RECENT RESEARCH ADVANCES ON THE LPMEOH PROCESS

T. H. HSIUNG T. C. GOLDEN R. P. UNDERWOOD

AIR PRODUCTS AND CHEMICALS, INC. ALLENTOWN, PA 18195

PRESENTED AT THE

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 H. Hsiung, T. C. Golden, and R. P. Underwood Air Products and Chemicals, Inc. Allentown, PA 18195

ABSTRACT

In April 1987, the United States Department of Energy awarded Air Products and Chemicals, Inc. the third consecutive contract on the development of Liquid Phase Methanol process. Key objectives are to demonstrate process simplifications and obtain long term (120 days) catalyst life data on the process development unit (PDU) at LaPorte, Texas. A parallel research program has been formulated to broaden the data base for the process. This paper describes the recent activities in the research program.

Significant progress has been accomplished since the start of the contract. Of the eight research subtasks, four are designed to support the PDU program and the others enhance the understanding of the technology. A new catalyst slurrying liquid and a new commercially available catalyst have been identified and recommended for PDU testing. The effects of CD₂ and H₂D on catalyst performance have been studied experimentally. Depending on the gas matrix, adjusting CO₂ and H₂D contents in the feed has the potential to enhance methanol production. The removal of process impurities in a typical coal gas was addressed by searching adsorbents to remove five prime catalyst poisons. A test of these adsorbents with real coal gas will be conducted later in the contract after a clean-up test unit is built.

INTRODUCTION

The Liquid Phase Methanol (LPMEON*) process differs from conventional gas-phase processes by introducing an inert liquid into the reactor system. Powdered or pelletized catalyst is suspended and well mixed in the liquid where it is contacted with the syngas. The slurrying liquid absorbs the reaction heat effectively, achieving isothermal conditions, to allow a higher conversion per pass than in gas-phase processes. In addition, the LPMEOH process is particularly well suited to coal-derived synthesis gas which is rich in carbon monoxide (1). These capabilities enable the process to be a potentially lower-cost conversion route to methanol, especially when methanol is coproduced in a coal-based integrated gasification combined cycle (IGCC) power plant.

Detailed history and process description are well documented in the literature. Espino and Pletzel (2) of Chem Systems Inc. conceived this concept in the mid-1970s. Initial development studies started in 1975 with most work funded by the Electric Power Research Institute (EPRI). The results of this early work are described in a series of EPRI reports (3, 4, 5). In 1981. Air Products and Chemicals, Inc. (APCI) joined efforts with Chem Systems to demonstrate the new technology at the process development unit (PDU) scale under the sponsorship of the United States Department of Energy (BOE). The first DOE contract (DE-AC22-B1PC30019) was awarded in September 1981 and the second contract (DE-AC22-B5PC80007) was awarded in July 1985. The results of these contracts were documented in the respective final reports of DOE and presented in previous DOE annual Contractors' Meetings (6-10).

In the prior contracts, several key process issues were addressed. The process was shown to be easy-to-operate with very high on-stream factor (98%+). The slurry mode of operation was confirmed as a highly efficient option. In-situ activation of catalyst in the slurry, especially for high slurry concentrations (e.g., >40 wt%), was developed in the laboratory and successfully demonstrated in the PDU at LaPorte, Texas. In addition, the poisoning impact of iron and nickel carbonyls was quantified, and led to piping changes in the PDU to eliminate their formation. A subsequent 40-day run of the LaPorte PDU demonstrated a much slower catalyst deactivation rate than that experienced with a gas phase operation.

The current contract will further the development of the LPMEON process at the POU scale. The primary goal is to develop the data required for the design and operation of a larger scale demonstration LPMEON plant that is reliable and easy to operate. Key emphasis of the contract is the POU modification and operation to demonstrate process simplifications and obtain catalyst life data. A research program is being carried out in parallel to address several outstanding issues of the process. This paper discusses the progress of the research program. Another paper by J. H. Frey et al will be presented in this meeting to detail the PDU program.

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RESEARCH PROGRAM

The focus of the research effort is clearly in support of the LaPorte PDU tests and future process scale-up. Figure 1 lists the eight subtasks under the research program. The Alternative Liquid (Subtask 3.1) and the Alternative Catalyst (Subtask 3.6 & 3.7) program are strategically important in that they signify the LPMEOH process is not limited to one catalyst and one liquid. The Effect of CO₂ (Subtask 3.2), In-situ Reduction Optimization (Subtask 3.3), and fundamental Modelling (Subtask 3.5) enhance the understanding of the process and are the basis for potential improvements. Catalyst Poisons Studies (Subtask 3.4) and Catalyst Poisons Field Test (Subtask 3.8) are critical to the commercialization of the process.

