTS ON DME/METHANOL MIXTURES

Three DME/methanol 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 measurements of flash point, Reid Vapor Pressure (RVP), and octane number. Results from these tests are compared with methanol produced at LaPorte and M85 (85 vol% methanol in gasoline) in Table 12. With small amounts of DME added, significant improvements in both flash point and RVP were observed over methanol. With a flash point of 7°C and an RVP of 6.4 psi, methanol alone has a cold-start problem in winter conditions. Adding DME to methanol brings those properties closer to those of M85, an acceptable automobile fuel. The

results indicate an average octane number 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/methanol mixtures would be worthwhile.

TABLE 12
SwRI Test Results on DME/Methanol Mixtures

Blend	DME, mol% nominal	DME, wt % Gravimetric	Flash Pt. °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 Methanol	NA	NA	7	6.4	111.1	87.0
M85	NA	NA	-65	10.3	108.8	85.6

SUMMARY AND CONCLUSIONS

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 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 significantly 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. In this study, three alternative methanol catalysts and five dehydration catalysts were investigated. A preferred catalyst system, consisting of a physical mixture of a methanol catalyst (81%) and a gamma alumina (19%) was identified. An improvement of about 50% in methanol equivalent productivity was achieved compared to the LPMEOH process. Improvement in methanol activity has the greatest potential to further enhance process performance.

A process variable study was completed with the preferred catalyst system. Results indicate that higher pressure and CO₂ removal benefit the process significantly. The "ideal" H₂/CO ratio in the feed for DME synthesis is 1 compared to 2 for methanol synthesis. Also, unlike methanol synthesis, DME synthesis does not need any CO₂ in the feed. Limited life studies were performed with the preferred catalyst system. Methanol catalyst appeared to deactivate somewhat higher than expected while the dehydration catalyst seemed to be stable. More work is needed to improve stability. However, the catalyst system is sufficiently stable to demonstrate the process at a larger scale in a slurry bubble column.

Sedimentation tests indicated only slightly lower settling rates for alumina compared to the methanol catalyst. Also, the two catalysts did not separate into two visible layers. Hence, the slurry property of the mixture was considered quite acceptable. The dehydration catalyst preparation was successfully scaled-up to produce larger quantities of material required for a demonstration at LaPorte.

Several DME/methanol mixtures were measured for their properties as a transportation fuel. With small amounts of DME added, significant improvements in both flash point and RVP were observed over methanol alone. With a flash point of 7°C and an RVP of 6.4 psi, methanol alone has a cold-start problem when the temperature becomes too low. Adding DME to methanol brings those properties closer to those of M85, an acceptable automobile fuel. These results are encouraging and more tests with DME/methanol mixtures would be worthwhile.

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

FUTURE PLANS

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' tall bubble column reactor. This facility has been used to successfully demonstrate slurry-phase methanol synthesis under previous DOE contracts. Production rates as high as 12 tons per day of methanol were attained, limited only by the capacity of the feed compressor.

In addition to demonstrating the feasibility of mixed DME/methanol synthesis in a single-stage, slurry reactor, the AFDU run would also verify that conclusions drawn in the laboratory are valid for 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.

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APPENDIX I
Air Products Memorandum from R. A. Byerley to B. Bhatt
25 May 1990

MEMORANDUM

AIR
PRODUCTS

To: B. Bhatt
From: R. A. Byerley
Date: 25 May 1990
Subject: Documentation for Iron Run Lab 17 Gas Chromatograph

Dept.: PSG Research
Dept./Ext.: CRSD-Analytical/6504
Chemical Separations Laboratory

cc: S. Gaul; T. Dahl; J. Frost; P. Clark; R. Mayo

INTRODUCTION

A Hewlett Packard 5890 gas chromatograph (GC) has been set-up to analyze reactor gas for light gases, methanol, dimethyl ether, methyl formate, and ethanol. The chromatograph, located in Iron Run lab 17, was originally configured by John Booker & Co., Austin, Texas. Modifications were performed to the chromatograph sampling system to improve the analysis of hydrogen in the reactor gas.

