

**DEVELOPMENT AND DEMONSTRATION OF A ONE-STEP SLURRY-PHASE
PROCESS FOR THE COPRODUCTION OF DIMETHYL-ETHER AND METHANOL**

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Contract Nos: DE-AC22-90PC89865, DE-AC22-91PC90018

ABSTRACT:

This report focuses on the work directed towards the demonstration of one-step, slurry-phase coproduction of dimethyl-ether (DME) and methanol.

First, process variable scans were completed in the laboratory on a dual-catalyst system which consisted of a physical mixture of a methanol catalyst and a dehydration catalyst. These tests were conducted in a slurry-phase autoclave and the results were used to aid in preparing a run plan and setting process targets for the AFDU demonstration. Among other things, this work demonstrated that the preferred dehydration catalyst proportion was between 5 and 25 wt%.

Next, modifications to the LaPorte facility were engineered and implemented. The plant was then reconfigured to make it possible to remove the product DME and byproduct carbon dioxide from the reactor effluent. New equipment was purchased and some existing equipment was recommissioned.

Finally, this technology was demonstrated in the 2 ft diameter, thirty foot tall, slurry reactor at the AFDU over the course of a three-week operating campaign. Three different proportions of dehydration catalyst were studied to illustrate the impact of dehydration catalyst concentration on per-pass syngas conversion and DME selectivity. Reactor conditions were maintained at 250°C and 750 psig with CO-Rich synthesis gas as feed; space velocity was varied at each separate catalyst proportion.

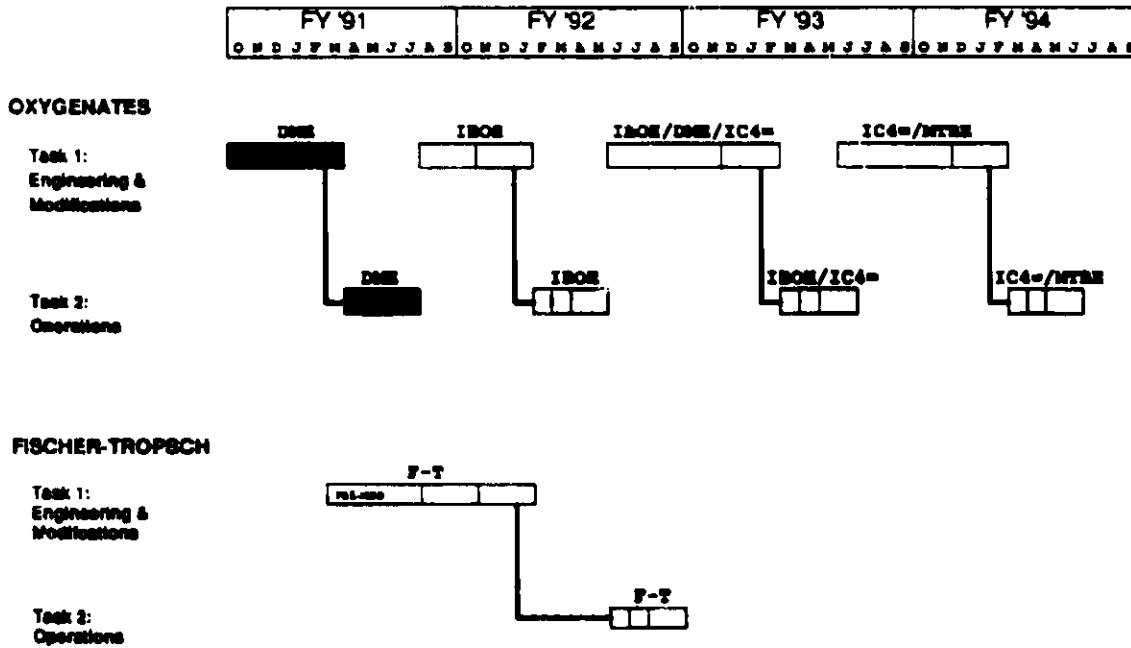
The results from both the laboratory and the AFDU confirm that dehydration catalyst concentration is a key process variable. Per-pass syngas conversion increases substantially (by at least 30% at commercial space velocities) with the addition of a small amount of dehydration catalyst.

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INTRODUCTION

Air Products and Chemicals, Inc. is currently working under a contract with the Department of Energy (DOE) entitled "Development of Alternative Fuels from Coal-Derived Syngas" to develop and demonstrate technologies which produce oxygenated fuels and additives. The schedule for this four year program, shown in Figure 1, calls for a series of plant modifications to, and operations at, the Alternative Fuels Development Unit (AFDU). This facility is owned by the DOE and operated by Air Products in LaPorte, Texas.

FIGURE 1: ALTERNATIVE FUELS DEMONSTRATION PLAN



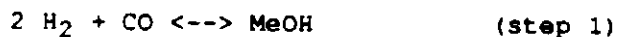
Some chemicals of interest include MTBE and its precursors: isobutanol and isobutylene. Dimethyl-ether (DME) is one of the key compounds in this oxygenated fuels portfolio. DME is perceived to have value as a reaction intermediate to fuels such as MTBE as well as an end product in its own right. The coproduction of DME and methanol also provides an opportunity for capital reduction when the synthesis is integrated with power generation in a Coal Gasifier Combined Cycle (CGCC) facility.

Researchers at Air Products demonstrated the single-step synthesis of DME from coal-derived syngas in 1986. Since that time, work has continued at Air Products, under contract with the DOE, to refine the technology and adapt it to a liquid-phase slurry process. This work resulted in a mixed catalyst system which was developed in the laboratory and demonstrated at a semi-works scale in the AFDU.