ALTERNATIVE LIQUID MEDIA:

The identification of an alternative slurrying media, preferably from alternate suppliers, is strategically important to the LPMEOH process. In the early stages of the process development, either Witco 40 or Freezene 100 was used as the liquid. Both were products of Witco Corporation. Freezene 100 was concluded to be a more stable oil for the process. All of the LaPorte POU runs prior to 1986 used Freezene 100. In mid-1985, Witco announced the discontinuation of Freezene 100 because of feedstock unavailability. A research effort was initiated in the second DOE contract to search for an alternate liquid medium. After evaluating six additional oils from four different suppliers, Witco 70 and LP-150 were identified as satisfactory alternate liquids. Again, both are products of Witco Corporation. The need to broaden the sources of the process oil still existed, especially when we discovered in mid-1987 that Witco has been planning to change one of its key production procedures from acid treatment to catalytic hydrogenation.

following the methodology established in the previous contract (10), nine potential conmercial liquid products were screened for their physical properties. Five candidate liquids from four different suppliers were then selected for further lab evaluations. Table 1 compares relevant properties of these candidates with those of Witco oils. These five oils were then individually tested for their compatibility with a standard methanol catalyst in a laboratory autoclave. The autoclave, manufactured by Autoclave Engineers, is made of 316 stainless steel and equipped with a Magnadrive II stirrer. A datailed description of the autoclave set-up can be found in Technical Progress Report No. 4 on the first contract. In-situ activation was performed on a 35 wt% slurry of a chosen candidate and the standard catalyst. This was followed immediately by activity tests in the autoclave with a CO-rich gas (51% CO, 35% N₂, 13% CO₂, and 1% N₂) simulating a clean coal gas from a Texaco gasifier. Figure 2 depicts the test results. Except for Mobil SHF 61, all other oil slurries exhibited acceptable activity in autoclave.

Based on price, availability, reliability, and plant experience, Drakeol 10 from Penreco was chosen for a 40-day autoclave life test. The oil was shown to be very compatible with the methanol catalyst, as the catalyst slurry exhibited stable performance over the 40-day experiment. A sample of the spent oil was analyzed by ASTM D2887-73 simulated distillation method. Figure 3 shows a comparison of the distillation curve of the spent oil with

that of a fresh oil. Only slight loss of the light ends was noted, suggesting Drakeol 10 is acceptably stable under the process conditions. Drakeol 10 was then recommended for the LaPorte PDU.

EFFECTS OF CO2 IN CO-RICH GAS:

The role of $\rm CO_2$ on methanol synthesis over copper/zinc oxide has attracted many interesting studies (11-13). Whether methanol is predominantly synthesized by $\rm CO$ or $\rm CO_2$ hydrogenation has brought some disagreement among the researchers. However, they seem to agree that both $\rm CO$ and $\rm CO_2$ have to coexist to show reasonable catalyst productivity for commercial interest.

In this subtask, lab experiments were designed to address the effects of varying CO₂ in a coal gas, usually rich in CO. Coal gas from a Texaco gasifier has a typical gas composition of 51% CO, 35% H₂, 13% CO₂, and 1% inerts (N₂ & CH₄). Table 2 lists the gas mixtures studied. Gas A is the standard CO-rich gas, and Gases B-E and Gas E simulate CO₂ addition or withdrawal from Gas A with H₂ and CO varying in a fixed ratio to compensate for the change of CO₂ content. Gas F which simulates the clean gas from a Shell gasifier provides some diversity to the program. Figure 4 depicts the data on the CO₂ effect. In general agreement with literature, the result indicates that CO₂ benefits methanol productivity when CO₂ content in the feed is relatively low. Figure 3 shows that methanol productivity reaches an optimum when the CO₂ content in the CO-rich gas feed lies around 8%, which suggests that CO₂ removal from the CO-rich gas (13% CO₂) can result in a 10-15% productivity improvement.

To complete the study, the effects of water on catalyst performance were also investigated. Water and $\rm CO_2$ are exchangeable to a large degree in a methanol reactor through the water gas shift reaction. The effect of water, however, has not been as extensively studied as the effect of $\rm CO_2$. Employing isotopes in methanol synthesis, Vedage et al (14) concluded that water was a primary reactant. The methanol synthesis rate over a $\rm Cu/ZnO$ catalyst was greatly enhanced by adding small amount of water to the $\rm H_2/CO$ feed gas. However, at higher concentrations, water retarded the methanol yield.

In this study, water was added to Gases A-D and Gas F of Table 2. Catalyst activity was measured in an autoclave. With Gas A (CO-rich gas), Figure 5 shows the effect of water on the standard methanol catalyst at two gas-hourly-space velocities (GHSV). At lower GHSV (5000 sl/kg-hr), the results showed an optimum in methanol productivity with approximately 2% water in the feed. However, at higher GHSV (10,000 sl/kg-hr), methanol productivity decreases with increasing water content. With Gas D (CO₂ free), water addition enhanced methanol productivity dramatically as depicted in Figure 6. Specifically, with 1 mol% water added, the methanol rate increased from 12.6 to 24.1 gmol/kg-hr at 10,000 GHSV. The productivity increased further to 30.6 gmol/kg-hr when 5 mol% water was added. The beneficial effect of water was less pronounced at 5,000 GHSV. With gases of intermediate CO₂ contents. Gases B and C, Figure 7 summarizes the results. As expected, the effect of water on catalyst performance depends on the CO₂ content of the feed.

Water can enhance methanol productivity when the feed gas contains relatively low ${\rm CO_2}$ and high ${\rm CO/H_2}$. Coal gas from a Shell gasifier is one such example. Gas f of Table 2 simulate the Shell coal gas. The results of water addition are shown in Figure B.

Mater and CO_2 effects were also salectively studied at 225°C. All these data will be incorporated in the earlier data base obtained in the prior contracts to establish a comprehensive model for better understanding and scale-up of the LPMEDH process. This modelling effort will be conducted in Subtask 3.5, Fundamental Modelling.