SYSTEM DESCRIPTION

Figure 1 is a block diagram of the chromatograph and integrator system. The original flame ionization (FID)/thermal conductivity detector (TCD) GC configuration was

Fig. 1. System Configuration

modified by replacing the FID with a TCD to perform a hydrogen analysis with nitrogen carrier. Both signals from the dual TCD arrangement are sent to the A/D (analog to digital) interface and are processed by the Nelson PC Integrator software.

FLOW PATHS

Figure 2 shows a diagram of the chromatograph in its ready state. Gas from the reactor (or calibration standard) enters the system from solenoid valve S4 passing through a 2 micron VALCO filter located inside the VALCO heated valve enclosure. The sample exits the system to vent after passing through a rotometer. All VALCO valves are shown in the load position with the sample stream purging the three 0.5 cc sample loops.

Helium and nitrogen carrier gasses are supplied to the GC from the Iron Run dock. Helium carrier is delivered to mass flow controllers (MFC) B1 and B2 at 50 psig. Nitrogen is supplied to MFC A at approximately 55 psig. Output flow of the three flow controllers is set to 20 ml/min. The B2 MFC regulates the helium carrier flow for VALCO valve V1, maintaining a column head pressure of 8 psig. Helium carrier flow for valve V2 is controlled by MFC B1, maintaining a head pressure of 18 psig. A column head pressure of 11 psig is maintained for valve V3 by MFC A. Figure 3 is a diagram of V1 in the inject mode with V2 and V3 in the load position. Figure 4 is a diagram showing valve V1 returned to the load position and V2 and V3 in the inject positions. V1 must be returned before injecting V2. Timed events for valve control are listed in Table 1 of Appendix A.1.

CHROMATOGRAPHY

Appendix A.2 lists the columns and conditions for the gas chromatograph system. Figure 5 is a chromatogram and Nelson report table of the V1 and V2 valve injections. Valve V1 with the attached Porapak T/ molecular sieve 13X column set is used for the separation of H₂, O₂/Ar, N₂, CH₄, and CO (H₂ quantitated on V3). The Porapak column is required to protect the molecular sieve column from heavy non-eluting components. After elution of the CO peak, valve V1 is returned and the Porapak T/ molecular sieve 13X column set is backflushed to vent.

Immediately after V1 is returned V2 is switched to inject. The Hayesep D column

connected to V2 separates a composite peak of air, H₂, and CO from CH₄, CO₂, H₂O, methanol, dimethyl ether, methyl formate, and ethanol. Valve V2 is returned after elution of ethanol, backflushing the Hayesep column to the detector. The valve switching times and other timed events for valves V1 and V2 are listed in Table 1 of Appendix A.1. Figure 6 is a chromatogram of the hydrogen analysis. Valve V3 is injected after V1 to allow for the V3 sample loop to reach equilibrium. The hydrogen analysis is very selective for hydrogen, giving a minimal response for O₂/Ar, N₂, CO, etc. Detector B (connected to V3) is used for the quantitation of hydrogen only. Valve switching times and other timed events for valve V3 are listed in Tables 1 and 2 of Appendix A.1.

The dual channel Nelson method naming convention is listed Table 2 of Appendix A.3. By convention, the first character of the second dual channel method must be named with the next logical letter or number. Table 1 of Appendix A.3 lists the Nelson PC Integrator parameters used for both detectors.

