APPENDIX C

Fluid Dynamic (Methanol) Run Authorizations

TEST AUTHORIZATION # 46

LaPorte Alternative Fuels Development Unit (AFDU)

Date : 06/03/95
By: BLB

RUN NUMBER: AF-A9
APPROX. START DATE: 3 June, 1995

TITLE: IN-SITU METHANOL CATALYST ACTIVATION USING DILUTE CO PRIOR TO HYDRODYNAMIC RUN

OBJECTIVE:
To activate the Liquid-Phase Methanol (LPMEOH) synthesis catalyst.

SUMMARY:
Approximately 1177 lbs of standard baseline catalyst is to be slurried with Drakeol-10 oil, transferred to the 27.20 reactor and activated with dilute CO (4% in nitrogen). Approximate run time is 2 days.

TEST DETAILS: See pages 2 to 4 for details.

ANALYTICAL COMMENTS: See page 4.

SAFETY IMPLICATIONS:
Operators should wear protective gear while loading catalyst to protect them from the dust and hot vapor which may be released from the loading nozzle. Protective gear including face shield should be worn during slurry sampling.

This operation will require the venting of unreacted CO. During a previous activation (performed under TEST AUTHORIZATION #29) the off-gas was blended with methane and burned in the flare. Previous calculations (for TA #23) indicated that in the event a combustible mixture could not be maintained, there would be no danger to personnel from venting. The reduction gas flow rates to be used in this run are less than those used in TA #23.

ENVIRONMENTAL IMPLICATIONS:
Minimal, a flame will be maintained at the flare. At 98% destruction efficiency, the CO emission rate would be 0.72 lb/hr.

SPECIAL REMARKS:
CO and H_2 concentrations in and out of the reactor must be monitored closely during the reduction. Reactor temperature must be closely monitored and controlled per the attached TEST DETAILS. The utility oil inlet temperature (TI 1244) to the 27.20 internal heat exchanger must not exceed a 200°F difference from the utility oil outlet temperature (TI-1246) or the reactor slurry temperature. These two temperature differentials are measured directly by TDI-1252 & TDI-1237. When adjusting flows or pressure, care should be taken to minimize catalyst carryover (caused by high gas velocity).

AUTHORIZATIONS:

E. C. Heydorn, Plant Mgr

B. L. Bhatt, Process Engr

TEST DETAILS:

1. This reduction procedure follows previous methanol catalyst reductions from the LPIII ER-6 reduction (TEST AUTHORIZATION #23), 1991 DME run (#25), 1992 LPSHIFT run (#29), and the 1994 methanol run (#37).

2. Charge the 28.30 prep tank with 1766 lb of oil (250 gallons of Drakeol-10 at 80°F). The oil should be transferred to drums and weighed using the scale for accurate measurement. As an approximation, meter the oil with FQI-334 using a meter correction factor of actual = 1.027 * meter (meter should read 243 gal). If the temperature differs from 80°F a corrected oil volume should be used. Heat this oil to 150-200°F.

3. Fill the 27.14 intermediate V/L separator to 25 nuts on LG-358 with approximately 100 gallons of Drakeol-10 oil from storage. Note the FQI-334 readings before and after the addition.

4. When the prep tank oil is at 150-200°F, add 1177 lb of baseline methanol catalyst (3 full drums and a small portion from a fourth drum). Add the catalyst very slowly to make a 40 wt% oxide slurry. Keep the slurry well stirred to prevent agglomeration of the catalyst.

5. Heat the slurry to 200°F and continue agitation, under nitrogen, for at least 2 hours to ensure good mixing.

6. When the catalyst and oil have been completely mixed, withdraw a sample of slurry.

7. Establish gas flow through the reactor using nitrogen through V-2627 to prevent slurry back-flow into the distributor. Vent the gas through PV-1261.

8. Pressure transfer the slurry to the reactor and verify operation by noting level with the nuclear density gauge (NDG- estimated level: 23 to 27 ft.)

9. Flush out the prep tank with 283 lb of oil (40 gallons of Drakeol-10 at 80°F). Measure the oil as in step 2 (meter should read approximately 38.9 gal). Pressure transfer the flush oil to the reactor and verify level with the NDG (LI-1242).

10. Close V-645 to prevent utility oil flow back to the prep tank and establish full utility oil flow through the 27.20 internal heat exchanger.

11. Pressurize the reactor loop to 67 psig.

12. Begin heating the slurry to 200°F, following TAVR on the DEC console. Check that the slurry temperatures are in reasonable agreement. Verify that the slurry is well mixed by performing a NDG scan.

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LaPorte Alternative Fuels Development Unit (AFDU)

Sheet: 3 of 4
Date : 06/03/95
By: BLB

13. Establish Dilute CO reduction gas flow at 12500 SCFH (on FI-126) and vent the flow through PV-170. Establish the following composition:

	Composition	Est. Flows (SCFH)
CO	4.0	500
N2	96.0	12000
	100.0	12500

MW = 28, SCF evaluated at 70°F, 14.7 psia
Target space velocity = 615 sL/h-kg; Target starting inlet superficial velocity = 0.48 ft/sec

14. When the reactor temperature reaches 200°F, bring reduction gas to the reactor slowly and close the nitrogen purge (V-2627). Establish a final flow to the reactor of 12,500 SCFH. Maintain flow and reducing gas composition as specified in step 13. The temperature-programmed activation consists of the following steps:

   - Heat the slurry at a target rate of 15°F/hr (no more than 18°F/hr, 10°C) until the slurry temperature reaches 464°F (240°C).

   H2 and CO concentrations are to be measured continuously for the feed and effluent streams. As long as the cumulative CO consumption minus H_2 Production at a given temperature is equal to or greater than the autoclave reduction data then the activation is proceeding well. Figure 1 shows the consumption profile vs temperature from the labs. If the cumulative consumption curve falls below the autoclave curve, consult the process or research engineer to reduce the heat up rate.

   If the CO concentration in the effluent falls below 0.1 mole %, increase the inlet CO concentration per the instructions of the process or research engineer. The objective here is to prevent reduction gas starvation.

   Once a slurry temperature of 392°F is reached decrease the dilute CO reduction gas flow to 9375 SCFH (on FI-126). Maintain the following composition:

	Composition	Est. Flows (SCFH)
CO	4.0	375
N2	96.0	9000
	100.0	9375

MW = 28, SCF evaluated at 70°F, 14.7 psia
Target space velocity = 461 sL/h-kg; Target starting inlet superficial velocity = 0.47 ft/sec

The reduction is expected to be complete before reaching 464°F. It may become necessary to hold slurry at this temperature until the difference between inlet and outlet CO concentration falls below 0.05 mole %.

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LaPorte Alternative Fuels Development Unit (AFDU)

Date : 06/03/95
By: BLB

15. The slurry level should be maintained between 90 and 95% of NDG range (approximately 40 ft.) by using LIC 1242 to control the makeup oil rate. Note that as the reactor is heated to 464 F, the slurry will expand. At the same time, some of the oil will be lost in the reactor effluent. If authorized by the process engineer or the plant manager, additional makeup oil can be added to the system via the 27.14 by following the standard procedure; FQI-334 readings and the change in level of the 27.14 should be recorded before and after each addition. It is important to note that the discharge valve of the 10.52.01 and 02 pumps should be used to throttle to the 67 psig reactor pressure. The pressure in the sump of the 21.11 should be at 150 psig or less.

16. Record any indication of density or viscosity change, such as a change in the pressure drop across the reactor or shaking of the reactor during heat up and reduction.

17. During the reduction, scan the reactor with the NDG, record levels in the 21.11 and 27.14 every 4 hrs. At the end of the reduction, add fresh oil to 27.14 to bring the level up to 25 nuts on LG-358. This charge should be drawn from storage; note the FQI-334 readings before and after addition.

TA #46 is done, consult TEST AUTHORIZATION #47 for the next step.

ANALYTICAL REQUIREMENTS:

1. Catalyst sampling requirements:

   - slurried oxide catalyst from prep tank before reduction,

   Exact quantities to be determined by operations, process, and research.

2. Composition sampling requirements:

   - reactor in and out continuously
   - H_2 and CO are critical
   - CO_2 and N_2 are also required

3. Flow measurement requirements:

   - reactor in at FI-126 and FI-299

REFERENCES:

1. TEST AUTHORIZATION # 23 : Procedure for previous in-situ activation.

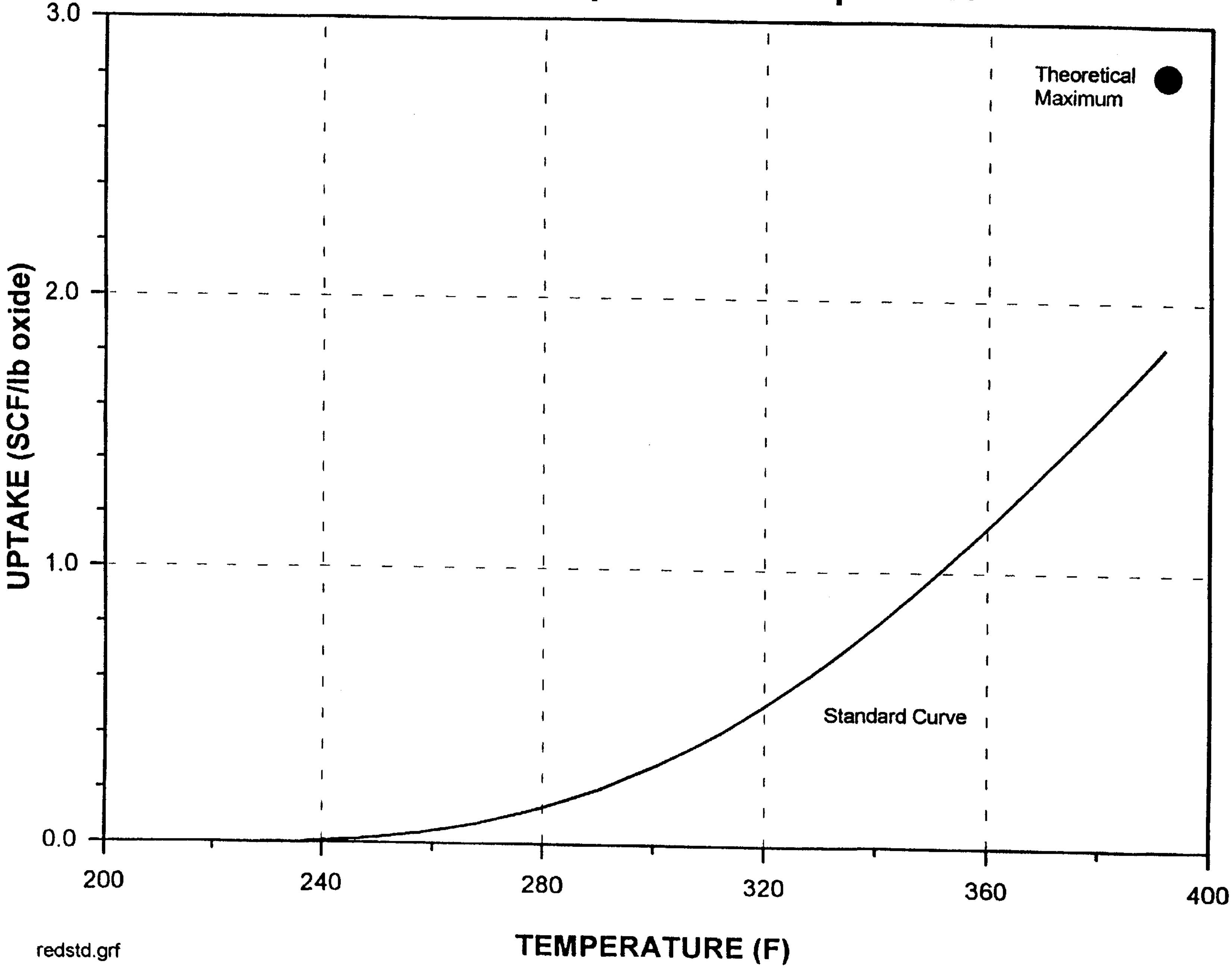
RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A9	AF-R13.1	AF-R.13.2	AF-R.13.3
Description	- - -	- - -	BSLN (REDTN)	BSLN (PVS)	BSLN (PVS)	BSLN (PVS)
Duration	- - -	days	1	2	3	2
Syngas	- - -	- - -	- - -	TEXACO	KINGSPORT	TEXACO
Inlet Space Velocity	- - -	sL/kg-hr	615	7,000	4,000	10,000
Reactor Pressure	PIC-1247	psig	67	750	735	750
REACTOR						
Pressure	PIC-1247	psig	67	750	735	750
Temperature	TI-1233	F	- - -	482	482	482
Heat Duty		MM BTU/hr	- - -	1.10	1.14	1.31
Inlet Superficial Velocity	- - -	ft/sec	0.62	0.83	0.48	1.20
Outlet Superficial Velocity	- - -	ft/sec	0.62	0.68	0.35	1.01
Liquid Level	LI-2142	% span	80%	100%	100%	100%
Catalyst Load	- - -	lb	1,177	1,177	1,177	1,177
Cat Weight Fraction	- - -	%	40%	42%	40%	43%
Vapor Void Fraction	- - -	%	24%	43%	35%	48%
FRESH FEED FLOWS						
LP H2	FIC-101	scfh	0	18,342	21,495	14,774
CO	FIC-104	scfh	500	15,217	11,995	18,598
CO2	FIC-107	scfh	0	1,185	1,040	1,373
N2	FIC-111	scfh	12,000	56	270	55
01.10 Total Flow	FI-726	scfh	12,500	34,800	34,800	34,800
HP H2	FIC-1200	scfh	0	7,283	2,467	17,837
01.20 Recycle	FIC-246	scfh	0	100,929	43,670	151,825
REACTOR FEED						
Target Feed Temp	TI-1253	F	- - -	362	392	357
Feed Dewpoint	- - -	F	- - -	89	78	91
Total Dry Flow	FI-1216	scfh	12,500	143,012	80,937	204,462
H2	- - -	mol%	0.0%	34.70%	60.90%	34.70%
CO	- - -	mol%	4.0%	50.56%	24.49%	50.56%
N2	- - -	mol%	96.0%	0.99%	3.90%	0.99%
CO2	- - -	mol%	0.0%	12.88%	10.02%	12.88%
MEOH	- - -	mol%	0.0%	0.71%	0.42%	0.75%
ETOH	- - -	mol%	0.0%	0.00%	0.00%	0.00%
PROH	- - -	mol%	0.0%	0.00%	0.00%	0.00%
C1	- - -	mol%	0.0%	0.00%	0.08%	0.02%
			100.0%	99.84%	99.81%	99.90%

RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A9	AF-R13.1	AF-R.13.2	AF-R.13.3
Description	- - -	- - -	BSLN (REDTN)	BSLN (PVS)	BSLN (PVS)	BSLN (PVS)
21.11 Feed/Product Exchanger						
Feed Inlet Temp	TI-1257	F	- - -	172	210	165
Feed Outlet Temp	TI-1263	F	- - -	402	402	402
Total Feed to 02.63 Temp	TI-1216	F	- - -	362	392	357
Reactor Eff. Inlet Temp	TI-1262	F	- - -	482	482	482
Reactor Eff. Outlet Temp	TIC-1260	F	- - -	280	280	280
Reactor Eff. Dew Temp	- - -	F	- - -	226	268	219
REACTOR EFFLUENT						
Total Flow	FI-196	scfh	- - -	118,117	59,152	172,712
H2	- - -	mol%	- - -	20.91%	46.47%	22.64%
CO	- - -	mol%	- - -	50.50%	14.66%	50.58%
N2	- - -	mol%	- - -	1.20%	5.36%	1.18%
CO2	- - -	mol%	- - -	15.79%	14.01%	15.35%
MEOH	- - -	mol%	- - -	11.09%	17.88%	9.87%
DME		mol%		0.09%	0.25%	0.05%
ETOH	- - -	mol%	- - -	0.08%	0.24%	0.06%
PROH	- - -	mol%	- - -	0.02%	0.08%	0.01%
C4OH	- - -	mol%	- - -	0.01%	0.03%	0.00%
IBOH	- - -	mol%	- - -	0.00%	0.01%	0.00%
C5OH+	- - -	mol%	- - -	0.01%	0.02%	0.00%
C1	- - -	mol%	- - -	0.04%	0.16%	0.03%
			- - -	99.73%	99.17%	99.77%
PRODUCT RECOVERY						
Syngas to Backend Flow	FI-682	scfh	- - -	None	None	None
22.11 to Flare Flow	FI-237	scfh	- - -	854	630	1,046
Main Flare Flow	FI-245	scfh	- - -	3,869	3,869	3,869
Product Flow	- - -	gpd	- - -	3,794	3,319	4,852
RECYCLE FEED						
H2	- - -	mol%	- - -	23.52%	57.66%	25.08%
CO	- - -	mol%	- - -	56.76%	18.13%	55.97%
N2	- - -	mol%	- - -	1.35%	6.65%	1.30%
CO2	- - -	mol%	- - -	17.13%	16.29%	16.48%
MEOH	- - -	mol%	- - -	1.01%	0.78%	1.01%
C1	- - -	mol%	- - -	0.04%	0.16%	0.03%
			- - -	99.81%	99.67%	99.87%

METHANOL CATALYST REDUCTION
Reduction Gas Uptake vs. Temperature



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TEST AUTHORIZATION # 47

LaPorte Alternative Fuels Development Unit (AFDU)

Date : 06/04/95
By: BLB

RUN NUMBER: AF-R13
APPROX. START DATE: 5 June, 1995

TITLE: METHANOL SYNTHESIS WITH BASELINE CATALYST

OBJECTIVE:
To study the performance of the baseline methanol catalyst in the 27.20 reactor train.

SUMMARY:
Upon completion of the activation step (AF-A9), the reactor feed will be adjusted to a Texaco gas composition (35% H2, 51% CO, 13% CO2, 1% N2). For approximately 2 days, the conditions will be targeted at 750 psig, 482°F, 7,000 sL/kg-hr space velocity, and 40 wt% oxide in oil. After 2 days, the gas composition will be switched to a Kingsport LPMEOH gas composition for three days of operation (60.7% H2, 24.4% CO, 10.0% CO2, 3.89% N2). Finally, a high velocity condition will be tested (1.2 ft/sec) with Texaco gas for 2 days. The main objective of this run is to evaluate the catalyst performance with the modified reduction procedure.

TEST DETAILS: See page 2.

ANALYTICAL COMMENTS: See page 3.

SAFETY IMPLICATIONS:
Protective gear including face shield should be worn during slurry sampling.

ENVIRONMENTAL IMPLICATIONS:
Minimal.

SPECIAL REMARKS:
The high pressure hydrogen pipe line will be in use during run AF-R13. The CO2 removal system will not be in operation. Special sample bombs will be used to collect samples of the methanol product produced during case AF-R13.2.

AUTHORIZATIONS:

E. C. Heydorn, Plant Mgr

B. L. Bhatt, Process Engr

<u>**TEST AUTHORIZATION # 47**</u>

LaPorte Alternative Fuels Development Unit (AFDU)

Date : 06/04/95
By: BLB

TEST DETAILS:

1. Upon completion of the catalyst activation (AF-A9), switch from reduction gas to Texaco-type gas by following the standard procedure. The CO2 removal section should NOT be operating during this run (V-2001,V-2003,V-2004,V-2006 shut; V-2000 open). In the event of a premature shut-down, consult TA #20 (RUN E-05) for appropriate standby conditions.

2. Increase the reactor pressure to 750 psig and control the slurry temperature at 482°F. Slowly increase the reactor feed rate to 25,000 SCFH while maintaining slurry level at 95% of NDG span. When the plant has lined out, the reactor feed composition should correspond closely to case AF-R13.1 (refer to Table). Once the compositions are lined out, slowly introduce recycle flow and back off the fresh feed flowrates until they match the targets outlined in the Table for case AF-R13.1. Note that the HP hydrogen pipeline is in service during all the three cases.

3. When the target feed rate has been achieved, put LIC-1242 in automatic to control slurry level at 95%. Adjust the fresh feed flow to achieve an initial purge flow rate of approximately 3,000 SCFH. Maintain reactor feed flow and reactor temperature and pressure at the case AF-R13.1 values for a nominal 24 hour period.

4. During the first 24 hours, the syngas conversion across the reactor will fall as the catalyst loses its hyperactivity. The purge flow will increase and the reactor feed composition will be changing during this period. When these rates of change diminish, fine tune the fresh feed flow to reach the desired reactor feed composition as specified for case AF-R13.1. The ultimate purge rate should be around 3,900 SCFH.

5. After the initial break-in period, begin to increase rates to maximize production of methanol. Monitor the air-cooler loading and temperature difference between the utility oil and the slurry and utility oil inlet & outlet using TDI-1237 and TDI-1252. Both of these temperature differences must be below 200°F.

6. The composition of the methanol product is to be monitored every 8 hours. The target oil content of the methanol product should be <=0.2 wt%. If the oil content is higher, lower the 21.11 effluent outlet TIC-1260 set point.

7. Maintain conditions for approximately 2 days. After conferring with the process engineer or plant manager, switch to AF-R13.2 run conditions (Kingsport gas). Run this data period for approximately 3 days.

8. Liquid samples of the methanol product will be collected in special sample bombs and shipped to Allentown for detailed analysis during case AF-R13.2. The samples will be collected downstream of the 22.11 separator. Consult with the process engineer and analytical representative for the frequency and manner of taking the samples.

9. After conferring with the process engineer or plant manager, switch to AF-R13.3 run conditions (Texaco gas). Run this data period for approximately 2 days.

10. When notified by the plant manager that case AF-R13.3 is complete, de-pressurize the plant, and drain the slurry from the 27.20 reactor using the prep tank as an intermediate hold point using the standard shutdown procedures. Drain the 22.10, 22.15 and 22.16. Proceed with TEST AUTHORIZATION #48.