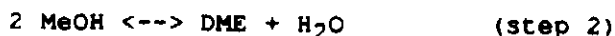
The historical developments in DME synthesis have been disclosed elsewhere (1,2) and will not be discussed here. Rather, an overview of the current state of our slurry-phase DME efforts will be put forth, followed by a discussion of recently completed works.

CHEMISTRY OF DIMETHYL-ETHER SYNTHESIS FROM H₂/CO SYNGAS

DME can be produced from syngas via a two-step reaction mechanism. In the first step syngas is converted to methanol (MeOH):



In the second step methanol is dehydrated to form DME:



Both these steps are reversible and exothermic. At equilibrium, the methanol production step is favored by higher pressure; the DME step is pressure neutral. Each of these steps is catalyzed by a different material: methanol is produced using a metal catalyst such as copper while DME is produced using a dehydration catalyst such as alumina.

The copper catalyst used also exhibits activity towards the water-gas shift reaction:



Shift is necessary to increase the hydrogen availability when processing CO-rich synthesis gases (CO/H₂ ratio greater than one).

Multistep processes, which use separate reactors for each step, cannot exploit the potential synergy of the three reactions. If these three reactions are conducted simultaneously, methanol synthesis drives the forward shift reaction, and DME synthesis drives both the methanol and shift reactions. Consequently, a one-step process is more flexible and can operate under a wider range of conditions than a multistep process. In addition, multistep processes require separate reactors, heat exchangers, and associated equipment.

CHARACTERISTICS OF SLURRY-PHASE DME SYNTHESIS

The work to-date has focused on slurry-mode operation using powdered catalysts, allowing researchers to draw significantly on the results from the successful LPMEOH program (3).

Commercial operating conditions include a pressure range of 1.5 MPa to 14 MPa, a temperature range of 200 to 350°C, and space velocities in the range of 1000 to 10,000 standard liters of synthesis gas per kilogram of catalyst per hour (sL/kg-hr). There is an opportunity to operate efficiently at lower pressures. The formation of DME will drive the equilibrium position of the methanol synthesis reaction well past the point achieved in a methanol-alone system, reducing the necessity for pressurized operation.

Because of the liquid-phase's ability to accommodate large exotherms resulting from high conversion levels, the process is thought to be particularly useful for synthesis gases which contain large quantities of carbon monoxide and hydrogen, even where the concentration of CO in the synthesis gas exceeds 50 vol %.

Catalyst loadings can vary from 5 wt % of the slurry to 60 wt. The catalyst is suspended in an inert hydrocarbon oil. Other types of liquids are known to work for liquid-phase processes, for example, oxygenated species such as alcohols, ethers, and polyethers. These oxygenated liquids should be inert and have a boiling point for single component liquids or boiling range for blended liquids of between 150 to 450°C.

LABORATORY RESEARCH

Commercially available catalysts have been used primarily, although some novel catalytic materials have also been examined. All catalysts were activated according to the procedure recommended by their manufacturers. They were slurried in either degassed WITCO 70 or degassed DRAKEOL 10, food grade mineral oils which are primarily C₁₈-C₃₁ paraffins. Slurry concentrations varied from 15 to 30 wt % catalyst (based on the total weight of the slurry).

Initial screening studies were carried-out on a number of catalyst pairs to identify the system with the greatest activity and mutual compatibility (2). The prototypical catalyst pair discussed here uses powdered BASF S3-86 to activate the methanol and shift steps and Catapal γ -alumina for the dehydration step.

A variety of process variable scans were conducted to characterize performance. Independent variables included: temperature, pressure, space velocity, feed gas composition, and catalyst proportions. The dependent variables include: productivity and selectivity. A summary of the range of process variables is included in Tables 1 and 2.

Table 1: Feed Gas Types Studied

TYPE	COMPOSITION (MOLE %)			
	H ₂	CO	N ₂	CO ₂
DOW	41	41	2	16
SHELL	30	66	1	3
TEXACO	35	51	1	13
H2-RICH	74	15	4	7
BALANCED	50	50	0	0

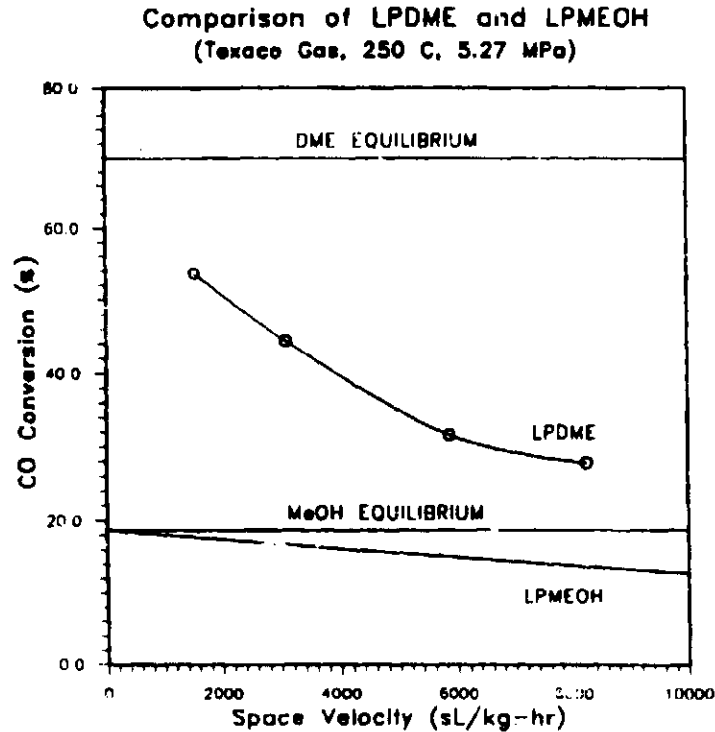
Table 2: Range of Process Variables

VARIABLE	RANGE
Temperature	250 - 280 °C
Pressure	5 - 10 MPa
Space Velocity	1500 - 10000 sL/kg-hr
Catalyst Proportion	0 - 50 (wt% alumina)