CALIBRATION

Instrument calibration should be checked by running standards as often as possible. Recalibration should be performed when the integrator report differs by more than 3 percent of the accepted standard values. An average of three injections should be used for calibration. The Nelson Integrator method given in Table 1 of Appendix A.3 is the same for all dual channel methods. Table 2 of Appendix A.3 lists the dual channel method names and the corresponding calibration standards. Since methanol and dimethyl ether are common to all process streams, the same methanol/dimethyl ether response factors are used for all methods listed in Appendix A.4. Response factors are also assumed for components that are not present in the calibration standards for a particular process stream. The assumed response factors provide a reasonable quantitative estimate since these components are usually insignificant. Refer to the notes at the bottom of each calibration listing of Appendix A.4 for the assumed response factors. However, if any of these components become

significant, then a response factor from an appropriate standard must be substituted into the calibration.

MAINTENANCE

The system requires minimal maintenance. It may be necessary to occasionally condition the molecular sieve 13X column for 1/2 hour @ 300 °C in order to improve separation. The charcoal column (in the 5890 oven) may also need conditioning for several hours @ 300 °C to remove accumulated material.

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R. A. Byerley

FIG. 3. Flow Diagram of Methanol Reactor GC

FIG. 4. Flow Diagram of Methanol Reactor GC

Fig. 5 Chromatogram of V1 and V2 Injections
A-10

EXTERNAL STANDARD TABLE							
PEAK NUM	RET TIME	PEAK NAME	CONCENTRATION in MOL%	NORMALIZED CONC	AREA	HEIGHT	AREA/ HEIGHT BL
1	0.862	hydrogen	73.4064	100.0000%	1880041	301049	6.2 1
TOTAL AMOUNT =			73.4064				

Fig. 6. Chromatogram of V3 injection

APPENDIX A.1

Table 1

NELSON TIMED EVENTS FOR VALVES V1, V2, V3,
(Detector A)

Ev#	Time	Event	Description	NOTE
1	0.01	1C	relay (Close)	Inject V1
2	0.05	PD-	Peak Detection (off)	
3	0.06	1O	relay (Open)	
4	0.30	6C	relay (Close)	Inject V3
5	0.40	6O	relay (Open)	
6	0.45	PD+	Peak Detection (on)	
7	2.85	PD-	Peak Detection (off)	
8	2.90	2C	relay (Close)	Return V1
9	2.90	3C	relay (Close)	Inject V2
10	3.20	2O	relay (Open)	
11	3.20	3O	relay (Open)	
12	3.35	PD+	Peak Detection (on)	
13	11.80	PD-	Peak Detection (off)	
14	11.85	4C	relay (Close)	Return V2
15	11.85	7C	relay (Close)	Return V3
16	11.95	4O	relay (Open)	
17	11.95	7O	relay (Open)	

Table 2

NELSON TIMED EVENTS FOR DETECTOR B
(hydrogen)

Ev#	Time	Event	Description
1	0.01	PD-	Peak Detection (off)
2	0.50	PD+	Peak Detection (on)
3	1.00	PD-	Peak Detection (off)

APPENDIX A.2

GAS CHROMATOGRAPHIC CONDITIONS

Instrument: Hewlett Packard 5890 Gas Chromatograph

Columns:

- (1) VALCO Valve V1 - 2' x 1/8" Porapak T 60/80 mesh in series with a 3' x 1/8" mole sieve 13X 40/50 mesh
- (2) VALCO Valve V2 - 5' x 1/8" Hayesep D(ip) acid washed 80/100 mesh
- (3) VALCO Valve V3 - 6' x 1/8" Activated Charcoal 60/80 mesh

Column Temperatures: Isothermal

Column 1 - Ambient temperature

Column 2 - 170 °C VALCO heated valve enclosure

Column 3 - 60 °C HP 5890 oven

Carrier Gas:

Column 1 (mass flow cont. B2) - 20 ml/min helium, 8 psig

Column 2 (mass flow cont. B1) - 20 ml/min helium, 18 psig

Column 3 (mass flow cont. A) - 20 ml/min nitrogen, 11 psig

Injection Volume: 0.5 cc for all three loops V1 - V3

Injection Mode: VALCO gas sampling valve

Detectors: Thermal Conductivity

A - 210 °C, refer. flow = 25 ml/min. helium, total flow = 45 ml/min.,
Low Sensitivity, Range = 0, Zero (typical) = 1.0