ANALYTICAL COMMENTS:

1. Catalyst sampling requirements:
   - slurried catalyst at end-of-run.

   Exact quantities to be determined by operations, process, and research.

2. Continuous composition sampling requirements (GC):
   - fresh feed,
   - reactor in,
   - reactor out,
   - recycle
   - 22.10 overheads

3. Periodic composition sampling requirements (GC):

   - 22.11 off-gas (frequency to be determined by operations & process)

   Periodic composition sampling requirements (LC):

   - methanol product (every 8 hours during first two days, twice a day thereafter)

4. Flow measurement requirements:

   - fresh feed,
   - reactor in,
   - reactor out,
   - recycle,
   - purge,
   - 22.11 off-gas,
   - methanol product

REFERENCES:

1. TEST AUTHORIZATION #20 - Procedures for reactor standby during shutdown.

2. STANDARD STARTUP PROCEDURES FOR MeOH-ONLY OPERATION

RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A9	AF-R13.1	AF-R.13.2	AF-R.13.3
Description	- - -	- - -	BSLN (REDTN)	BSLN (PVS)	BSLN (PVS)	BSLN (PVS)
Duration	- - -	days	1	2	3	2
Syngas	- - -	- - -	- - -	TEXACO	KINGSPORT	TEXACO
Inlet Space Velocity	- - -	sL/kg-hr	615	7,000	4,000	10,000
Reactor Pressure	PIC-1247	psig	67	750	735	750
REACTOR						
Pressure	PIC-1247	psig	67	750	735	750
Temperature	TI-1233	F	- - -	482	482	482
Heat Duty		MM BTU/hr	- - -	1.10	1.14	1.31
Inlet Superficial Velocity	- - -	ft/sec	0.62	0.83	0.48	1.20
Outlet Superficial Velocity	- - -	ft/sec	0.62	0.68	0.35	1.01
Liquid Level	LI-2142	% span	80%	100%	100%	100%
Catalyst Load	- - -	lb	1,177	1,177	1,177	1,177
Cat Weight Fraction	- - -	%	40%	42%	40%	43%
Vapor Void Fraction	- - -	%	24%	43%	35%	48%
FRESH FEED FLOWS						
LP H2	FIC-101	scfh	0	18,342	21,495	14,774
CO	FIC-104	scfh	500	15,217	11,995	18,598
CO2	FIC-107	scfh	0	1,185	1,040	1,373
N2	FIC-111	scfh	12,000	56	270	55
01.10 Total Flow	FI-726	scfh	12,500	34,800	34,800	34,800
HP H2	FIC-1200	scfh	0	7,283	2,467	17,837
01.20 Recycle	FIC-246	scfh	0	100,929	43,670	151,825
REACTOR FEED						
Target Feed Temp	TI-1253	F	- - -	362	392	357
Feed Dewpoint	- - -	F	- - -	89	78	91
Total Dry Flow	FI-1216	scfh	12,500	143,012	80,937	204,462
H2	- - -	mol%	0.0%	34.70%	60.90%	34.70%
CO	- - -	mol%	4.0%	50.56%	24.49%	50.56%
N2	- - -	mol%	96.0%	0.99%	3.90%	0.99%
CO2	- - -	mol%	0.0%	12.88%	10.02%	12.88%
MEOH	- - -	mol%	0.0%	0.71%	0.42%	0.75%
ETOH	- - -	mol%	0.0%	0.00%	0.00%	0.00%
PROH	- - -	mol%	0.0%	0.00%	0.00%	0.00%
C1	- - -	mol%	0.0%	0.00%	0.08%	0.02%
			100.0%	99.84%	99.81%	99.90%

RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A9	AF-R13.1	AF-R.13.2	AF-R.13.3
Description	- - -	- - -	BSLN (REDTN)	BSLN (PVS)	BSLN (PVS)	BSLN (PVS)
21.11 Feed/Product Exchanger						
Feed Inlet Temp	TI-1257	F	- - -	172	210	165
Feed Outlet Temp	TI-1263	F	- - -	402	402	402
Total Feed to 02.63 Temp	TI-1216	F	- - -	362	392	357
Reactor Eff. Inlet Temp	TI-1262	F	- - -	482	482	482
Reactor Eff. Outlet Temp	TIC-1260	F	- - -	280	280	280
Reactor Eff. Dew Temp	- - -	F	- - -	226	268	219
REACTOR EFFLUENT						
Total Flow	FI-196	scfh	- - -	118,117	59,152	172,712
H2	- - -	mol%	- - -	20.91%	46.47%	22.64%
CO	- - -	mol%	- - -	50.50%	14.66%	50.58%
N2	- - -	mol%	- - -	1.20%	5.36%	1.18%
CO2	- - -	mol%	- - -	15.79%	14.01%	15.35%
MEOH	- - -	mol%	- - -	11.09%	17.88%	9.87%
DME		mol%		0.09%	0.25%	0.05%
ETOH	- - -	mol%	- - -	0.08%	0.24%	0.06%
PROH	- - -	mol%	- - -	0.02%	0.08%	0.01%
C4OH	- - -	mol%	- - -	0.01%	0.03%	0.00%
IBOH	- - -	mol%	- - -	0.00%	0.01%	0.00%
C5OH+	- - -	mol%	- - -	0.01%	0.02%	0.00%
C1	- - -	mol%	- - -	0.04%	0.16%	0.03%
			- - -	99.73%	99.17%	99.77%
PRODUCT RECOVERY						
Syngas to Backend Flow	FI-682	scfh	- - -	None	None	None
22.11 to Flare Flow	FI-237	scfh	- - -	854	630	1,046
Main Flare Flow	FI-245	scfh	- - -	3,869	3,869	3,869
Product Flow	- - -	gpd	- - -	3,794	3,319	4,852
RECYCLE FEED						
H2	- - -	mol%	- - -	23.52%	57.66%	25.08%
CO	- - -	mol%	- - -	56.76%	18.13%	55.97%
N2	- - -	mol%	- - -	1.35%	6.65%	1.30%
CO2	- - -	mol%	- - -	17.13%	16.29%	16.48%
MEOH	- - -	mol%	- - -	1.01%	0.78%	1.01%
C1	- - -	mol%	- - -	0.04%	0.16%	0.03%
			- - -	99.81%	99.67%	99.87%

TEST AUTHORIZATION # 48

LaPorte Alternative Fuels Development Unit (AFDU)

Date : 06/12/95
By: BLB

RUN NUMBER: AF-A10
APPROX. START DATE: 12 June, 1995

TITLE: IN-SITU METHANOL CATALYST ACTIVATION USING DILUTE CO PRIOR TO HYDRODYNAMIC RUN

OBJECTIVE:
To activate the Liquid-Phase Methanol (LPMEOH) synthesis catalyst.

SUMMARY:
Approximately 1177 lbs of an alternate methanol catalyst is to be slurried with Drakeol-10 oil, transferred to the 27.20 reactor and activated with dilute CO (4% in nitrogen). Approximate run time is 2 days.

TEST DETAILS: See pages 2 to 4 for details.

ANALYTICAL COMMENTS: See page 4.

SAFETY IMPLICATIONS:
Operators should wear protective gear while loading catalyst to protect them from the dust and hot vapor which may be released from the loading nozzle. Protective gear including face shield should be worn during slurry sampling.

This operation will require the venting of unreacted CO. During a previous activation (performed under TEST AUTHORIZATION #29) the off-gas was blended with methane and burned in the flare. Previous calculations (for TA #23) indicated that in the event a combustible mixture could not be maintained, there would be no danger to personnel from venting. The reduction gas flow rates to be used in this run are less than those used in TA #23.

ENVIRONMENTAL IMPLICATIONS:
Minimal, a flame will be maintained at the flare. At 98% destruction efficiency, the CO emission rate would be 0.72 lb/hr.

SPECIAL REMARKS:
CO and H_2 concentrations in and out of the reactor must be monitored closely during the reduction. Reactor temperature must be closely monitored and controlled per the attached TEST DETAILS. The utility oil inlet temperature (TI 1244) to the 27.20 internal heat exchanger must not exceed a 200°F difference from the utility oil outlet temperature (TI-1246) or the reactor slurry temperature. These two temperature differentials are measured directly by TDI-1252 & TDI-1237. When adjusting flows or pressure, care should be taken to minimize catalyst carryover (caused by high gas velocity).

AUTHORIZATIONS:

E. C. Heydorn, Plant Mgr.   B. L. Bhatt, Process Engr

TEST DETAILS:

1. This reduction procedure follows previous methanol catalyst reductions from the LPIII ER-6 reduction (TEST AUTHORIZATION #23), 1991 DME run (#25), 1992 LPSHIFT run (#29), 1994 methanol run (#37) and the recent hydrodynamic run with baseline catalyst (#46).

2. Charge the 28.30 prep tank with 1766 lb of oil (250 gallons of Drakeol-10 at 80°F). The oil should be transferred to drums and weighed using the scale for accurate measurement. As an approximation, meter the oil with FQI-334 using a meter correction factor of actual = 1.027 * meter (meter should read 243 gal). If the temperature differs from 80°F a corrected oil volume should be used. Heat this oil to 150-200°F.

3. Fill the 27.14 intermediate V/L separator to 25 nuts on LG-358 with approximately 100 gallons of Drakeol-10 oil from storage. Note the FQI-334 readings before and after the addition.

4. When the prep tank oil is at 150-200°F, add 1177 lb of alternate methanol catalyst (10 full drums and a portion from an eleventh drum). Add the catalyst very slowly to make a 40 wt% oxide slurry. Keep the slurry well stirred to prevent agglomeration of the catalyst.

5. Heat the slurry to 200°F and continue agitation, under nitrogen, for at least 2 hours to ensure good mixing.

6. When the catalyst and oil have been completely mixed, withdraw a sample of slurry.

7. Establish gas flow through the reactor using nitrogen through V-2627 to prevent slurry back-flow into the distributor. Vent the gas through PV-1261.

8. Pressure transfer the slurry to the reactor and verify operation by noting level with the nuclear density gauge (NDG- estimated level: 23 to 27 ft.)

9. Flush out the prep tank with 283 lb of oil (40 gallons of Drakeol-10 at 80°F). Measure the oil as in step 2 (meter should read approximately 38.9 gal). Pressure transfer the flush oil to the reactor and verify level with the NDG (LI-1242).

10. Close V-645 to prevent utility oil flow back to the prep tank and establish full utility oil flow through the 27.20 internal heat exchanger.

11. Pressurize the reactor loop to 67 psig.

12. Begin heating the slurry to 200°F, following TAVR on the DEC console. Check that the slurry temperatures are in reasonable agreement. Verify that the slurry is well mixed by performing a NDG scan.