The characteristic behavior of Liquid-Phase DME (LPDME) is contrasted with Liquid-Phase Methanol (LPMEOH) in Figure 2 which presents the CO conversion as a function of space velocity. The CO conversion in LPDME is

up to twice as high as that in LPMEOH and much higher than the equilibrium conversion achievable from the methanol reaction alone. Interestingly, the gap between DME equilibrium and the DME performance curve indicates that there is still substantial room for catalyst improvement.

FIGURE 2:



As one would expect, raising the reactor temperature increases the activity of both catalysts. However the rate of dehydration is more strongly affected by temperature, such that overall, DME selectivity increases. This effect is illustrated in Figure 3.

Pressure has a pronounced impact on overall productivity. By increasing the pressure, the first of the two sequential steps can be driven forward at a greater rate. The result is increased productivity for both components (see Figure 4). The response of selectivity to increasing pressure is dependent on the space velocity. At lower space velocity, selectivity to DME increases with increasing pressure; at higher space velocity, the reverse is so.

FIGURE 3:

Effect of Temperature on DME Synthesis (Texaco Gas, 5.27 MPa, 8100 sL/kg-hr, 18.7% Al₂O₃)

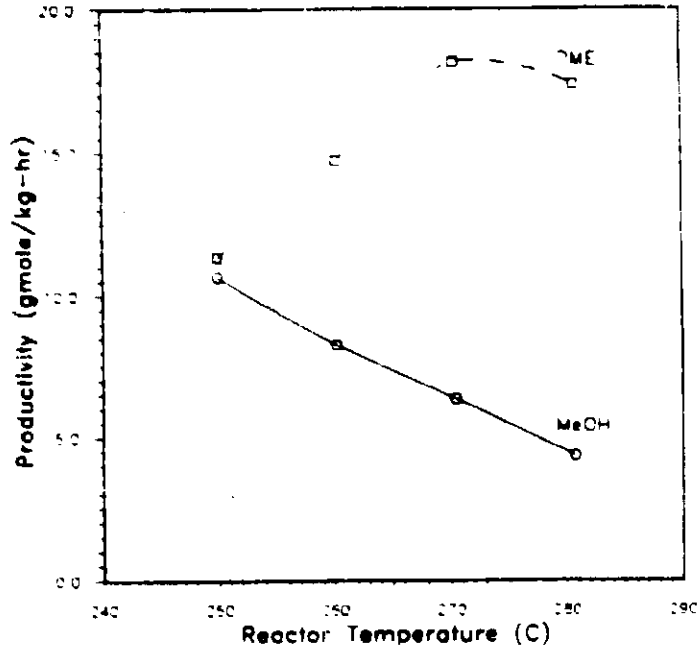
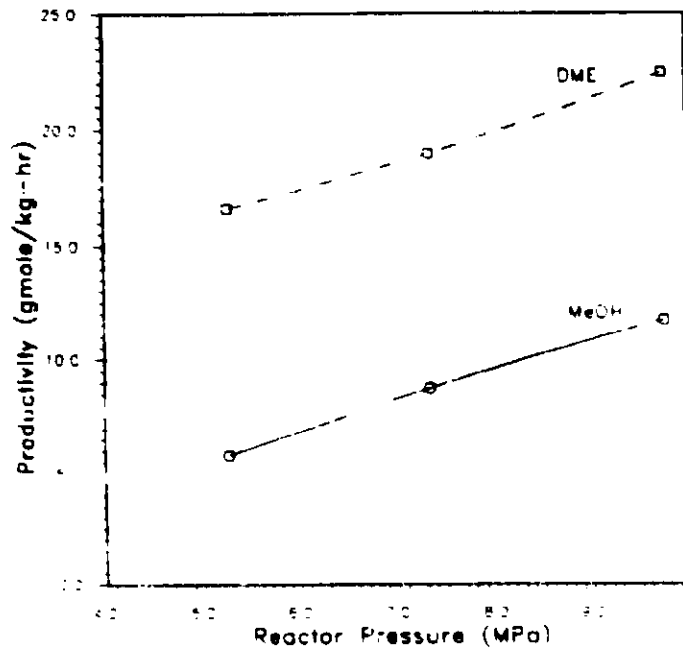


FIGURE 4:

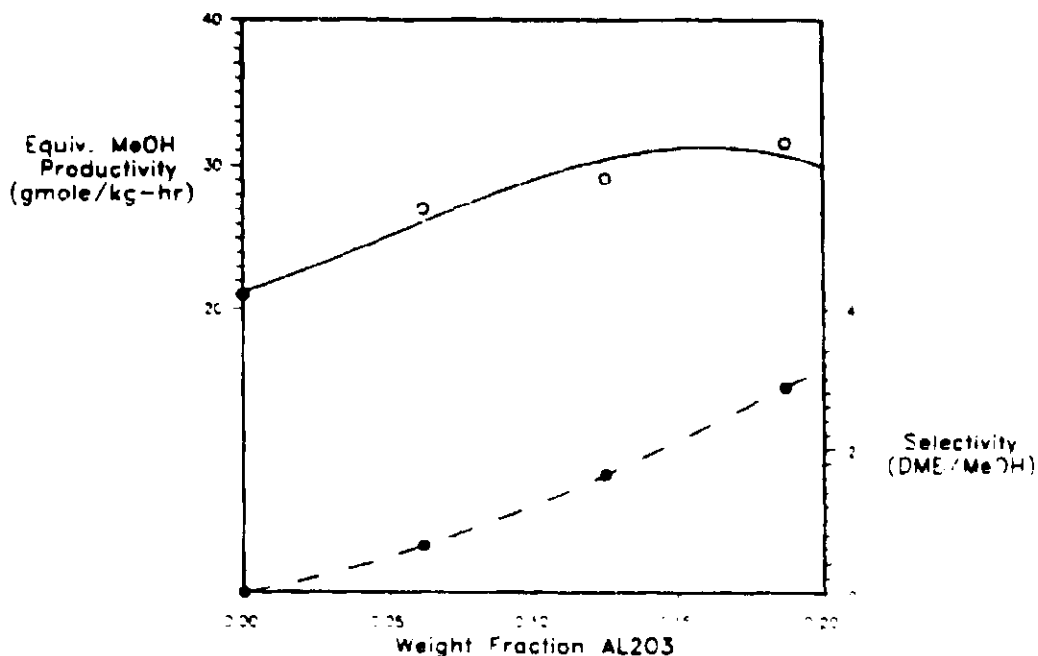
Effect of Pressure on DME Synthesis (Shell Gas, 250 C, 9500 sL/kg-hr, 18.7% Al₂O₃)



The relative proportion of S3-86 and alumina has a profound impact on the process performance (see Figure 5). As would be expected, increasing the percentage of dehydration catalyst increases selectivity to DME. In addition, at very low proportions of alumina, increasing its relative amount increases overall, per-pass equivalent MeOH productivity significantly (equivalent productivity is defined as productivity of MeOH plus twice the productivity of DME). If one continues to increase the proportion of dehydration catalyst the incremental increase in productivity declines until a maximum is reached. Beyond this point, continued increases in the alumina proportion results in a reduction in productivity. The composition which corresponds to the maximum productivity is a function of pressure, temperature, catalyst types and syngas composition. Commercially, one must consider both selectivity and productivity before deciding on the appropriate catalyst proportion.

FIGURE 5:

Effect of Catalyst Proportion on Productivity & Selectivity
(Texaco Gas, 250 C, 5.27 MPa, 5900 sL/kg-hr)



SLURRY-PHASE DME SCALE-UP

The laboratory screening and process variable studies successfully identified the attractive operating envelope for DME synthesis. The next logical step is to address the commercial scale-up issues. A major question which cannot be resolved in mechanically stirred autoclaves is how homogenized the dual-catalyst system will remain when agitated within a bubble column reactor. Improper mixing and/or stratification of the two catalysts will introduce mass transfer resistances and reduce productivity. Other issues which are appropriate to this technology include: catalyst preparation and handling, startup, and shutdown. Finally, hydrodynamic data such as vapor hold-up and catalyst agglomeration are important.

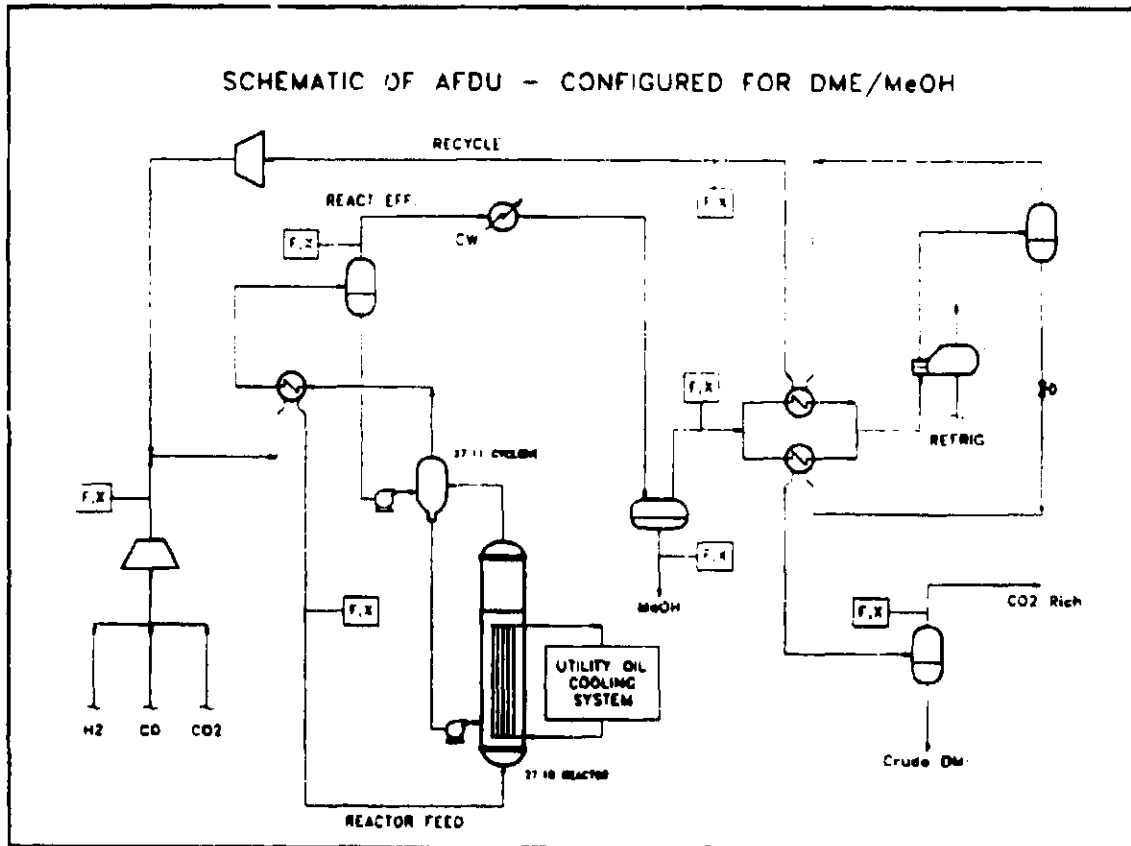
Under a previous contract with the DOE, Air Products has operated a semi-works scale high pressure bubble column reactor which is capable of processing a syngas of virtually any composition. This facility, the AFDU, has been used to demonstrate the LPMEOH technology at a maximum production rate of 12 tons/day of methanol.