B - 100 °C refer. flow = 25 ml/min. helium, total flow = 45 ml/min.,
Low Sensitivity, Range = 0, Zero (typical) = -9.2

Negative Polarity

Data System: Nelson PC Integrator

Integration Parameters:

Noise Threshold	5	microvolts/sec
Peak Width	3	seconds
Area Threshold	300	microvolts*sec
Sampling Rate	0.2	seconds/sample
Peak Area Rejection	0	microvolt-sec

Quantitation Method: External Standard, mole %

APPENDIX A.3

Table 1

Nelson Integrator Method (Dual Chanel) For Detectors A and B

ACQUISITION PARAMETERS

SINGLE OR DUAL CHANNEL (1 OR 2)	2.00
RUN TIME (minutes)	12.00
END TIME FOR PLOTS (default=RUN TIME)	12.00
SOLVENT DELAY TIME (minutes)	0.00
PEAK DETECTION THRESHOLD (microv/sec)	5.00
Area Threshold	300.00
MINIMUM PEAK WIDTH (seconds)	3.00
TIME FOR ONE SAMPLE (seconds)	0.20
NUMBER OF REAL TIME CRT PAGES TO PLOT (0 TO 99)	1.00
REAL TIME PLOT FULL SCALE FOR CH.0 (millivolts)	50.00
REAL TIME FULL SCALE FOR CH.1 (millivolts)	50.00
HARD COPY REAL TIME PLOT	NO
AUTO ZERO REAL TIME PLOT	YES
Pre Version 4 method	NO
RECORD AREA TABLES ON DISK	YES
RECORD RAW DATA	YES
NUMBER OF CRT PAGES FOR REPLOT (1 TO 99)	1.00
VERTICAL SCALE FACTOR FOR REPLOT (units of largest peak)	0.00
OFFSET FOR THE REPLOT (millivolts)	5.00
PUT NAMES ON REPLOT?	YES
PRINT AREA PERCENT REPORT	NO
PRINT EXTERNAL STANDARD REPORT	YES
PRINT INTERNAL STANDARD REPORT	NO
FINAL REPORT AREA REJECT (microvolt-sec)	500.00
LINK TO USER PROGRAM	NO
FORCE DROP LINE INTEGRATION	NO
FORCE COMMON BASE LINE	NO
FULL SCALE RANGE FOR A.D.C. (3=1VOLT, 1=2VOLT, 0=10VOLT)	3.00
AREA REJECT FOR REFERENCE PEAKS?	0.00
% RET TIME WINDOW FOR REFERENCE PEAKS	15.00
RET TIME WINDOW IN SECONDS FOR REF. PEAKS	15.00
AREA OR PEAK HEIGHT QUANTITATION (0 OR 1)	0.00
PRINT GROUP REPORT	NO
NUMBER OF CALIBRATION LEVELS (1 TO 6)	1.00
LIST COMPONENTS NOT FOUND IN SAMPLE?	YES
INCLUDE UNKNOWN PEAKS IN REPORTS?	YES
UPDATE RESPONSE FACTORS WITH REPLACEMENT (0) OR AVERAGE (1)	0.00
DEFAULT DILUTION FACTOR	1.00
DEFAULT SAMPLE WEIGHT	1.00
DEFAULT AMOUNT INJECTED	1.00
DEFAULT AMOUNT OF INTERNAL STANDARD	1.00
PRINT GPC MW DISTRIBUTION	NO
PRINT SIMULATED DISTILLATION REPORT	NO

NOTE: Both methods in a dual chanel configuration must have the same integration parameters and run time. Tined events may be different for each.

Table 2

Method Naming Convention

<u>Calibration Standards</u>	<u>Detector A</u>	<u>Detector B</u>
Dakota Syngas	DAKSYN.MET	EAKSYN.MET
Unbalanced	UNBAL.MET	VNBAL.MET
Balanced	BAL.MET	CAL.MET
H ₂ Rich	H2RICH.MET	I2RICH.MET

NOTE: First character of second dual channel method must be named with the next logical letter or number. Detector B is used for determination of hydrogen only.