TEST AUTHORIZATION # 48

LaPorte Alternative Fuels Development Unit (AFDU)

13. Establish Dilute CO reduction gas flow at 12500 SCFH (on FI-126) and vent the flow through PV-170. Establish the following composition:

	Composition	Est. Flows (SCFH)
CO	4.0	500
N2	96.0	12000
	100.0	12500

MW = 28, SCF evaluated at 70°F, 14.7 psia
Target space velocity = 615 sL/h-kg; Target starting inlet superficial velocity = 0.48 ft/sec

14. When the reactor temperature reaches 200°F, bring reduction gas to the reactor slowly and close the nitrogen purge (V-2627). Establish a final flow to the reactor of 12,500 SCFH. Maintain flow and reducing gas composition as specified in step 13. The temperature-programmed activation consists of the following steps:

- Heat the slurry at a target rate of 15°F/hr (no more than 18°F/hr, 10°C) until the slurry temperature reaches 464°F (240°C).

H2 and CO concentrations are to be measured continuously for the feed and effluent streams. As long as the cumulative CO consumption minus H_2 Production at a given temperature is equal to or greater than the autoclave reduction data then the activation is proceeding well. Figure 1 shows the consumption profile vs temperature from the labs. If the cumulative consumption curve falls below the autoclave curve, consult the process or research engineer to reduce the heat up rate.

If the CO concentration in the effluent falls below 0.1 mole %, increase the inlet CO concentration per the instructions of the process or research engineer. The objective here is to prevent reduction gas starvation.

Once a slurry temperature of 392°F is reached decrease the dilute CO reduction gas flow to 9375 SCFH (on FI-126). Maintain the following composition:

	Composition	Est. Flows (SCFH)
CO	4.0	375
N2	96.0	9000
	100.0	9375

MW = 28, SCF evaluated at 70°F, 14.7 psia
Target space velocity = 461 sL/h-kg; Target starting inlet superficial velocity = 0.47 ft/sec

The reduction is expected to be complete before reaching 464°F. It may become necessary to hold slurry at this temperature until the difference between inlet and outlet CO concentration falls below 0.05 mole %.

15. The slurry level should be maintained between 90 and 95% of NDG range (approximately 40 ft.) by using LIC 1242 to control the makeup oil rate. Note that as the reactor is heated to 464 F, the slurry will expand. At the same time, some of the oil will be lost in the reactor effluent. If authorized by the process engineer or the plant manager, additional makeup oil can be added to the system via the 27.14 by following the standard procedure; FQI-334 readings and the change in level of the 27.14 should be recorded before and after each addition. It is important to note that the discharge valve of the 10.52.01 and 02 pumps should be used to throttle to the 67 psig reactor pressure. The pressure in the sump of the 21.11 should be at 150 psig or less.

16. Record any indication of density or viscosity change, such as a change in the pressure drop across the reactor or shaking of the reactor during heat up and reduction.

17. During the reduction, scan the reactor with the NDG, record levels in the 21.11 and 27.14 every 4 hrs. At the end of the reduction, add fresh oil to 27.14 to bring the level up to 25 nuts on LG-358. This charge should be drawn from storage; note the FQI-334 readings before and after addition.

TA #48 is done, consult TEST AUTHORIZATION #49 for the next step.

ANALYTICAL REQUIREMENTS:

1. Catalyst sampling requirements:

    - slurried oxide catalyst from prep tank before reduction,

   Exact quantities to be determined by operations, process, and research.

2. Composition sampling requirements:

    - reactor in and out continuously
    - H_2 and CO are critical
    - CO_2 and N_2 are also required

3. Flow measurement requirements:

    - reactor in at FI-126 and FI-299

REFERENCES:

1. TEST AUTHORIZATION # 23 : Procedure for previous in-situ activation.

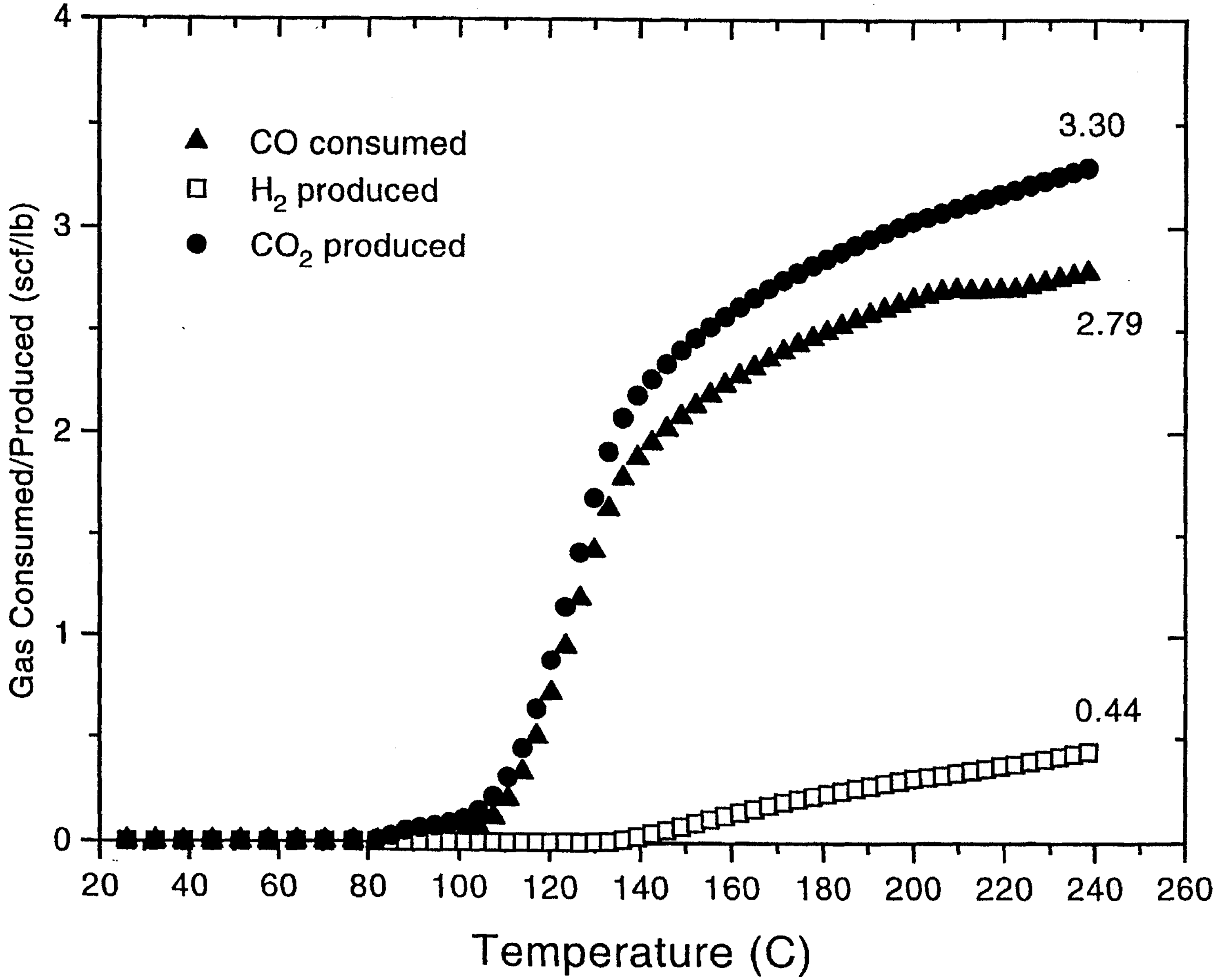
RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A10	AF-R14.1	AF-R14.2	AF-R14.3	AF-R14.4	AF-R14.5	AF-R14.6	AF-R14.7	AF-R14.8
Description	- - -	- - -	ALT (REDTN)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (TRC)	ALT (TRC)	ALT (TRC)
Duration	- - -	days	1	2	3	1.5	1.5	1	1	1	1
Syngas	- - -	- - -	- - -	TEXACO	KINGSPORT	KINGSPORT	TEXACO	TEXACO	TEXACO	TEXACO	KINGSPORT
Inlet Space Velocity	- - -	sL/kg-hr	615	7,000	4,000	10,000	4,000	7,000	7,000	4,000	7,000
Reactor Pressure	PIC-1247	psig	67	750	735	735	750	750	750	750	520
REACTOR											
Pressure	PIC-1247	psig	67	750	735	735	750	750	750	750	520
Temperature	TI-1233	F	- - -	482	482	482	482	482	482	482	482
Heat Duty		MM BTU/hr	- - -	1.10	1.14	2.00	0.73	1.10	1.10	0.73	
Inlet Superficial Velocity	- - -	ft/sec	0.62	0.83	0.48	1.21	0.47	0.83	0.83	0.47	1.18
Outlet Superficial Velocity	- - -	ft/sec	0.62	0.68	0.35	0.95	0.38	0.68	0.68	0.38	0.94
Liquid Level	LI-2142	% span	80%	100%	100%	100%	100%	100%	100%	100%	100%
Catalyst Load	- - -	lb	1,177	1,177	1,177	1,177	1,177	1,177	1,177	1,177	1,158
Cat Weight Fraction	- - -	%	40%	42%	40%	41%	41%	42%	42%	41%	44%
Vapor Void Fraction	- - -	%	24%	43%	35%	42%	39%	43%	43%	39%	49%
FRESH FEED FLOWS											
LP H2	FIC-101	scfh	0	18,342	21,495	11,080	16,029	18,342	18,342	16,029	1,620
CO	FIC-104	scfh	500	15,217	11,995	21,420	10,469	15,217	15,217	10,469	10,000
CO2	FIC-107	scfh	0	1,185	1,040	2,050	914	1,185	1,185	914	772
N2	FIC-111	scfh	12,000	56	270	250	56	56	56	56	61
01.10 Total Flow	FI-726	scfh	12,500	34,800	34,800	34,800	27,468	34,800	34,800	27,468	12,453
HP H2	FIC-1200	scfh	0	7,283	2,467	33,730	0	7,283	7,283	0	18,930
01.20 Recycle	FIC-246	scfh	0	100,929	43,670	134,220	54,113	100,929	100,929	54,113	110,160
REACTOR FEED											
Target Feed Temp	TI-1253	F	- - -	362	392	373	369.0	362	362	369.0	373
Feed Dewpoint	- - -	F	- - -	89	78	86	87.0	89	89	87.0	86
Total Dry Flow	FI-1216	scfh	12,500	143,012	80,937	203,230	81,581	143,012	143,012	81,581	141,690
H2	- - -	mol%	0.0%	34.70%	60.90%	60.92%	34.68%	34.70%	34.70%	34.68%	60.92%
CO	- - -	mol%	4.0%	50.56%	24.49%	24.50%	50.54%	50.56%	50.56%	50.54%	24.50%
N2	- - -	mol%	96.0%	0.99%	3.90%	3.90%	0.99%	0.99%	0.99%	0.99%	3.90%
CO2	- - -	mol%	0.0%	12.88%	10.02%	10.03%	12.88%	12.88%	12.88%	12.88%	10.03%
MEOH	- - -	mol%	0.0%	0.71%	0.42%	0.53%	0.67%	0.71%	0.71%	0.67%	0.53%
ETOH	- - -	mol%	0.0%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
PROH	- - -	mol%	0.0%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
C1	- - -	mol%	0.0%	0.00%	0.08%	0.04%	0.04%	0.00%	0.00%	0.04%	0.04%
			100.0%	99.84%	99.81%	99.92%	99.80%	99.84%	99.84%	99.80%	99.92%

RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A10	AF-R14.1	AF-R14.2	AF-R14.3	AF-R14.4	AF-R14.5	AF-R14.6	AF-R14.7	AF-R14.8
Description	- - -	- - -	ALT (REDTN)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (TRC)	ALT (TRC)	ALT (TRC)
21.11 Feed/Product Exchanger											
Feed Inlet Temp	TI-1257	F	- - -	172	210	197	180	172	172	180	197
Feed Outlet Temp	TI-1263	F	- - -	402	402	402	403	402	402	403	402
Total Feed to 02.63 Temp	TI-1216	F	- - -	362	392	373	369	362	362	369	373
Reactor Eff. Inlet Temp	TI-1262	F	- - -	482	482	482	482	482	482	482	482
Reactor Eff. Outlet Temp	TIC-1260	F	- - -	280	280	280	280	280	280	280	280
Reactor Eff. Dew Temp	- - -	F	- - -	226	268	247	232	226	226	232	
REACTOR EFFLUENT											
Total Flow	FI-196	scfh	- - -	118,117	59,152	172,712	66,177	118,117	118,117	66,177	116,380
H2	- - -	mol%	- - -	20.91%	46.47%	50.31%	19.50%	20.91%			
CO	- - -	mol%	- - -	50.50%	14.66%	18.18%	50.29%	50.50%			
N2	- - -	mol%	- - -	1.20%	5.36%	4.93%	1.23%	1.20%			
CO2	- - -	mol%	- - -	15.79%	14.01%	12.27%	16.28%	15.79%			
MEOH	- - -	mol%	- - -	11.09%	17.88%	13.64%	11.94%	11.09%			
DME		mol%		0.09%	0.25%	0.04%	0.18%	0.09%			
ETOH	- - -	mol%	- - -	0.08%	0.24%	0.01%	0.12%	0.08%			
PROH	- - -	mol%	- - -	0.02%	0.08%	0.00%	0.03%	0.02%			
C4OH	- - -	mol%	- - -	0.01%	0.03%	0.00%	0.01%	0.01%			
IBOH	- - -	mol%	- - -	0.00%	0.01%	0.00%	0.00%	0.00%			
C5OH+	- - -	mol%	- - -	0.01%	0.02%	0.00%	0.01%	0.01%			
C1	- - -	mol%	- - -	0.04%	0.16%	0.07%	0.07%	0.04%			
			- - -	99.73%	99.17%	99.45%	99.66%	99.73%			
PRODUCT RECOVERY											
Syngas to Backend Flow	FI-682	scfh	- - -	None	None	None	None	None	None	None	None
22.11 to Flare Flow	FI-237	scfh	- - -	854	630	1,050	552	854	854	552	500
Main Flare Flow	FI-245	scfh	- - -	3,869	3,869	3,869	3,869	3,869	3,869	3,869	1,000
Product Flow	- - -	gpd	- - -	3,794	3,319	6,510	2,337	3,794	3,794	2,337	3,247
RECYCLE FEED											
H2	- - -	mol%	- - -	23.52%	57.66%	58.53%	22.20%	23.52%			
CO	- - -	mol%	- - -	56.76%	18.13%	21.22%	57.21%	56.76%			
N2	- - -	mol%	- - -	1.35%	6.65%	5.72%	1.40%	1.35%			
CO2	- - -	mol%	- - -	17.13%	16.29%	13.65%	17.82%	17.13%			
MEOH	- - -	mol%	- - -	1.01%	0.78%	0.81%	1.01%	1.01%			
C1	- - -	mol%	- - -	0.04%	0.16%	0.06%	0.06%	0.04%			
			- - -	99.81%	99.67%	99.99%	99.70%	99.81%			

CO Reduction Profiles of Alternate Catalyst



1419177-scf/lb

TEST AUTHORIZATION # 49

LaPorte Alternative Fuels Development Unit (AFDU)

Sheet: 1 of 3
Date : 06/13/95
By: BLB

RUN NUMBER: AF-R14
APPROX. START DATE: 13 June, 1995

TITLE: METHANOL SYNTHESIS WITH ALTERNATE CATALYST

OBJECTIVE:
To study the performance of the alternate methanol catalyst in the 27.20 reactor train.

SUMMARY:
Upon completion of the activation step (AF-A10), the reactor feed will be adjusted to a Texaco gas composition (35% H2, 51% CO, 13% CO2, 1% N2). For approximately 2 days, the conditions will be targeted at 750 psig, 482°F, 7,000 sL/kg-hr space velocity, and 40 wt% oxide in oil. The gas composition will then be switched to a Kingsport LPMEOH gas composition for three days of operation (60.7% H2, 24.4% CO, 10.0% CO2, 3.89% N2). A high velocity condition will be tested next (1.2 ft/sec) with Kingsport gas for 1.5 days. Over following 3 days, two different gas velocity will be studied with Texaco gas. The initial baseline condition will then be repeated to check for any catalyst deactivation. A tracer study (Run Authorization #50) will follow the process variable study.

The main objectives of this run are to evaluate the alternate catalyst performance in comparison with the baseline catalyst and perform hydrodynamic studies on the reactor.

TEST DETAILS: See page 2.

ANALYTICAL COMMENTS: See page 3.

SAFETY IMPLICATIONS:
Protective gear including face shield should be worn during slurry sampling.

ENVIRONMENTAL IMPLICATIONS:
Minimal.

SPECIAL REMARKS:
The high pressure hydrogen pipe line will be in use during run AF-R14. The CO2 removal system will not be in operation. Special sample bombs will be used to collect samples of the methanol product produced during case AF-R14.2.

AUTHORIZATIONS:

E. C. Heydorn, Plant Mgr

B. L. Bhatt, Process Engr

TEST DETAILS:

1. Upon completion of the catalyst activation (AF-A10), switch from reduction gas to Texaco-type gas by following the standard procedure. The CO_2 removal section should NOT be operating during this run (V-2001,V-2003,V-2004,V-2006 shut; V-2000 open). In the event of a premature shut-down, consult TA #20 (RUN E-05) for appropriate standby conditions.

2. Increase the reactor pressure to 750 psig and control the slurry temperature at 482°F. Slowly increase the reactor feed rate to 25,000 SCFH while maintaining slurry level at 95% of NDG span. When the plant has lined out, the reactor feed composition should correspond closely to case AF-R14.1 (refer to Table). Once the compositions are lined out, slowly introduce recycle flow and back off the fresh feed flowrates until they match the targets outlined in the Table for case AF-R14.1. Note that the HP hydrogen pipeline is in service during all the cases.

3. When the target feed rate has been achieved, put LIC-1242 in automatic to control slurry level at 95%. Adjust the fresh feed flow to achieve an initial purge flow rate of approximately 3,000 SCFH. Maintain reactor feed flow and reactor temperature and pressure at the case AF-R14.1 values for a nominal 24 hour period.

4. During the first 24 hours, the syngas conversion across the reactor will fall as the catalyst loses its hyperactivity. The purge flow will increase and the reactor feed composition will be changing during this period. When these rates of change diminish, fine tune the fresh feed flow to reach the desired reactor feed composition as specified for case AF-R14.1. The ultimate purge rate should be around 3,900 SCFH.

5. After the initial break-in period, begin to increase rates to maximize production of methanol. Monitor the air-cooler loading and temperature difference between the utility oil and the slurry and utility oil inlet & outlet using TDI-1237 and TDI-1252. Both of these temperature differences must be below 200°F.

6. The composition of the methanol product is to be monitored every 8 hours. The target oil content of the methanol product should be <=0.2 wt%. If the oil content is higher, lower the 21.11 effluent outlet TIC-1260 set point.

7. Maintain conditions for approximately 2 days. After conferring with the process engineer or plant manager, switch to AF-R14.2 run conditions (Kingsport gas). Run this data period for approximately 3 days.

8. Liquid samples of the methanol product will be collected in special sample bombs and shipped to Allentown for detailed analysis during case AF-R14.2. The samples will be collected downstream of the 22.11 separator. Consult with the process engineer and analytical representative for the frequency and manner of taking the samples.

9. After conferring with the process engineer or plant manager, switch to AF-R14.3 run conditions (Kingsport gas). Run this data period for approximately 1.5 days.

10. After conferring with the process engineer or plant manager, switch to AF-R14.4 run conditions (Texaco gas). Run this data period for approximately 1.5 days.

11. After conferring with the process engineer or plant manager, switch to AF-R14.5 run conditions (Texaco gas). Run this data period for approximately 1 day.

10. When notified by the plant manager that case AF-R14.5 is complete, refer to Run Authorization #50 to proceed to the tracer study.

ANALYTICAL COMMENTS:

1. Catalyst sampling requirements:
   - slurried catalyst at end-of-run.

   Exact quantities to be determined by operations, process, and research.

2. Continuous composition sampling requirements (GC):
   - fresh feed,
   - reactor in,
   - reactor out,
   - recycle
   - 22.10 overheads

3. Periodic composition sampling requirements (GC):
   - 22.11 off-gas (frequency to be determined by operations & process)

   Periodic composition sampling requirements (LC):
   - methanol product (every 8 hours during first two days, twice a day thereafter)

4. Flow measurement requirements:
   - fresh feed,
   - reactor in,
   - reactor out,
   - recycle,
   - purge,
   - 22.11 off-gas,
   - methanol product

REFERENCES:

1. TEST AUTHORIZATION #20 - Procedures for reactor standby during shutdown.

2. STANDARD STARTUP PROCEDURES FOR MeOH-ONLY OPERATION

RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A10	AF-R14.1	AF-R14.2	AF-R14.3	AF-R14.4	AF-R14.5	AF-R14.6	AF-R14.7	AF-R14.8
Description	- - -	- - -	ALT (REDTN)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (TRC)	ALT (TRC)	ALT (TRC)
Duration	- - -	days	1	2	3	1.5	1.5	1	1	1	1
Syngas	- - -	- - -	- - -	TEXACO	KINGSPORT	KINGSPORT	TEXACO	TEXACO	TEXACO	TEXACO	KINGSPORT
Inlet Space Velocity	- - -	sL/kg-hr	615	7,000	4,000	10,000	4,000	7,000	7,000	4,000	7,000
Reactor Pressure	PIC-1247	psig	67	750	735	735	750	750	750	750	520
REACTOR											
Pressure	PIC-1247	psig	67	750	735	735	750	750	750	750	520
Temperature	TI-1233	F	- - -	482	482	482	482	482	482	482	482
Heat Duty		MM BTU/hr	- - -	1.10	1.14	2.00	0.73	1.10	1.10	0.73	
Inlet Superficial Velocity	- - -	ft/sec	0.62	0.83	0.48	1.21	0.47	0.83	0.83	0.47	1.18
Outlet Superficial Velocity	- - -	ft/sec	0.62	0.68	0.35	0.95	0.38	0.68	0.68	0.38	0.94
Liquid Level	LI-2142	% span	80%	100%	100%	100%	100%	100%	100%	100%	100%
Catalyst Load	- - -	lb	1,177	1,177	1,177	1,177	1,177	1,177	1,177	1,177	1,158
Cat Weight Fraction	- - -	%	40%	42%	40%	41%	41%	42%	42%	41%	44%
Vapor Void Fraction	- - -	%	24%	43%	35%	42%	39%	43%	43%	39%	49%
FRESH FEED FLOWS											
LP H2	FIC-101	scfh	0	18,342	21,495	11,080	16,029	18,342	18,342	16,029	1,620
CO	FIC-104	scfh	500	15,217	11,995	21,420	10,469	15,217	15,217	10,469	10,000
CO2	FIC-107	scfh	0	1,185	1,040	2,050	914	1,185	1,185	914	772
N2	FIC-111	scfh	12,000	56	270	250	56	56	56	56	61
01.10 Total Flow	FI-726	scfh	12,500	34,800	34,800	34,800	27,468	34,800	34,800	27,468	12,453
HP H2	FIC-1200	scfh	0	7,283	2,467	33,730	0	7,283	7,283	0	18,930
01.20 Recycle	FIC-246	scfh	0	100,929	43,670	134,220	54,113	100,929	100,929	54,113	110,160
REACTOR FEED											
Target Feed Temp	TI-1253	F	- - -	362	392	373	369.0	362	362	369.0	373
Feed Dewpoint	- - -	F	- - -	89	78	86	87.0	89	89	87.0	86
Total Dry Flow	FI-1216	scfh	12,500	143,012	80,937	203,230	81,581	143,012	143,012	81,581	141,690
H2	- - -	mol%	0.0%	34.70%	60.90%	60.92%	34.68%	34.70%	34.70%	34.68%	60.92%
CO	- - -	mol%	4.0%	50.56%	24.49%	24.50%	50.54%	50.56%	50.56%	50.54%	24.50%
N2	- - -	mol%	96.0%	0.99%	3.90%	3.90%	0.99%	0.99%	0.99%	0.99%	3.90%
CO2	- - -	mol%	0.0%	12.88%	10.02%	10.03%	12.88%	12.88%	12.88%	12.88%	10.03%
MEOH	- - -	mol%	0.0%	0.71%	0.42%	0.53%	0.67%	0.71%	0.71%	0.67%	0.53%
ETOH	- - -	mol%	0.0%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
PROH	- - -	mol%	0.0%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
C1	- - -	mol%	0.0%	0.00%	0.08%	0.04%	0.04%	0.00%	0.00%	0.04%	0.04%
			100.0%	99.84%	99.81%	99.92%	99.80%	99.84%	99.84%	99.80%	99.92%

RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A10	AF-R14.1	AF-R14.2	AF-R14.3	AF-R14.4	AF-R14.5	AF-R14.6	AF-R14.7	AF-R14.8
Description	- - -	- - -	ALT (REDTN)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (TRC)	ALT (TRC)	ALT (TRC)
21.11 Feed/Product Exchanger											
Feed Inlet Temp	TI-1257	F	- - -	172	210	197	180	172	172	180	197
Feed Outlet Temp	TI-1263	F	- - -	402	402	402	403	402	402	403	402
Total Feed to 02.63 Temp	TI-1216	F	- - -	362	392	373	369	362	362	369	373
Reactor Eff. Inlet Temp	TI-1262	F	- - -	482	482	482	482	482	482	482	482
Reactor Eff. Outlet Temp	TIC-1260	F	- - -	280	280	280	280	280	280	280	280
Reactor Eff. Dew Temp	- - -	F	- - -	226	268	247	232	226	226	232	
REACTOR EFFLUENT											
Total Flow	FI-196	scfh	- - -	118,117	59,152	172,712	66,177	118,117	118,117	66,177	116,380
H2	- - -	mol%	- - -	20.91%	46.47%	50.31%	19.50%	20.91%			
CO	- - -	mol%	- - -	50.50%	14.66%	18.18%	50.29%	50.50%			
N2	- - -	mol%	- - -	1.20%	5.36%	4.93%	1.23%	1.20%			
CO2	- - -	mol%	- - -	15.79%	14.01%	12.27%	16.28%	15.79%			
MEOH	- - -	mol%	- - -	11.09%	17.88%	13.64%	11.94%	11.09%			
DME		mol%		0.09%	0.25%	0.04%	0.18%	0.09%			
ETOH	- - -	mol%	- - -	0.08%	0.24%	0.01%	0.12%	0.08%			
PROH	- - -	mol%	- - -	0.02%	0.08%	0.00%	0.03%	0.02%			
C4OH	- - -	mol%	- - -	0.01%	0.03%	0.00%	0.01%	0.01%			
IBOH	- - -	mol%	- - -	0.00%	0.01%	0.00%	0.00%	0.00%			
C5OH+	- - -	mol%	- - -	0.01%	0.02%	0.00%	0.01%	0.01%			
C1	- - -	mol%	- - -	0.04%	0.16%	0.07%	0.07%	0.04%			
			- - -	99.73%	99.17%	99.45%	99.66%	99.73%			
PRODUCT RECOVERY											
Syngas to Backend Flow	FI-682	scfh	- - -	None	None	None	None	None	None	None	None
22.11 to Flare Flow	FI-237	scfh	- - -	854	630	1,050	552	854	854	552	500
Main Flare Flow	FI-245	scfh	- - -	3,869	3,869	3,869	3,869	3,869	3,869	3,869	1,000
Product Flow	- - -	gpd	- - -	3,794	3,319	6,510	2,337	3,794	3,794	2,337	3,247
RECYCLE FEED											
H2	- - -	mol%	- - -	23.52%	57.66%	58.53%	22.20%	23.52%			
CO	- - -	mol%	- - -	56.76%	18.13%	21.22%	57.21%	56.76%			
N2	- - -	mol%	- - -	1.35%	6.65%	5.72%	1.40%	1.35%			
CO2	- - -	mol%	- - -	17.13%	16.29%	13.65%	17.82%	17.13%			
MEOH	- - -	mol%	- - -	1.01%	0.78%	0.81%	1.01%	1.01%			
C1	- - -	mol%	- - -	0.04%	0.16%	0.06%	0.06%	0.04%			
			- - -	99.81%	99.67%	99.99%	99.70%	99.81%			

TEST AUTHORIZATION # 50

LaPorte Alternative Fuels Development Unit (AFDU)

Date : 06/20/95
By: BLB

RUN NUMBER: AF-R14.6/14.7/14.8
APPROX START DATE: 21 JUNE, 1995

TITLE: TRACER STUDY FOR LIQUID PHASE METHANOL DEMONSTRATION RUN WITH ALTERNATE CATALYST

OBJECTIVE:
To conduct a 3-day radioactive tracer study for the Methanol synthesis run in a bubble column reactor.

SUMMARY:
A slurry of an alternate methanol catalyst and Penreco Drakeol-10 oil will be activated in the reactor (Test Authorization # 48). Upon completion of the activation, a process variable study will be conducted (Test Authorization # 49). A three day tracer study will follow the process variable study. Radioactive gas and liquid tracers will be injected at three process conditions to study the mixing in both the phases. The unit will be shut down following the tracer study.

TEST DETAILS: See pages 2 to 4 for details.

ANALYTICAL COMMENTS: See page 4.

SAFETY IMPLICATIONS:
Safety information available from ICI Tracerco is attached (Letters from D. A. Bucior to B. L. Bhatt, "Radiation Safety Analysis of Proposed Methanol Reactor Residence Time and Distribution Study", 3 June 1993; "Radiation Safety Analysis of Proposed LaPorte Pilot Plant Radioactive Tracer Study", 10 February 1994; "Tracerco Radiation Analysis", 15 June 1995). Barricades will be erected by ICI Tracerco to prevent access to areas containing radioactive materials. Radiation film badges will be worn by all personnel present during the study.

ENVIRONMENTAL IMPLICATIONS:
A flame will be maintained at the flare.

SPECIAL REMARKS:
The radioactive tracer injection will be performed by ICI Tracerco personnel using their injection equipment. APCI personnel will be present during the injection and operate AFDU equipment.

AUTHORIZATIONS:

E. C. Heydorn, Plant Mgr

B. L. Bhatt, Process Engr

TEST DETAILS:

1. Upon completion of the Process Variable Study (Run AF-R14.1 thru 14.5), start the Tracer Study. A vapor residence time distribution study will be performed by injecting Argon-41 into the inlet gas line and monitoring its progress through the reactor by several detectors. Three different gas velocities will be tested. Also, four injections of radioactive Mn_2O_3 will be made in the reactor slurry at each condition to study liquid phase mixing.

   ICI Tracerco is licensed to conduct these tests and will conform to guidelines prescribed by the Texas Department of Health. Texas A&M will irradiate the Argon and Manganese on the morning of the tests, and it will be delivered to the LaPorte site by courier. The radioactive Ar-41 has a half life of 1.8 hrs and will be injected into the reactor and vented to the atmosphere in levels acceptable to the Texas Department of Health. The radioactive manganese is expected to have a half life of 2.5 hours; only small amounts acceptable to the Texas Department of Health will be injected. An irradiation test will be performed on Mn_2O_3 by Texas A&M to ensure that the radiation will decay to very low levels within several days.

2. Operating conditions of Run Nos. AF-R14.6, 14.7 and 14.8 will be studied. Process and control targets for the study are tabulated in the attached table. The run descriptors are presented below:

RUN NO.	INJECTIONS	SPACE VEL SL/HR - KG CAT	PRESSURE PSIG	TEMPERATURE DEG C	INLET GAS VEL, FT/SEC
AF-R14.6A	GAS-INLET (2)	7000	750	250	0.83
AF-R14.6B	LIQUID-TOP (2) CENTER/WALL	7000	750	250	0.83
AF-R14.6C	LIQUID-BOT (2) CENTER/WALL	7000	750	250	0.83
AF-R14.7A	GAS-INLET (2)	4000	750	250	0.47
AF-R14.7B	LIQUID-TOP (2) CENTER/WALL	4000	750	250	0.47
AF-R14.7C	LIQUID-BOT (2) CENTER/WALL	4000	750	250	0.47
AF-R14.8A	GAS-INLET (2)	7000	520	250	1.20
AF-R14.8B	LIQUID-TOP (2) CENTER/WALL	7000	520	250	1.20
AF-R14.8C	LIQUID-BOT (2) CENTER/WALL	7000	520	250	1.20

3. The slurry level should be maintained between 80 and 100% of NDG range, as specified in Table 1. Leave the Nuclear Density Gauge at the normal controlling reactor height. Shut off the gauge for 10-15 minutes during the injections as cross-interference is expected. Put LIC-1242 on manual during the injections but bring it back on auto between runs. Pump 10.52.02 should be on all the time to bring oil back to the reactor. Pump 10.52.01 should be on all the time to circulate oil thru 27.14. Maintain 27.14 separator between 270-290^{o}F. Maintain 22.10 separator between 90-115^{o}F.