CATALYST POISONS STUDIES:

Purification of coal-derived syngas is one outstanding issue not only for the LPMEOF process but also for other methanol processes using copper based catalyst. Anticipated process impurities and their respective levels in a coal gas were best estimated by APCI as shown in Table 3. Also included in Table 3 are the catalyst design specifications for these impurities.

The objective of the Catalyst Poisons Studies is to recommend the most efficient adsorbents for the removal of five prime catalyst poisons in the process gas. These catalyst poisons are iron and nickel carbonyls, hydrogen sulfide, carbonyl sulfide, and hydrogen chloride. A corollary objective is to develop fast and reliable analytical methods for the quantifications of these impurities at the parts-per-million (ppm) and parts-per-billion (ppb) level. Yet, another objective of this task is to investigate whether or not COS is a catalyst poison. The incorporation of the last objective was precipitated by the studies of Wood et al (15) who reported that COS did not poison Cu/ZnO methanol catalysts at a concentration range of 0.6-9 ppmV.

Analytical Method Development:

In the first DDE contract, a gas chromatography (GD) method was developed for detecting from and nickel carbonyls at the ppbV levels. This GC method uses a squalane column and an electron capture detector (ECD). Details of this GC/ECD method and its development can be found in the final report (16).

Additional analytical methods are needed for fast and reliable analyses of COS, H₂S, and HCl. After a comprehensive literature search, the analytical chemists at APCI recommended another GC method for the quantification of COS and H₂S. This method uses a 4' Hayesep Q column heated to 50°C using He carrier gas with a flow rate of 30 ml/min. The eluted gases are detected with a photoionization detector equipped with an 11.7 ev lamp. A typical chromatogram is shown in Figure 9. The method is fine-tuned for the detection of both COS and H₂S in the low ppbV ranges.

Attempts to develop a GC method for HCl analysis were not successful. For the analytical requirement on HCl adsorbent screening, an on-line FI-IR instrument was used. This IR analyzer was a Nicolet 100X instrument with a sensitivity range of 1 to 10 ppmy.

In addition to the instrumental methods of analyses, complementary wet chemical methods were also developed for COS and HC! quantifications in synthesis gas. The emphasis was to develop methods that can consistently quantify these impurities in the sub-ppm concentration range. These wet chemical methods have been developed and will be documented in the final report.

2. Autoclave Test of COS Poisoning on Methanol Catalyst:

Carbonyl sulfide was tested in the APCI laboratory to see if it would deactivate a Cu/ZnO/Al₂O₃ methanol catalyst. A slurry of a commercial methanol catalyst and Drakeol 10 oil was prepared and loaded into the autoclave. After in-situ activation, the catalyst was exposed to the CO-rich gas at 250°C and 750 psig to establish a baseline before the introduction of COS. The inlet concentration of COS was measured by the GC/ECD method to be around 5 ppmV.

The test results are summarized in Figure 10. The catalyst deactivation was observed almost immediately with the introduction of COS. After 70 hours on 5 ppm COS, the catalyst lost over 50% of its original activity as the methanol productivity dropped from 32 to 15 gmol/kg-hr. The GHSV was 10,000 sl/kg-hr. COS is concluded to be detrimental to a methanol catalyst.

During the COS experiment, the exit stream was constantly monitored for COS breakthrough. No COS was detected by the GC for the entire duration. The spent catalyst was washed with cyclohexane and submitted for sulfur analysis. Elemental analysis by Inductively Coupled Plasma (ICP) revealed 0.58 wt% S on the spent catalyst, which agreed well with the 0.55 wt% number calculated assuming that all the S put in the reactor stayed on the catalyst. The spent catalyst was also analyzed by XRD. Although no sulfur compound was detected, the crystallite sizes for Cu (156 A) and ZnO (>1000 A) were much larger than expected for normal liquid phase operation.

3. Adsorbents Screening for Poisons Removal:

A recirculating adsorption apparatus was used to screen adsorbents for the removal of the five key process impurities. Equilibrium and kinetic adsorption characteristics of various adsorbents can be obtained using this unit. A schematic of this apparatus is shown in Figure 11. The adsorption vessel is made of 1/2° stainless tubing and can house up to 10 ml of adsorbent. A Teflon diaphragm pump is used to circulate the gas inside the apparatus.

The recirculating apparatus is capable of screening adsorbents efficiently. A fixed volume of gas containing a known initial concentration of catalyst poison is continuously circulated through the adsorbent bed of known weight until a final equilibrium concentration is reached. The amount adsorbed at equilibrium conditions is a data point for an adsorption isotherm. The approach to equilibrium with respect to time yields kinetic data. With the adsorption isotherm and the kinetic data, an adsorber design can be accomplished.

Many adsorbents were screened in the adsorption unit for the individual removal of $Fe(CO)_5$, $Ni(CO)_4$, COS, H_2S , and HCI. The concentration targets of these process impurities are shown in Table 3. In addition to the

equilibrium capacities of these adsorbents, their regenerability was also tested. A summary of the best adsorbents resulting from this study is presented in Table 4.

The results of this study will be incorporated into the design of a clean-up test rig for further evaluations with a real coal gas. The issue of interaction of multicomponent adsorption/desorption will be addressed. This Catalyst Poisons Field Test will be conducted later under the current DDE contract.