As part of the current contract with the DOE, modifications have been made to the plant to facilitate the demonstration of DME in the slurry phase. Most notably, unit operations were added to allow the product DME and co-product carbon dioxide to be removed from the reactor effluent - a refrigerated, partial condensation process was used.

A schematic of the AFDU flowsheet is shown in Figure 6. Hydrogen, carbon monoxide, and carbon dioxide are blended and compressed, then mixed with recycle gas to form the desired syngas composition and flow. This reactor feed is preheated then introduced to the bottom of the slurry reactor. The syngas flows upward through the slurry (catalyst-mix plus mineral oil) and is partially converted to products and by-products. The heat of reaction is absorbed by the oil and then rejected to an internal heat exchanger. The gross reactor effluent is passed through a cyclone to remove catalyst fines, then cooled to condense traces of slurry oil. The resultant vapor is considered to be the net reactor effluent and contains MeOH, DME, CO₂, H₂O, and unreacted reactor feed. This stream is subsequently chilled against cooling water, and introduced to a separator where the bulk of the methanol and any water is recovered as a liquid. The remaining vapor portion is cooled in a series of heat recovery and refrigerant exchangers then directed to a second separator where DME and a portion of CO₂ is removed as liquid. The vapor from this separator is rewarmed, compressed, and recycled to the front-end. The DME-bearing liquid is flashed to a lowered pressure and vaporized to reject CO₂ and partially concentrate the DME.

Flows and composition are measured at various strategic points in the process. The two key points are: reactor feed and reactor effluent. The additional process points are measured to provide information which can be used to resolve the material balance.

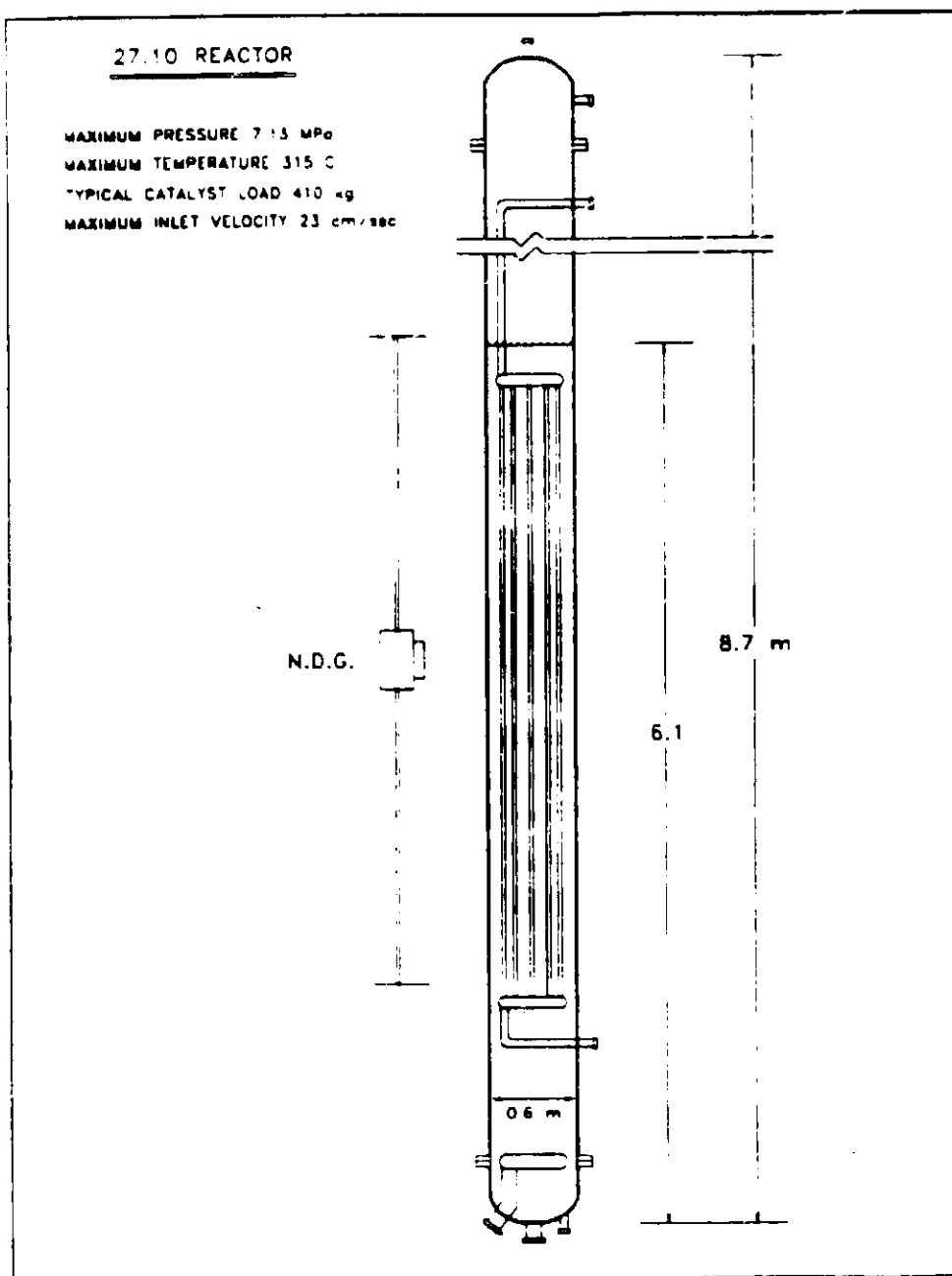
FIGURE 6:



The bubble column reactor, shown schematically in Figure 7, is 8.7 meters top to bottom and 0.6 meters inside diameter. The maximum slurry level is approximately 6.1 meters; the remainder is vapor disengagement space. The reactor is fitted with an internal heat exchanger which consists of 10, 1" tubes. These tubes occupy less than 5% of the reactor cross-section.

The reactor is fitted with a number of thermocouples, located at various elevations. A nuclear density gauge is mounted on an external track and spans the space occupied by the internal exchanger. The "Nuke" is used to determine gas holdup. The relief pressure for this reactor is 7.1 MPa; at this pressure the maximum temperature is 315°C. Maximum temperature can be increased by derating the relief pressure. Typically, the reactor can hold up to 410 kg of catalyst. The maximum superficial inlet velocity is 23 cm/sec. This limitation is set by the capacity of the compression capacity.

FIGURE 7:



AFDU DEMONSTRATION RESULTS

The modified AFDU was recommissioned in April 91; this was followed by a period of operations in May. The objective of the demonstration was to operate at conditions similar to those of the lab and compare performance.

Emphasis was placed on understanding the variation in productivity and selectivity with catalyst proportion.

The demonstration consisted of three major operations:

- baseline MeOH production with 100% BASF S3-86 (run AF-R1)
- mixed DME/MeOH production with 93.6% BASF S3-86 and 6.4% Catapal γ -alumina (run AF-R2)
- mixed DME/MeOH production with 81.2% BASF S3-86 and 18.8% Catapal γ -alumina (run AF-R3)

The reactor feed used here was CO-Rich (35% H₂, 51% CO and 11-13% CO₂, balance N₂/CH₄/MeOH/DME). Since this gas was produced by combining recycle with the fresh feed, small amounts of MeOH and DME were present.

Reactor pressure and temperature were maintained at 5.27 MPa and 250°C, respectively, during all three production runs. The catalyst charge was maintained at 220 kg (oxide basis).

A total of 8 process conditions were investigated during this demonstration. These conditions are summarized in Table 3.

Table 3: Identification of Run Conditions

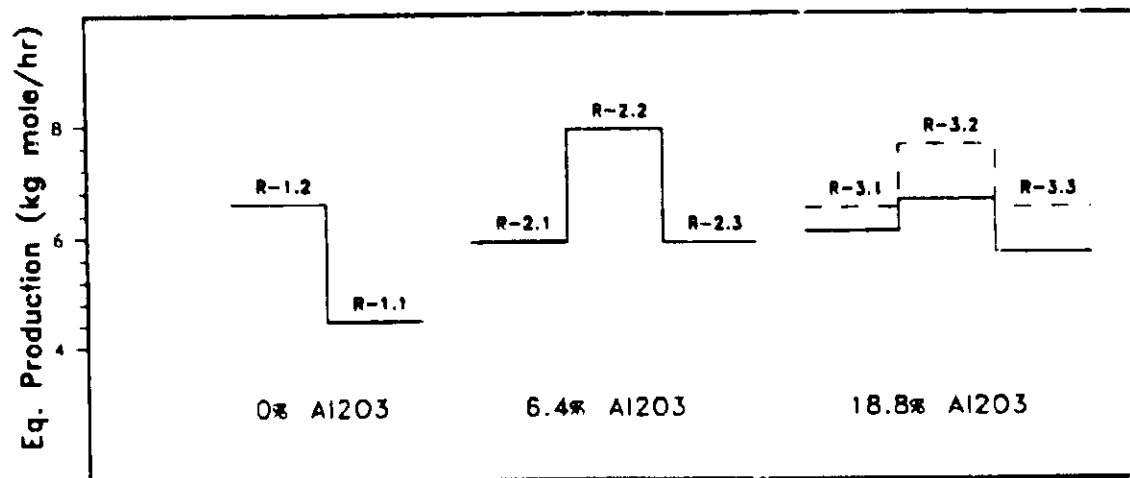
RUN #	Wt% Alumina Catalyst	Inlet Velocity (cm/sec)	Slurry Level (%)
AF-R1.1	0.0	4.9	75
AF-R1.2	0.0	7.3	100
AF-R2.1	6.4	4.9	100
AF-R2.2	6.4	7.3	100
AF-R2.3	6.4	4.9	75
AF-R3.1	18.8	4.9	100
AF-R3.2	18.8	7.3	100
AF-R3.3	18.8	4.9	75