4. Day 1 (Approx. Date: 6/21/95)

Preparation and initial testing of the equipment will be conducted on the last day of the Process Variable Study. The electronic equipment includes 28 detectors connected to a data acquisition system. The process equipment includes a gas sample cylinder with adequate valves to allow filling of the cylinder with Ar-41 and subsequent injection into the reactor via a nitrogen flush. The Ar-41 will be injected thru valve V-2462. The radioactive manganese will be sluried in Drakeol-10 and injected with a hand-powered piston pump. The liquid injections will be made at two locations on the side of the reactor: Top N1-nozzle and Bottom N2-nozzle.

During day 1, the electronic equipment will be connected and power supplied to it. A preliminary calibration will be performed to verify the equipment is operational. Arrangements will be made to support the detectors in their proper location, detectors will not be placed until day 2.

Personnel available during the study will include two persons from Tracerco, one operator, one PSG process engineer and the plant manager. A catalyst inventory will be determined during day 1 using the nuclear density gauge with no gas flow through the reactor.

Day 2 (Approx. Date: 6/22/95)

Prior to day 2, arrangements will be made to irradiate Ar-41 and Mn_2O_3 in a reactor at Texas A&M. The irradiation will take place on the morning of day 2 and be transported to LaPorte by 1 pm. The radioactive materials produced during day 2 can only be used during this day since the half life of these compounds is less than three hours.

During the morning of day 2, the Tracerco crew will calibrate and hang the 28 detectors at the LaPorte AFDU. Each detector will be subjected to a gamma-ray source, and the response will be measured. All the detectors will then be normalized relative to the most sensitive detector.

After the calibration is complete, the detectors will be placed at specified locations. Conditions of Run No. AF-R14.6 will be studied during the day. Two Ar-41 injections will be made into the feed gas. A reasonable amount of time must exist between injections so that either Ar-41 has left the system or a steady level of radiation is available to use as a baseline. Two liquid injections will be made at the top nozzle (one near the wall and another half way between the wall and the center). Two more injections (wall and center) will be made at the bottom.

At the beginning and end of each condition, liquid level, gas hold up and slurry concentration will be measured with the nuclear density gauge (NDG). Two sets of detectors below the liquid level will have to be removed for the NDG measurements.

Day 3 (Approx. Date: 6/23/95)

Conditions of Run No. AF-R14.7 will be studied during the day. Two Ar-41 injections will be made into the feed gas. Two liquid injections will be made both at the top and the bottom.

Day 4 (Approx. Date: 6/24/95)

Conditions of Run No. AF-R14.8 will be studied during the day. Two Ar-41 injections will be made into the feed gas. Two liquid injections will be made both at the top and the bottom.

After completing the study, Tracerco will remove their equipment from the LaPorte site.

5. Upon completion of the Tracer Study, the plant will be shut down.

ANALYTICAL COMMENTS:

Since the gas and liquid will contain radioactive materials, NO sampling will be done while the tracers are being injected. Reactor feed gas analysis will be conducted between two process conditions. According to calculations performed by ICI Tracerco, the gas is safe to analyze 6 hours after the last gas injection (see attached letter dated 6/15/95).

RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A10	AF-R14.1	AF-R14.2	AF-R14.3	AF-R14.4	AF-R14.5	AF-R14.6	AF-R14.7	AF-R14.8
Description	- - -	- - -	ALT (REDTN)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (TRC)	ALT (TRC)	ALT (TRC)
Duration	- - -	days	1	2	3	1.5	1.5	1	1	1	1
Syngas	- - -	- - -	- - -	TEXACO	KINGSPORT	KINGSPORT	TEXACO	TEXACO	TEXACO	TEXACO	KINGSPORT
Inlet Space Velocity	- - -	sL/kg-hr	615	7,000	4,000	10,000	4,000	7,000	7,000	4,000	7,000
Reactor Pressure	PIC-1247	psig	67	750	735	735	750	750	750	750	520
REACTOR											
Pressure	PIC-1247	psig	67	750	735	735	750	750	750	750	520
Temperature	TI-1233	F	- - -	482	482	482	482	482	482	482	482
Heat Duty		MM BTU/hr	- - -	1.10	1.14	2.00	0.73	1.10	1.10	0.73	
Inlet Superficial Velocity	- - -	ft/sec	0.62	0.83	0.48	1.21	0.47	0.83	0.83	0.47	1.18
Outlet Superficial Velocity	- - -	ft/sec	0.62	0.68	0.35	0.95	0.38	0.68	0.68	0.38	0.94
Liquid Level	LI-2142	% span	80%	100%	100%	100%	100%	100%	100%	100%	100%
Catalyst Load	- - -	lb	1,177	1,177	1,177	1,177	1,177	1,177	1,177	1,177	1,158
Cat Weight Fraction	- - -	%	40%	42%	40%	41%	41%	42%	42%	41%	44%
Vapor Void Fraction	- - -	%	24%	43%	35%	42%	39%	43%	43%	39%	49%
FRESH FEED FLOWS											
LP H2	FIC-101	scfh	0	18,342	21,495	11,080	16,029	18,342	18,342	16,029	1,620
CO	FIC-104	scfh	500	15,217	11,995	21,420	10,469	15,217	15,217	10,469	10,000
CO2	FIC-107	scfh	0	1,185	1,040	2,050	914	1,185	1,185	914	772
N2	FIC-111	scfh	12,000	56	270	250	56	56	56	56	61
01.10 Total Flow	FI-726	scfh	12,500	34,800	34,800	34,800	27,468	34,800	34,800	27,468	12,453
HP H2	FIC-1200	scfh	0	7,283	2,467	33,730	0	7,283	7,283	0	18,930
01.20 Recycle	FIC-246	scfh	0	100,929	43,670	134,220	54,113	100,929	100,929	54,113	110,160
REACTOR FEED											
Target Feed Temp	TI-1253	F	- - -	362	392	373	369.0	362	362	369.0	373
Feed Dewpoint	- - -	F	- - -	89	78	86	87.0	89	89	87.0	86
Total Dry Flow	FI-1216	scfh	12,500	143,012	80,937	203,230	81,581	143,012	143,012	81,581	141,690
H2	- - -	mol%	0.0%	34.70%	60.90%	60.92%	34.68%	34.70%	34.70%	34.68%	60.92%
CO	- - -	mol%	4.0%	50.56%	24.49%	24.50%	50.54%	50.56%	50.56%	50.54%	24.50%
N2	- - -	mol%	96.0%	0.99%	3.90%	3.90%	0.99%	0.99%	0.99%	0.99%	3.90%
CO2	- - -	mol%	0.0%	12.88%	10.02%	10.03%	12.88%	12.88%	12.88%	12.88%	10.03%
MEOH	- - -	mol%	0.0%	0.71%	0.42%	0.53%	0.67%	0.71%	0.71%	0.67%	0.53%
ETOH	- - -	mol%	0.0%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
PROH	- - -	mol%	0.0%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
C1	- - -	mol%	0.0%	0.00%	0.08%	0.04%	0.04%	0.00%	0.00%	0.04%	0.04%
			100.0%	99.84%	99.81%	99.92%	99.80%	99.84%	99.84%	99.80%	99.92%

RUN PLAN FOR FLUID DYNAMIC / METHANOL RUN (JUNE, 1995)

RUN			AF-A10	AF-R14.1	AF-R14.2	AF-R14.3	AF-R14.4	AF-R14.5	AF-R14.6	AF-R14.7	AF-R14.8
Description	- - -	- - -	ALT (REDTN)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (PVS)	ALT (TRC)	ALT (TRC)	ALT (TRC)
21.11 Feed/Product Exchanger											
Feed Inlet Temp	TI-1257	F	- - -	172	210	197	180	172	172	180	197
Feed Outlet Temp	TI-1263	F	- - -	402	402	402	403	402	402	403	402
Total Feed to 02.63 Temp	TI-1216	F	- - -	362	392	373	369	362	362	369	373
Reactor Eff. Inlet Temp	TI-1262	F	- - -	482	482	482	482	482	482	482	482
Reactor Eff. Outlet Temp	TIC-1260	F	- - -	280	280	280	280	280	280	280	280
Reactor Eff. Dew Temp	- - -	F	- - -	226	268	247	232	226	226	232	
REACTOR EFFLUENT											
Total Flow	FI-196	scfh	- - -	118,117	59,152	172,712	66,177	118,117	118,117	66,177	116,380
H2	- - -	mol%	- - -	20.91%	46.47%	50.31%	19.50%	20.91%			
CO	- - -	mol%	- - -	50.50%	14.66%	18.18%	50.29%	50.50%			
N2	- - -	mol%	- - -	1.20%	5.36%	4.93%	1.23%	1.20%			
CO2	- - -	mol%	- - -	15.79%	14.01%	12.27%	16.28%	15.79%			
MEOH	- - -	mol%	- - -	11.09%	17.88%	13.64%	11.94%	11.09%			
DME		mol%		0.09%	0.25%	0.04%	0.18%	0.09%			
ETOH	- - -	mol%	- - -	0.08%	0.24%	0.01%	0.12%	0.08%			
PROH	- - -	mol%	- - -	0.02%	0.08%	0.00%	0.03%	0.02%			
C4OH	- - -	mol%	- - -	0.01%	0.03%	0.00%	0.01%	0.01%			
IBOH	- - -	mol%	- - -	0.00%	0.01%	0.00%	0.00%	0.00%			
C5OH+	- - -	mol%	- - -	0.01%	0.02%	0.00%	0.01%	0.01%			
C1	- - -	mol%	- - -	0.04%	0.16%	0.07%	0.07%	0.04%			
			- - -	99.73%	99.17%	99.45%	99.66%	99.73%			
PRODUCT RECOVERY											
Syngas to Backend Flow	FI-682	scfh	- - -	None	None	None	None	None	None	None	None
22.11 to Flare Flow	FI-237	scfh	- - -	854	630	1,050	552	854	854	552	500
Main Flare Flow	FI-245	scfh	- - -	3,869	3,869	3,869	3,869	3,869	3,869	3,869	1,000
Product Flow	- - -	gpd	- - -	3,794	3,319	6,510	2,337	3,794	3,794	2,337	3,247
RECYCLE FEED											
H2	- - -	mol%	- - -	23.52%	57.66%	58.53%	22.20%	23.52%			
CO	- - -	mol%	- - -	56.76%	18.13%	21.22%	57.21%	56.76%			
N2	- - -	mol%	- - -	1.35%	6.65%	5.72%	1.40%	1.35%			
CO2	- - -	mol%	- - -	17.13%	16.29%	13.65%	17.82%	17.13%			
MEOH	- - -	mol%	- - -	1.01%	0.78%	0.81%	1.01%	1.01%			
C1	- - -	mol%	- - -	0.04%	0.16%	0.06%	0.06%	0.04%			
			- - -	99.81%	99.67%	99.99%	99.70%	99.81%			

Tracerco

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RECEIVED
JUN 07 1993
PROCESS ENGINEERING

June 3, 1993

Mr. Bharat Bhatt
Air Products and Chemicals
7201 Hamilton Blvd.
Allentown, PA 18195

RE: RADIATION SAFETY ANALYSIS OF PROPOSED METHANOL REACTOR RESIDENCE TIME AND DISTRIBUTION STUDIES

Dear Mr. Bhatt:

The proposed radiotracer fluid distribution studies of the Methanol Reactor will be performed under ICI Tracerco's Texas Radioactive Materials License, L03096. I have included a copy of our current license for your files.