TESTING ALTERNATIVE CATALYSTS:

The objective of this task is to identify alternative commercial low temperature methanol catalysts for the LPMEDH process. Representative catalyst samples, before pelletizing, were requested from vendors and tested in APCI laboratories. The criteria for an acceptable alternate catalyst is not only the intrinsic catalyst activity but also its ability to be effectively used in a slurry reactor. For example, the catalyst should have lower porosity to allow higher catalyst loading in a given reactor so that the reactor volume productivity can be increased, and the catalyst should exhibit low fouling tendency in the slurry so that heat exchanger tubes and reactor internals will not be coated with stagnant catalyst. Slurry rheology, which affects reactor hydrodynamics, also influences reactor productivity. In the second contract, the rheology of catalyst slurries was studied (16). The slurries exhibited yield stress and shear-thinning behavior. Both increased exponentially with volume fraction of solids.

Three commercially available methanol catalyst samples were evaluated. All three catalysts showed high methanol activity in autoclave tests as exhibited in Figure 11. Physical properties of these samples are compared with those of the standard catalyst in Table 5. Catalyst F21/DE75-43, which has the lowest slurry viscosity and the lowest packed volume in oil should have the best slurry properties for the process. The catalyst was, therefore, recommended for a life test in the autoclave before being tested in the PDU at LaPorte.

AUTOCLAVE LIFE TEST - ALTERNATE CATALYST:

Catalyst F21/0675-43 was subjected to a 40-day life test in the autoclave with a 15 wt% slurry of this catalyst in Drakeo? 10 off. Test conditions were 250°C and 750 psig. The CO-rich gas was fed at a GHSV of 5400 s1/kg-hr. Figure 13 summarizes the results of both the methano? productivity and exit methanol concentration plotted against time on sympas. Due to serious 60 problems, earlier activity data are missing. However, consistent and frequent data were obtained after 575 hours on stream. A total run time of 1050 hours was achieved.

From this figure, the decline of methanol productivity (and reactor exit methanol concentration) seems to be leveling off with time on stream. Using the data obtained after 600 hours on stream, a linear deactivation rate of 0.0016 productivity units per hour can be estimated. This rate of decline compares favorably against the standard catalyst. The equivalent rate of decline was about 0.0024 productivity units per hour from the data reported in the final Report of the prior 005 contract (17).

The spent catalyst was analyzed for Cu and ZnO crystallite sizes. Moderate growth was noted on both Cu and ZnO, as indicated in Table 6.

The catalyst is concluded to be acceptable for the LPMEOH process and recommended for further testing in the PDU at LaPorte, Texas.

CONCLUSIONS

Significant progress has been achieved toward the research objectives of this contract. Both Drakeol 10 oil and F21/DE75-43 catalyst have been successfully tested in the LaPorte PDU. The PDU results will be presented by J. Frey. The data obtained from the CO2 and H20 studies will be incorporated in the Fundamental Modelling task to better understand and control the reaction system. The results from the Catalyst Poisons Studies will be the basis for further work on a test rig, currently under construction, to treat a real coal gas for the LPMEOH process. In addition, a simple method of storing activated catalyst slurry is recommended to LaPorte for later catalyst addition and withdrawal practice. Furthermore, more simplistic catalyst activation schemes are being investigated to improve the existing in-situ activation procedure.

At the completion of this contract, we shall have a solid design basis to confidently engineer a LPMEOH process at a demonstration or commercial scale.

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Figure 1. DOE LP III RESEARCH PROGRAM (TASK 3)

OBJECTIVE:

enhance the likelihood of commercialization of the LPMEOH process. To extend the data base of the LPMEOH process technology and

SUBTASKS:

.1 Alternate liquid media studies

3.2 Effects of CO2 in CO-rich gas

3.3 In-situ reduction optimization

3.4 Catalyst poisons studies

3.5 Fundamental modelling

3.6 Testing afternate catalysts

3.7 Autoclave life test - alternate catalyst

3.8 Catalyst poisons field test

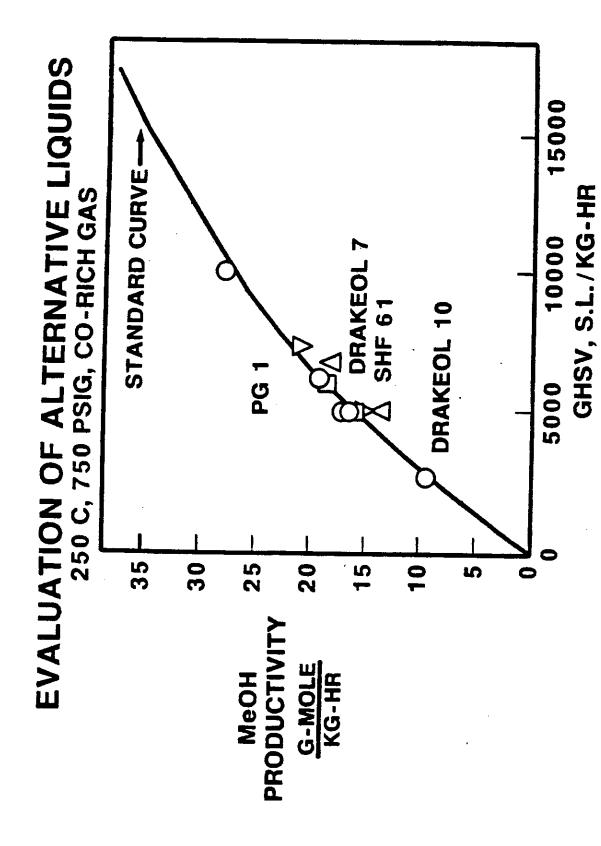
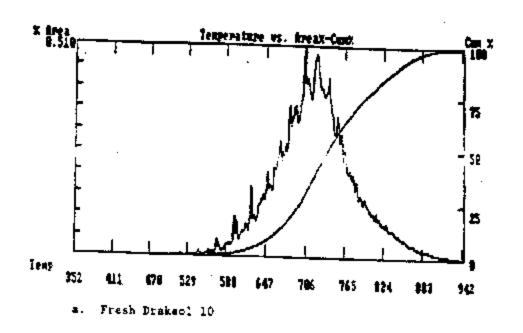
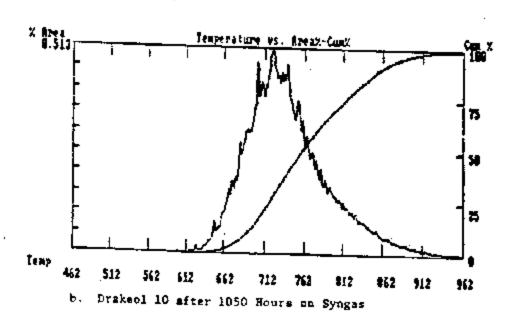
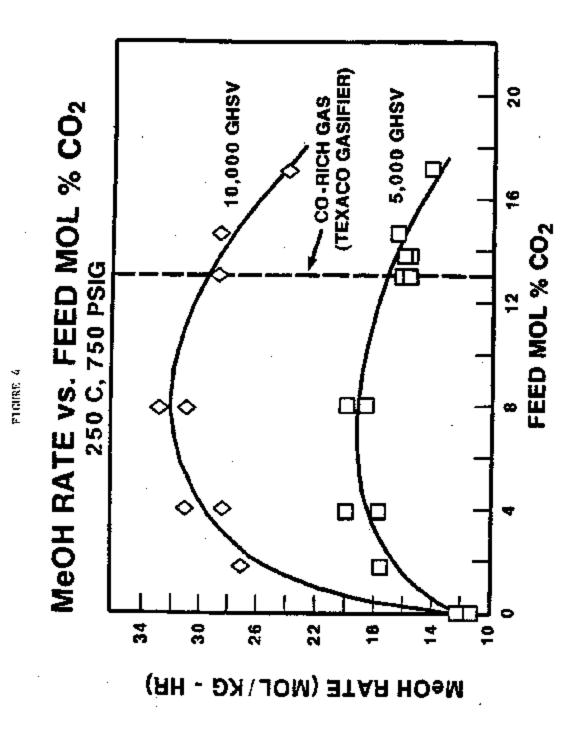
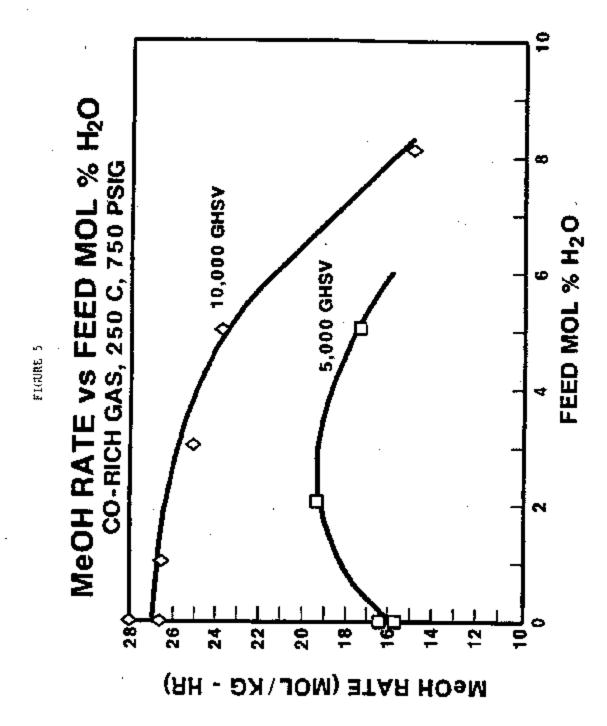


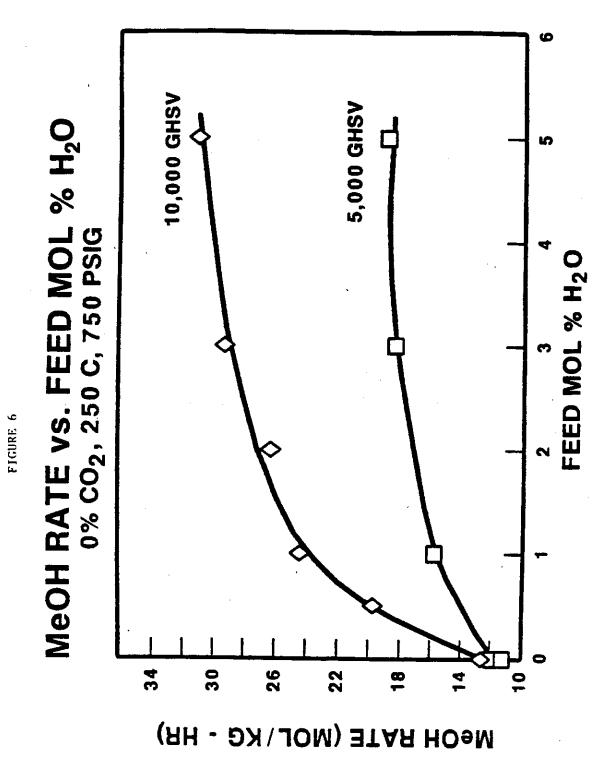
Figure 3 - Simulated Distillation of Drakeol 10 011 (ASTM 2887-73)