The same S3-86 catalyst was used for all three runs. This was done to avoid having to activate new lots of methanol catalyst which, in turn, would have added uncertainty when comparing system productivities. Additionally, the mass of total catalyst within the reactor (on an as-charged basis) was the same for each of the process conditions. Therefore, at equivalent space velocity, all three campaigns could be carried-out at the same inlet velocity and roughly the same slurry concentration. This would minimize the introduction of additional independent variables which could potentially cloud the results. As a consequence, it was necessary to withdraw catalyst-slurry from the reactor following each major run before fresh alumina catalyst could be added.

A schematic of the run chronology is presented in Figure 8. The bar chart depicts equivalent MeOH production rate (in kg mole/hr). Tabulated within the figure is the superficial inlet velocity, U_g , the selectivity, DME/MeOH, and the slurry level.

FIGURE 8:

RUN CHRONOLOGY



Ug (cm/sec)	7.5	4.9	4.9	7.5	4.9	4.9	7.5	4.9
DME/MeOH			0.7	0.4	0.5	2.6	1.1	1.8
Level (%)	100	75	100	100	75	100	100	75

The first campaign (AF-R1) was used to establish the base-line productivity of the methanol catalyst. Prior to this run, the S3-86 was activated within the reactor using procedures established during the LPMEOH program. Production rates for this run were much as expected. Following this operation, a fraction of the slurry was withdrawn to allow the addition of dehydration catalyst.

The second campaign (AF-R2) demonstrated the concept of enhanced syngas conversion which results by adding a relatively small quantity of pre-dried dehydration catalyst. The results of tests showed that at equivalent inlet velocity, production increased by 32% (lower inlet velocity) and 18% (higher inlet velocity) when compared to AF-R1.

The final campaign (AF-R3) was to demonstrate a higher level of DME selectivity. The plant came up at the low velocity point, 100% level. The equivalent production rate increased, as did the selectivity. However, rates were somewhat below expectations (indicated by the dashed line). As time-into-run continued, the disparity between the data and expectations continued.

Post-run inspection of the reactor revealed that approximately 9% of the catalyst charge had sunk into the bottom head (below the gas sparger), and become lodged. Furthermore, elemental analysis of this catalyst showed it to be of a composition commensurate with 18 wt% alumina.

This information indicates two things. First, the settling was irreversible, otherwise it would simply have drained from the reactor

following shutdown. Second, such settling did not occur in the first two runs, otherwise elemental analysis would have revealed a lower alumina content.

It was found that correcting for the "lost" catalyst is sufficient to bring the results in-line with expectations.

A run summary is contained in Table 4.

TABLE 4:

**DMEMeOH DEMONSTRATION - LAPORTE AFDU, SPRING 81
PRELIMINARY RUN SUMMARY**

Run No.		R-1.1	R-1.2	R-2.1	R-2.2	R-2.3	R-3.1	R-3.2	R-3.3
Time from Start (hrs)	(1)	119	72	193	231	260	312	347	375
Space Vel. (SI/hr, kg-cat)		5511	8581	5371	8640	5486	5915	9222	5958
Cat. Proportion (wt% AL ₂ O ₃)		0	0	6.4	6.4	6.4	18.8	18.8	18.8
Inlet Gas Velocity (cm/sec)		4.9	7.5	4.9	7.5	4.9	4.9	7.5	4.9
Reactor Level (m)		4.6	6.0	6.0	6.0	4.5	6.0	6.0	4.6
Syngas Conversion (%)		29.2	27.5	38.8	31.9	37.8	39.3	27.8	36.4
Eq. Prod. (gmol/hr, kg-cat)	(2)	20.4	30.3	27.0	35.3	26.7	30.1	33.0	28.1
Gross MeOH Make (kg/day)		3423	5076	1907	3632	2179	726	1544	998
Gross DME Make (kg/day)		0	0	1907	1725	1725	2815	2542	2482
Fuel Production (kW)	(3)	789	1170	1061	1400	1065	1085	1185	1029

Standard Reactor Conditions:		Standard Reactor Feed Composition (mole%):	
Temperature (C)	250	hydrogen	35
Pressure (MPa)	5.27	carbon monoxide	51
		carbon dioxide	13
		other	1

NOTES:

- 1 This is the time since the catalyst was first activated and reflects the average for the run period. Run period durations averaged 26 hours.
- 2 Eq. Prod. = Gross methanol productivity = MeOH productivity + 2*DME productivity
- 3 Fuel Production Rate evaluated using lower heating value for liquid at 25°C

The data obtained from the AFDU are compared to expectations in Figures 9 (lower inlet velocity) and 10 (higher inlet velocity). The expectations were computed from kinetic and mixing models. The kinetic model was developed to correlate the laboratory DME data; the reactor mixing model was developed during the previous LPMEOH program.

The computed space velocities in Figures 9 and 10 reflect the run AF-R3 correction for settled catalyst. Therefore, at equivalent inlet velocities, the space velocity of AF-R3 is necessarily 10% greater than those from AF-R1 and AF-R2 - hence the discontinuity in the predicted productivity curves.