ICI Tracerco operates within strict guidelines, established by the Texas Bureau of Radiation Control, regarding how radioactive materials are to be handled, how much activity may be injected into the process system, exposure limits for non-radiation workers, and barricades around the area in which radiation is being used.

By regulation, barricades must be posted such that radiation exposure to non-radiation workers will not exceed 2 millirem in any 1 hour and/or 100 millirem in any seven consecutive seven days. Radiation workers, such as Tracerco employees, are limited to exposures of 1250 millirem per calendar quarter.

ICI Tracerco's operating standards are considerably higher than those required by law. We operate under the ALARA radiation principal. ALARA, simply put, states the any radiation exposure will be limited to *As Low As Reasonably Achievable*. An example of this philosophy in action is that should a Tracerco employee receive 1/10th the acceptable regulatory limit in a calendar quarter, an internal investigation will be performed to determine the cause of the "excessive" exposure. As you will appreciate, the principals of ALARA are equally applicable to possible radiation exposures of non-radiation workers. During our on-site investigation, we establish our radiation barricades such that possible exposures of non-radiation workers would be considerably less than legally allowable.

At Air Products request, radiation dosimetry was provided for each non-radiation worker on the plant site during the 1989 studies. Included is a copy of the radiation exposure analysis. There was no recordable radiation exposure to any plant employees during the study.

The other potential concern regarding the radiation safety of the project addresses the allowable concentration of the residual activity of the radiotracers and environmental impact. All accounting and

ICI Tracerco

disposal of radioactive materials are accomplished under provisions of ICI Tracerco's License. Again, ICI Tracerco is guided by regulations established by the State of Texas. (Incidentally, the applicable concentration limits are identical to those established as "fit" for human consumption.)

Two radiotracers will be used during the studies of the reactor. Vapor phase studies will be performed using Ar-41, an inert gas with a half-life of 1.8 hours. The liquid phase studies will be performed using Mn-56. Mn-56 has a half-life of 2.5 hours.

The Ar-41 radiotracer will vent the system via a 35 foot tall stack downstream of the reactor. Texas regulations allow an Ar-41 disposable concentration of $4*10^{-8}$ uCi/mL. This equates to an allowable injection of 2880 mCi per 8 hour day. The actual amount of radiotracer required during the previous studies was approximately 1/10 the allowable limit.

Disposal of the Mn-56 liquid tracer will be accomplished via dilution of the radiotracer within the 550 gallon liquid inventory and then via decay. Texas regulations allow a Mn-56 concentration of $3*10^{-3}$ uCi/mL. A strict dilution into product inventory allows injection of 6.2 mCi. The 1989 project required injection of 3 mCi Mn-56. When decay of the radioisotope is factored into the equation, the actual radiotracer concentration is considerably lower. For instance assuming 6.2 mCi were injected into the system, in 24 hours the actual concentration will be $3.8 * 10^{-6}$ uCi/mL, or 1000 times lower than the applicable regulatory limit.

I hope that I have addressed all you concerns. Please contact us if you need further information.

During the 1989 study, Air Produces provided "Manganese Oxide of a proper particle size", which we then irradiated and mixed in solution to provide the liquid radiotracer. I have limited details of the base stock, particularly regarding partial size. Can you look into providing a sample. We would want to perform a test irradiation prior to the project to insure proper decay and no undesirable by-products. I will continue researching our records as well.

Sincerely,

David A. Bucior
Senior Project Leader

DAB/jls
93-016.dab
1007

Tracerco

cc ECH
BAT

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February 10, 1994

Dr. Bharat L. Bhatt
Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501

RE: RADIATION SAFETY ANALYSIS OF PROPOSED LAPORTE PILOT PLANT RADIOTRACER STUDY

Dear Dr. Bhatt:

On January 25, 1994, a preliminary safety analysis associated with performing a radiotracer diagnostic flow distribution study of the reactor in the La Porte Pilot Plant was held. Present at the meeting were Dr. Bharat Bhatt, Dr. Bernie Tosland, Edward Heydorn and myself.

Three areas of concern were identified which required further investigation. These included worst case scenarios where all catalyst radiotracer injected would accumulate in 1 filter or ended up in the product stream exiting the column. The third concern was the amount of vapor phase tracer which could be absorbed into the catalyst slurry.

The calculations presented in this text are based upon consuming an identical amount of radiotracer as during a study of this equipment preformed in August 1993. The catalyst radiotracer was Mn-56 with has a half-life of 2.5 hours. The vapor radiotracer was Ar-41 with a half-life of 1.8 hours.

Reactor Slurry & Product Stream

During the August studies 2 mCi of Mn-56 were consumed during each days testing. Given the reactor volume of 550 gallon the radiotracer concentration upon mixing with the reactor volume:

$$\frac{2\ \text{mCi}}{550\ \text{Gal}} * \frac{1\ \text{Gal}}{3{,}785\ \text{ml}} * \frac{1000\ \mu\text{Ci}}{1\ \text{mCi}} = 9.6\ \text{E-04}\ \mu\text{Ci/ml}$$

The maximum concentration at which the general public may contact Mn-56 allowable under Texas Regulations is 7 E-05 μCi/ml. The previous study showed considerable mixing occurring in the reactor. Since the product draw is located so high on the reactor I believe it safe to assume that product stream concentration would not be greater than the mixed inventory concentration.

It will be necessary to allow 10 hours to elapse after test completion prior to allowaing non-radiation personnel to come into direct contact with the reactor slurry and/or product stream. This will allow the injected material to have passed through 4 half-lives. After 10 hours decay the Mn-56 concentration will be 6 E-05 μCi/ml.

Filter

Four filters are in place on the slurry stream. The following analysis is based upon all Mn-56 injected short circuiting the reactor and collecting in one filter. It is assumed that the radiotracer material is deposited on the filter in combination with a 1/8" thick "cake" layer of density 70 lbs/ft^3. This would result in an accumulation of 193.17 grams of material. Thus the initial concentration would be:

$$\frac{2\ mCi}{193.17\ g} * \frac{1000\ \mu Ci}{mCi} = 10.35\ \mu Ci/g$$

Texas Regulations establish a concentration of 7 E-04 μCi/ml for solid Mn-56 as acceptable for contact by the general public. Therefore, if all material was deposited in one filter, 36 hours would be required (after injection) for the material deposited on the filters to decay to the regulatory limit. If all tracer material were trapped on four filters, 31 hours would be required (after injection) to decay to the regulator limit.

In an alternate scenario, after 4 hours of circulation (inventory turnover time), 4 hours of filter cooling time, and all four filters in operation; the filters would be acceptable for immediate handling provided less than 2.5 percent of the total tracer injected was trapped on the filters.

Vapor Tracer Solubility

A final concern was the potential for Ar-41, the vapor phase tracer, being absorbed into the catalyst slurry stream. I have insufficient information to calculate a realistic Argon absorption in the reactor. During each process rate study approximately 0.025 moles of Argon with a radiation activity of 250 mCi will be consumed. If you can calculate what percentage of the injected material might be absorbed by the process stream, the radiation concentration would be in an identical ratio. The available information indications that Argon absorption, if any, would be minimal.

According to D. Vermeer and R. Krishna's "Hydrodynamics and Mass Transfer in Bubble Columns Operating in the Churn-Turbulent Regime", we may expect some Argon absorption. Figure 1 of the paper showed an Argon mole fraction of 0.00235 dissolved in turpentine 5 at 1 atmosphere. I assume this represented a saturation concentration. To saturate 550 gallons of slurry, we would have to inject 31 moles of argon.

A more practical representation was presented in Figure 4, which showed Residence Time Distributions (pulse injections) with tracer

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gases of varying solubility. During these studies Argon cleared the test vessel in approximately 30 seconds.

This was also the observation during the previous studies of the reactor. If any argon was absorbed, its' concentration was lower than the detectable limits using our extremely sensitive equipment.

Argon is not typically recognized as being a soluble material. Texas Regulations for the Control of Radioactive Materials provide no concentration limits for Ar-41 being in anything other than a vapor phase, i.e.; there are no regulatory provisions which address Argon being in either a solution or solid mixture.

I trust that I have addressed your concerns. Please contact us if we may be of further service.

Sincerely,

David A. Bucior
Senior Project Leader

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TRACERCO RADIATION SAFETY ANALYSIS

AIR PRODUCTS AND CHEMICALS
Alternate Fuels Pilot Plant
Pasadena, TX

Job Description

Flow distribution studies of the Pilot Plant High Pressure Reactor. Testing will be performed on three consecutive days, June 22, 23, & 24. Each day's study will consist of two injections of 25 mCi Ar^{41} into the reactor feed and four injections of 1 mCi Mn^{56} into the reactor liquid.

Details of Disposal

Vapor Traffic - Ar^{41}

The system inventory is approximately 15000 SCF with a purge rate of 5000 SCFH.

$$\frac{50\ mCi}{15000\ Ft^3} * \frac{10^3\ uCi}{mCi} * \frac{Ft^3}{2.832 * 10^4\ ml} = 1.17 * 10^{-4}\ uCi/ml$$

Argon Decay Halflife = 1.8 Hr & System Purge Rate Halflife = 1.7 Hr

Therefore, every 1.8 hours the system concentration will be reduced by 75%, resulting in:

Time After Injection (Hr)	Concentration (uCi/ml)	Regulatory Limits
1.8	4.2 E-5	DAC = 3 E^{-6}
3.6	1.0 E-5	Effluent Release = 1 E^{-8}
5.4	2.6 E-6	
7.2	6.6 E-7	
9.0	1.6 E-7	
10.8	4.1 E-8	
12.6	1.0 E-8	

Liquid Traffic - Mn^{56} (Halflife = 2.5 Hr)

4 mCi Mn^{56} diluted into 375 gallon inventory

$$\frac{4\ mCi}{375\ gal} * \frac{10^3\ uCi}{mCi} * \frac{gal}{3.785\ l} * \frac{1}{10^3\ ml} = 2.81\ E^{-3}\ uCi/ml$$

2.81 E^{-3} uCi/ml will decay to regulatory release limit of 7.0 E^{-5} in 13 hours and 22 minutes.

System Accumulation is negligible.

Time Hr	New Addition	Concentration at start	Concentration At End
0	2.81 E^{-3}	0	2.81 E^{-3}
24	2.81 E^{-3}	3.62 E^{-6}	2.81 E^{-3}
36	2.81 E^{-3}	3.62 E^{-6}	2.81 E^{-3}
48	0	3.62 E^{-6}	

Prepared by June 15 1995

David A. Bucior Senior Project Leader