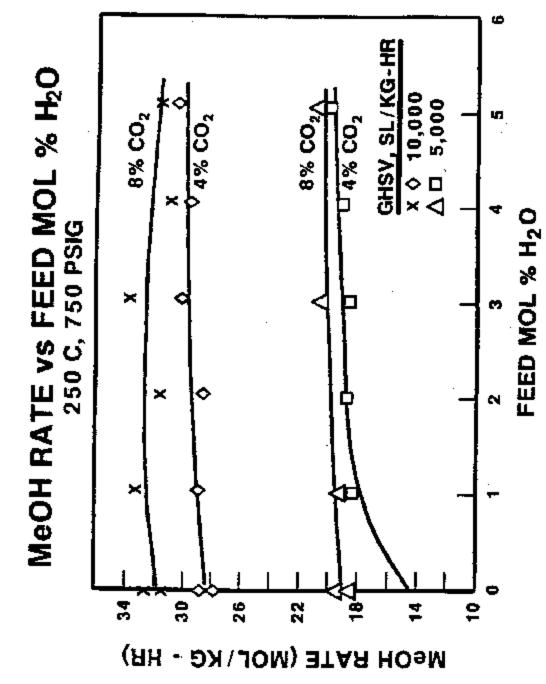












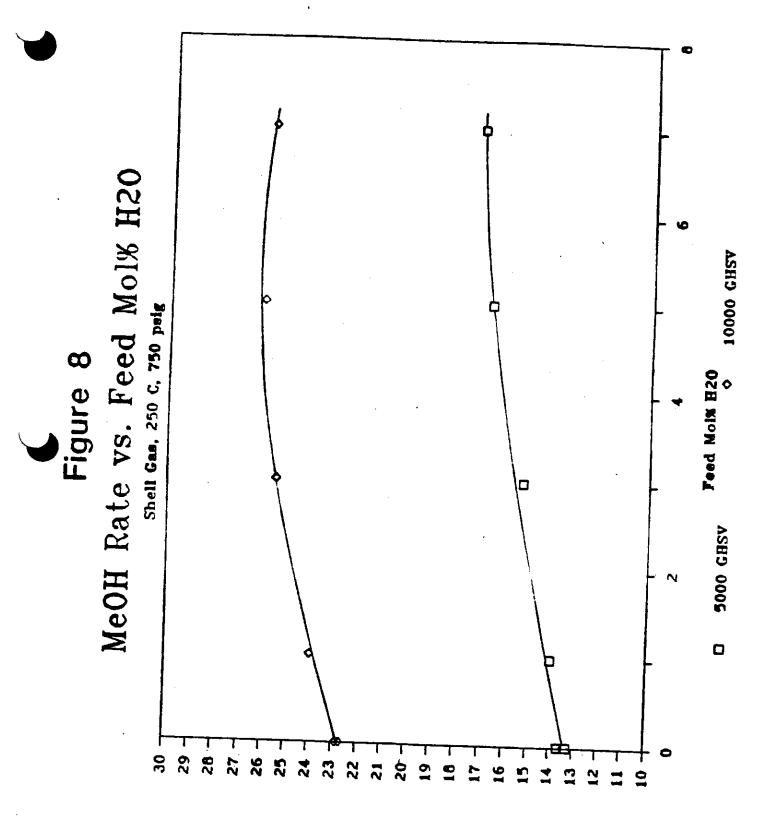


Figure 9. GC METHOD FOR PPM H2S AND COS ANALYSIS

METHOD

- . COLUMN: 4' HAYSEP Q
- . DETECTOR: PHOTO IONIZATION DETECTOR (PID)
- . CARRIER: HE @ 30 CC/MIN
- . OVEN TEMPERATURE: 50°C

CHROMATOGRAM:

GAS SAMPLE		
HYDROGEN NITROGEN CARBON MONOXIDE HYDROGEN SULFIDE CARBONYL SULFIDE CARBON DIOXIDE	29.7% 19.8% 9.72% 2 PPM 8 PPM BALANCE	STOP RUH # 158 OCT 21, 1987 16:37:08 START IF 1.915 8 ₂ \$ 2.525 COS
		STOP
	,	31UF
		RUHH 150 OCT 21, 1987 (6:37:68
		AREAR RT AREA TYPE WIDTH AREAR 1.915 66377 86 .131 28.59723 3.525 165814 88 .275 71.41274 TOTAL PREA= 232191 NUL FACTOR=1.88886486