FIGURE 9:

MeOH and DME Productivities in AFDU Reactor
(SV=5500-6000, prediction based on 2 CSTR mixing model)

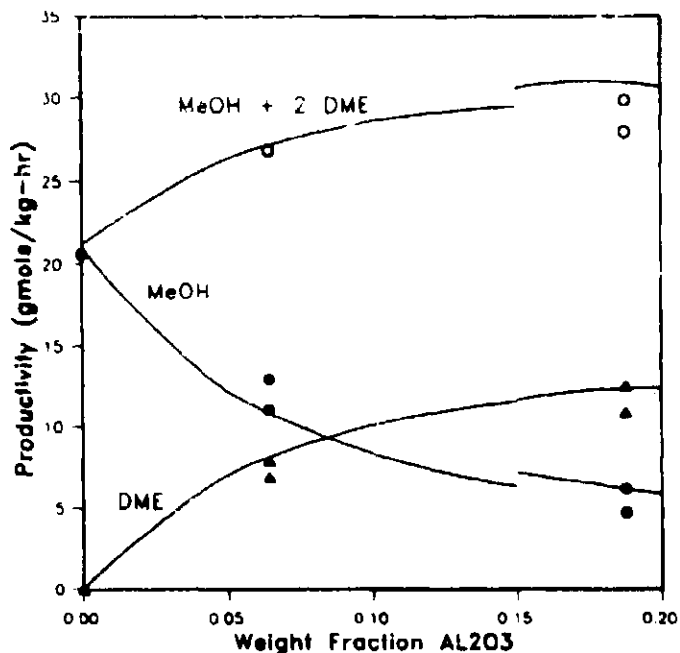
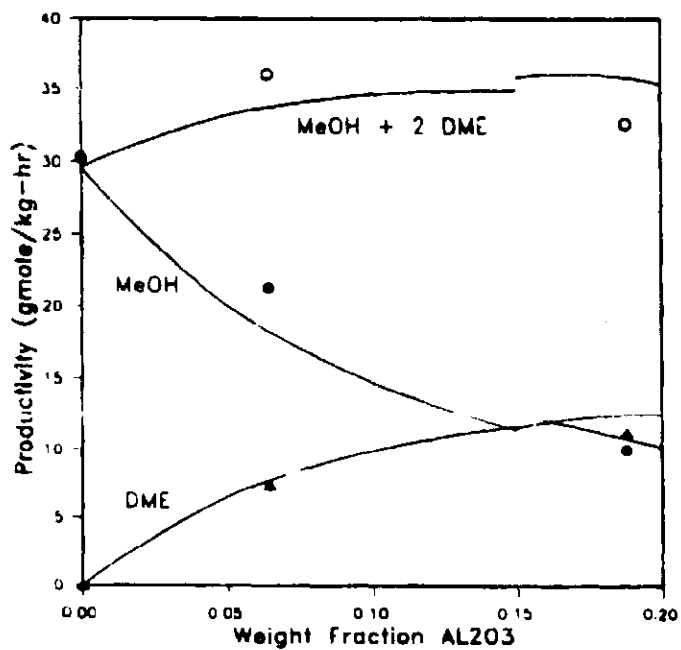


FIGURE 10:

MeOH and DME Productivities in AFDU Reactor
(SV=8600-9300, prediction based on 2 CSTR mixing model)



The trends observed were as expected. Increasing the relative amount of dehydration catalyst initially increases the overall productivity by removing methanol from the system and thereby eliminating the equilibrium constraint of the syngas-to-methanol reaction step. However, the productivity gain diminishes if the concentration of dehydration catalyst is increased beyond a certain level. Overall, a predictable link between the laboratory autoclaves and AFDU bubble column reactor has been confirmed.

SUMMARY

The principle of enhanced syngas conversion was successfully demonstrated. The plant reached the target 32% increase in equivalent productivity at 6.4% alumina - this being accomplished at a 6 TPD scale of operation.

Variation in performance with catalyst proportion as previously demonstrated in the autoclaves was confirmed. Within the regions of operation, both selectivity and productivity increased with dehydration catalyst proportion.

No significant catalyst maldistribution was discernable, confirming that the hydrodynamic performance of the bubble column reactor is generally satisfactory for this catalyst blend. However, an apparent variability in slurry properties with alumina loading has been identified. This conclusion comes from the observation of catalyst "settling" in the third run. It has been postulated that the gas distributor had not induced sufficient velocity to sweep slurry from the bottom head. This was unexpected since the reactor previously operated at such low gas velocities in the past (on methanol catalyst alone). Indeed, the first two runs did not appear to suffer from low flow. It is important to note that such subtle slurriability variations are not easily identified in mechanically stirred autoclaves. Before future runs, a supplemental distributor will be installed to better handle low-flow operation.

FUTURE WORK

With the successfully demonstrated scale-up of liquid-phase DME synthesis, the first building block technology to an ether product (MTBE) has been secured. Chemistries which will convert DME to the precursor to MTBE (isobutanol and/or isobutylene) are currently under investigation in the lab and is hoped to be ready for demonstration in 1993/94. In parallel, the liquid-phase synthesis of higher (C₄) alcohols directly from syngas is also under development. An anticipated demonstration of selective isobutanol synthesis is scheduled for 1992.

ACKNOWLEDGEMENTS

The authors wish to thank their coworkers for numerous contributions to the work reported here and in particular, those who helped recommission and operate the AFDU. They would also like to thank DOE/PETC for their financial backing and project support.

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