APPENDIX A.4
CALIBRATION LISTINGS FOR DETECTOR A
Method: DAKSYN

Response factor for unknowns= 1.0000E+00

Component Units = MOL%

1 O2/Ar	Ret. Time = 0.56 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 15.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	930911	18.00000000	0.00001934	
2 N2	Ret. Time = 0.96 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 15.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	930911	18.00000000	0.00001934	
3 CH4	Ret. Time = 1.35 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	930911	18.00000000	0.00001934	
4 CO	Ret. Time = 1.94 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	1311880	19.39999960	0.00001479	
5 CO2	Ret. Time = 3.43 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	48720	1.00000000	0.00002053	
6 H2O	Ret. Time = 3.90 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	449767	7.80000020	0.00001734	
7 MeOH	Ret. Time = 5.32 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	49024	1.10000002	0.00002244	
8 DME	Ret. Time = 5.69 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	449767	7.80000020	0.00001734	
9 Methylformate	Ret. Time = 8.46 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	449767	7.80000020	0.00001734	
10 EtOH	Ret. Time = 9.80 min.	Fit.type = 1			
Ref. peak: CO	Int Std: CO			Window size: 5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	449767	7.80000020	0.00001734	

NOTE: Response factors for N₂, O₂/Ar were taken as CH₄ of the DAKSYN STD.
Response factors for H₂O, Methyl Formate, and EtOH were taken as DME of the
MEOH/DME standard.

APPENDIX A.4 (cont'd)
Method: UNBAL

Response factor for unknowns= 1.0000E+00

Component Units = MOL%

1 O2/Ar	Ret. Time =	0.54 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	15.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	77649	1.02999997	0.00001326	
2 N2	Ret. Time =	0.81 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	20.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	77649	1.02999997	0.00001326	
3 CH4	Ret. Time =	1.35 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	3491471	49.16999800	0.00001408	
4 CO	Ret. Time =	1.65 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	20.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	3491471	49.16999800	0.00001408	
5 CO2	Ret. Time =	3.38 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	676637	13.00000000	0.00001921	
6 H2O	Ret. Time =	3.90 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	499098	7.80000020	0.00001563	
7 MeOH	Ret. Time =	5.06 min.	Fit.type =	1	
Ref. peak: MeOH	Int Std: MeOH		Window size:	5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	168323	3.59999990	0.00002139	
8 DME	Ret. Time =	5.41 min.	Fit.type =	1	
Ref. peak: DME	Int Std: DME		Window size:	5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	499098	7.80000020	0.00001563	
9 Methylformate	Ret. Time =	8.46 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	499098	7.80000020	0.00001563	
10 EtOH	Ret. Time =	9.80 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
	LEVEL	AREA	AMOUNT	RATIO (amount/area)	
	1	499098	7.80000020	0.00001563	

NOTE: Response factor for O₂/Ar was taken as N₂ of the UNBALANCED standard.
Response factor for CH₄ was taken as CO of the UNBALANCED std. Response factors for H₂O, Methyl Formate, and EtOH were taken as DME of the MECH/DME standard.

APPENDIX A.4 (cont'd)

Method: BAL

Response factor for unknowns= 1.0000E+00

Component Units = MOL%

1 O2/Ar	Ret. Time =	0.56 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	15.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	276008	21.00000000	0.00007608		
2 N2	Ret. Time =	0.89 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	15.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	276008	21.00000000	0.00007608		
3 CH4	Ret. Time =	1.35 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	1023628	19.10000040	0.00001866		
4 CO	Ret. Time =	2.06 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	1023628	19.10000040	0.00001866		
5 CO2	Ret. Time =	3.43 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	7.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	350208	5.02000000	0.00001433		
6 H2O	Ret. Time =	3.90 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	449767	7.80000020	0.00001734		
7 MeOH	Ret. Time =	5.32 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	49024	1.10000002	0.00002244		
8 DME	Ret. Time =	5.69 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	449767	7.80000020	0.00001734		
9 Methylformate	Ret. Time =	8.46 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	449767	7.80000020	0.00001734		
10 EtOH	Ret. Time =	9.80 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	449767	7.80000020	0.00001734		