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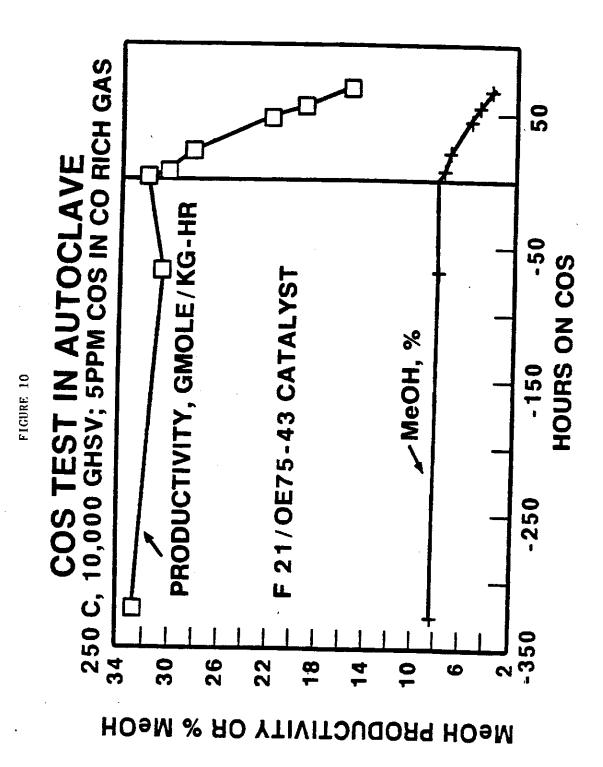


FIGURE 11

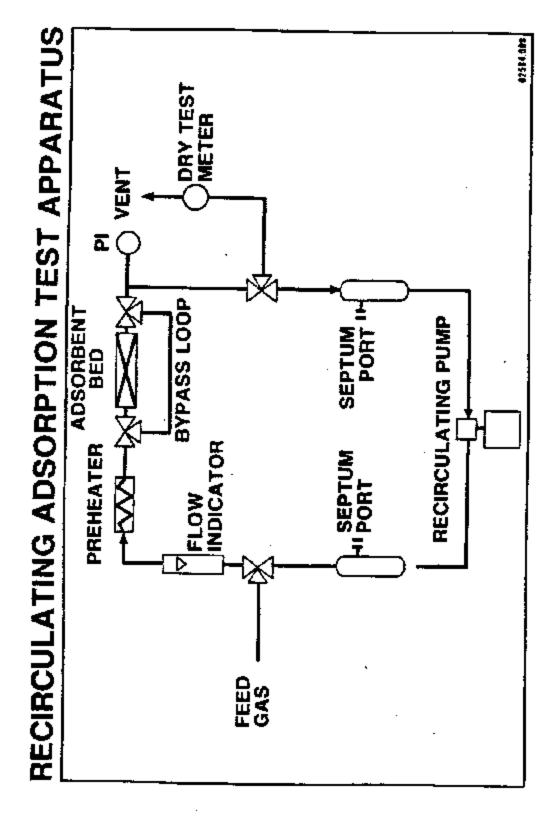
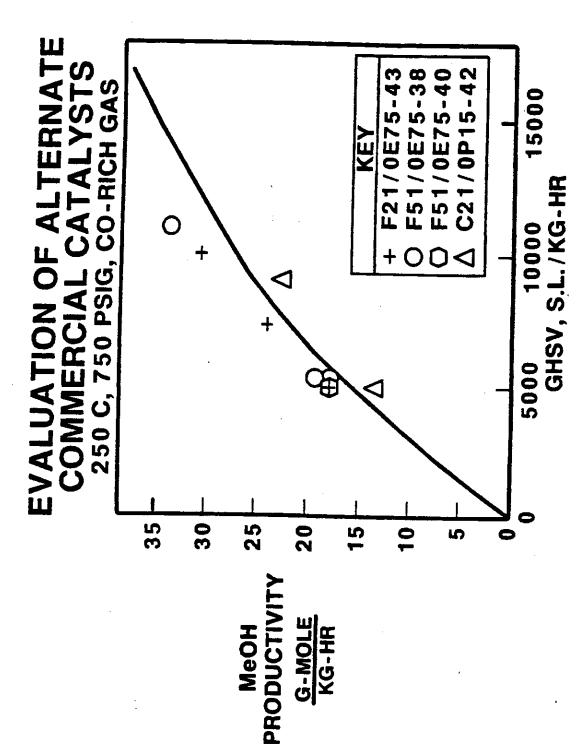


FIGURE 12



FICURE 13

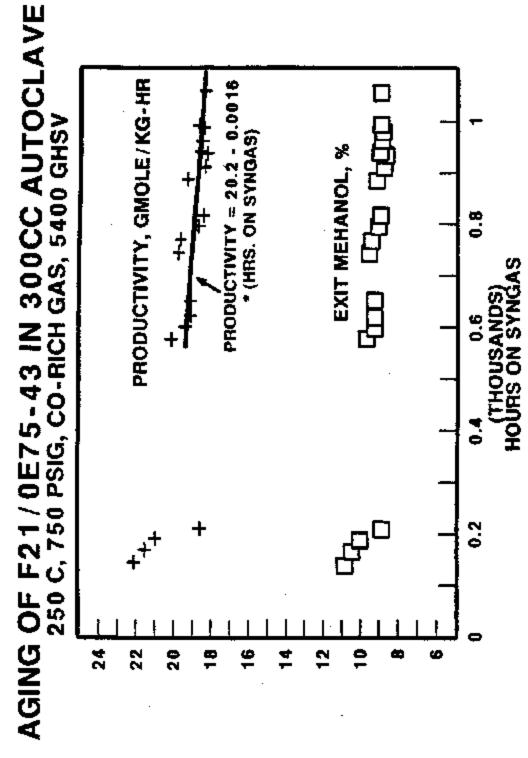


Table 1

LPMEDH Process Alternate Liquid Properties

	Freezene-100	Witco-40	Witco Witco-70	LP-150	Penreco Drakeol 7		Multitherm	Mob ! 1
Average Molecular Weight	340	245			323	366	2 5	SHF61
Distillation (ASTM D1160), *C 18P 10% 50% 90% EP	263 317 369 473	268 294 318 341 380	310 338 396 419	348 379 390 447	316 328 374 449 512	263 353 407	95 9E	B
Specific Gravity, g/ml 25°c 6 75°c	0.854	0.815	0.830	0.856	0.838	0.849	0.866	0.825
Hydrocarbon Type (PONA) % Paraffinic/Naphthenic	001	<u>8</u>	001	8	66/34	65/35	66, 1/13.9	* 00.
Surface Tension, DYNE/CM 25°C 250°C	30.2 16.5	28.2 13	29.6	30.4	\$.5	8	50.0	
Viscosity, cP 25°C 75°C	34.0	6.0 -	19.5	57.0 9.1	17.9	31.2	8	
Pour Pint, *C	'n	-36	15	32	7	ŗ	7	ᅏ
Flash Point, *C)10 01.<	011 <	2110) 110 011<	179	S	171	×210
Vapor Pressure, psia 250°C	6: 1						•	

Table 2. GASES FOR CO2 EFFECT STUDIES

Convents	CO-rich gas, Texaco Gasiller	CO-rich gas, with CO2 removal	CO-rich gas, with CO2 removal	CO-rich gas, with CO2 removal	CO-rich gas, with CO2 addition	Shell Gasifier	CO-rich gas, with CO2 removal
					•		
mole %	-	_		_	 -	_	
N2.							
H2, mote % CO2, mote % N2, mote %	13	ಕು	*	0	19	က	CV
٥							
H2, mate %	35	37	38.7	40.3	33	30	39.5
Gas CO, mole %	13	54	56.3	58.7	48	99	57.5
Gas	< <	:	ပ	۵	ш	ш	<u> </u>

TABLE 3

MAJOR TRACE CONTAMINANTS IN LPMEOH SYNGAS FEED

	_Design Conce	ntration, ppmv
Trace Component	Adsorber Feed Limit	Catalyst Design Limit
Sulfur Compounds*		
H ₂ S COS	5	
Total Sulfur	10	
Total Sallur	15	0.06
Halides	•	
Chloride	20	
Fluoride	5	
Total Halides	•	0.01
Hydrocarbons		
Ethylene, Benzene and		
Other Unsaturates	•	
Acetylene	2	300
	. •	5.0
Nitrogen Compounds	•	
NH ₃	5	10.0
NOX	0.001	0.1
HCN	6	0.01
Salaval /aslustbules		
Selexol (polyethylene) glycol dimethyl ether)		
gracor dimethyr ether)	0.02**	
Iron, as Fe(CO)s	Ę	
Nickel, as Ni(CO)4	5 1	0.01
	ī	0.01

^{*} Much higher levels have been reported. Limit set based on apparent economic operating range of guard bed materials.

0455N

^{**} Based on a vapor pressure of 0.0007 mm Hg at 77°F, and assuming no entrainment of liquid.

A SUMMARY OF ADSORBENT SCREENING STUDIES Table 4.

Impurity	Expected impurity Conc., ppmV	# of Adsorbent Tested	Recommended Adsorbent	# of Adsorbent Recommended Capacity @75 F Tested Adsorbent mmol/gm	Regenerable © 500 F N2
Fe(CO)5	ĸ	6	BPL carbon H-Y zeolite	0.96	no yes
N(CO)4	-	~	BPL cerbon	0.048	ye9
4ZS	ĸ	o	spent cat. FCA carbon	2.1 2.2	5 5
SOO	9	6 0	FCA carbon	- 2900	y69
Ŧ	50	,	spent cat. FCA carbon	7.44 @ 5ppm 2.7	SP 55

TABLE 5

PHYSICAL PROPERTIES OF ALTERNATE CATALYSTS

	F2'	1/0E75	F51	/0E75
	* -44	* -43	* -38	* -40
LOI, wt%	11.5	14.5	13.9	20.5
BET, m2/gm	84.6	87.4	103.3	70.1
Viscosity, mPas, #	136	64	212	173
Stlg Rate cc/min, ##	2.07	2.27	0.53	0.53
Packed Vol% @20 wt% in Freezene	38	29	46	46
Pore Vol% cc/gm	0.785	0.588	1.17	0.988
Skeletal (He) Density, g/cc	4.7 4.21	4.55	4.99 4.47	4.31 3.81

[#] Apparent viscosity of 35 wt% slurry @ 25°C and 100/sec shear rate.

^{##} Initial setting rate of 20 wt% slurry in Freezene at room temperature.

Table 6

XRD RESULTS ON F21/0E75-43 CATALYSTS

Cu, Å Zno, Å	90 20	132 62
HRS. ON GAS	0	1050
#NOW	FRESH CATALYST	9397-36-EOR