NOTE: Response factor for O₂/Ar was taken as N₂ of the BALANCED standard.
 Response factor for CH₄ was taken as CO of the BALANCED std. Response
 factors for H₂O, Methyl Formate, and EtOH were taken as DME of the MECH/DME
 standard.

APPENDIX A.4 (cont'd)
Method: H2RICH

Response factor for unknowns= 1.0000E+00

Component Units = MOL%

1 O2/Ar	Ret. Time =	0.56 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	15.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	276008	4.04000000	0.00001464		
2 N2	Ret. Time =	0.89 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	15.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	276008	4.04000000	0.00001464		
3 CH4	Ret. Time =	1.35 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	1023628	15.10000040	0.00001475		
4 CO	Ret. Time =	2.06 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	1023628	15.10000040	0.00001475		
5 CO2	Ret. Time =	3.43 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	7.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	350208	7.05000020	0.00002013		
6 H2O	Ret. Time =	3.90 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	449767	7.80000020	0.00001734		
7 MeOH	Ret. Time =	5.32 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	49024	1.10000002	0.00002244		
8 DME	Ret. Time =	5.69 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	449767	7.80000020	0.00001734		
9 Methylformate	Ret. Time =	8.46 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	449767	7.80000020	0.00001734		
10 EtOH	Ret. Time =	9.80 min.	Fit.type =	1	
Ref. peak: CO	Int Std: CO		Window size:	5.0%	
LEVEL	AREA	AMOUNT	RATIO (amount/area)		
1	449767	7.80000020	0.00001734		

NOTE: Response factor for O₂/Ar was taken as N₂ of the H2 RICH standard. Response factor for CH₄ was taken as CO of the H2 RICH std. Response factors for H2O, Methyl Formate, and EtOH were taken as DME of the MECH/DME standard.

APPENDIX A.4 (cont'd)
HYDROGEN METHODS

METHOD: EAKSYN

Response factor for unknowns= 1.0000E+00

Component Units = MOL%

1 hydrogen	Ret. Time =	0.82 min.	Fit.type =	1	
Ref. peak: hydrogen		Int Std: hydrogen			Window size: 10.0%
	LEVEL	AREA	AMOUNT		RATIO (amount/area)
	1	1571592	61.59999800		0.00003920

METHOD: VNBAL

Response factor for unknowns= 1.0000E+00

Component Units = MOL%

1 hydrogen	Ret. Time =	0.83 min.	Fit.type =	1	
Ref. peak: hydrogen		Int Std: hydrogen			Window size: 20.0%
	LEVEL	AREA	AMOUNT		RATIO (amount/area)
	1	945398	36.79999900		0.00003893

METHOD: CAL

Response factor for unknowns= 1.0000E+00

Component Units = MOL%

1 hydrogen	Ret. Time =	0.87 min.	Fit.type =	1	
Ref. peak: hydrogen		Int Std: hydrogen			Window size: 10.0%
	LEVEL	AREA	AMOUNT		RATIO (amount/area)
	1	1890377	54.88000100		0.00002903

METHOD: I2RICH

Response factor for unknowns= 1.0000E+00

Component Units = MOL%

1 hydrogen	Ret. Time =	0.87 min.	Fit.type =	1	
Ref. peak: hydrogen		Int Std: hydrogen			Window size: 10.0%
	LEVEL	AREA	AMOUNT		RATIO (amount/area)
	1	1890377	73.80999800		0.00003905

**DATE
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