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APPENDIX A

TEST AUTHORIZATIONS

Memorandum

AIR PRODUCTS

	Distribution	Dept./Loc.:	
From:	E. S. Schaub/E. C. Heydorn	Dept./Ext.:	PSG Process/LaPorte AFDU
Date:	3 March 1994		
Subject:	Test Authorizations # 37,38, 389, & 40 for the LaPorte AFDU Methanol and Isobutanol Runs		

Distribution:

W. C. Allen
D. P. Bernhard
B. L. Bhatt/K. G. Freidl/C. Chen
D. M. Brown/W. R. Brown
D. P. Drown
V. E. Stein/J. M. Repasky
R. P. Underwood/B. A. Toseland

Attached for your information are the 4 Test Authorizations for the upcoming Isobutanol/Mixed Alcohols Demonstration and the 5 LPMEOH run which will be used as a shakedown period prior to the Isobutanol run.

If you have any questions, please contact either of us at (713) 479-5485.

Elizabeth Schaub ESH

E. S. Schaub/E. C. Heydorn

TEST AUTHORIZATION # 37

LaPorte AAlternative Fuels Development Unit (AFDU)

Date : 03/02/94
By: ESS

RUN NUMBER: AF-A5
APPROX. START DATE: 14 March, 1994

TITLE: IN-SITU METHANOLL CATALYST ACTIVATION PRIOR TO SPRING 94 RUN USING DILUTE CO-RICH REDUCTION GAS

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

SUMMARY:
Approximately 1250 lbs of BASF S3-86 oxide is to be slurried with Drakeol-10 oil, transferred to the 27.20 reactor and activated with dililute CO-Rich syngas (3.5% 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 ggear while loading catalyst to protect them from the dust and hot vapor which may be released from n the loading nozzle. Protective gear including face shield should be worn during slurry sampling.

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

ENVIRONMENTAL IMPLICATIONSS:
Minimal, a flame will be maintained d at the flare. At 98% destruction efficiency, the CO emission rate would be 0.67 lb/hr.

SPECIAL REMARKS:
Hydrogen and CO concentrations ir in and out of the reactor must be monitored closely during the reduction. Reactor temperature muust be closely monitored and controlled per the attached TEST DETAILS. The utility oil inlet tempeerature (TI 1244) to the 27.20 internal heat exchanger must not exceed a 200°F difference from thee utility oil outlet temperature (TI-1246) or the reactor slurry temperature. These two temperatuure 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. l Heydorn, Plant Mgr

E. S. Schaub, 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), and the 1992 LPSHIFT run (#29).

2. Charge the 28.30 prep tank with 1875 lb of oil (265 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 258.2 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 1250 lb of methanol catalyst (BASF S3-86- 2 full drums of Lot 851-1642 and the balance (3+) drums of Lot 553-5072). 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: 25 to 28 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 (LILI-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 1000 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.

13. Establish CO-Rich reduction ggas flow at 25,910 SCFH (on FI-126) and vent the flow through PV-170. Establish the following ccomposition:

	Composition	Est. Flows (SCFH)
H2	1.2%	311
CO	1.8	466
CO2	0.5	130
N2	96.5	25,003
	100.0	25,910

MW == 27.8, SCF evaluated at 70°F, 14.7 psia
Target space velocity = 1 1200 sL/h-kg; Target starting inlet superficial velocity = 0.73 ft/sec

14. When the reactor temperaturee reaches 200°F, bring reduction gas to the reactor slowly and close the nitrogen purge (V-2627). I Establish a final flow to the reactor of 25,910 SCFH. Maintain flow and reducing gas compositionn as specified in step 13. The temperature-programmed activation consists of the following stepss:

- Heat the slurry at a targeget rate of 15°F/hr (no more than 18°F/hr, 10°C) until the slurry temperature reaches 3992°F (200°C).
- Hold the slurry temperatature at 392°F for 12 hours.
- Heat the slurry at 15°F/hhr until the slurry temperature reaches 464°F (240°C).
- Hold the slurry temperatature at 464°F for 1 hour (or longer if syngas uptake is still apparent).

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

If the H2+CO concentration inn the effluent falls below 0.1 mole %, increase the inlet H2+CO concentration per the instructitions of the process or research engineer. The objective here is to prevent reduction gas starvatition.

During the 392°F hold period, I, it may become necessary to maintain this temperature beyond 12 hours until the difference betwween inlet and outlet H2+CO concentration falls below 0.05 mole %.

15. The slurry level should be maiaintained between 90 and 95% of NDG range (approximately 40 ft.) by using LIC 1242 to control tthe makeup oil rate. Note that as the reactor is heated to 464 F, the slurry will expand. At the samme time, some of the oil will be lost in the reactor effluent. If authorized by the process engngineer or the plant manager, additional makeup oil can be added to the system via the 27.14 by fofollowing 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 2.01 and 02 pumps should be used to throttle to the 100 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 heatup and reduction.

17. When reduction has been completed, scan the reactor with the NDG. Record levels in the 21.11 and 27.14. Add fresh oil to 27.114 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 #37 is done, consult TEST AUTHORIZATION #38 for the next step.

ANALYTICAL REQUIREMENTS:

1. Catalyst sampling requirements:

   - slurried oxide catalyst from prep tank before reduction, and,
   - from the reactor, slurried reduced catalyst

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

2. Composition sampling requirements:

   - reactor in and out continuously
   - H2 and CO are critical
   - CO2 and N2 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 SPRING 1994 IBOH DEMONSTRATION

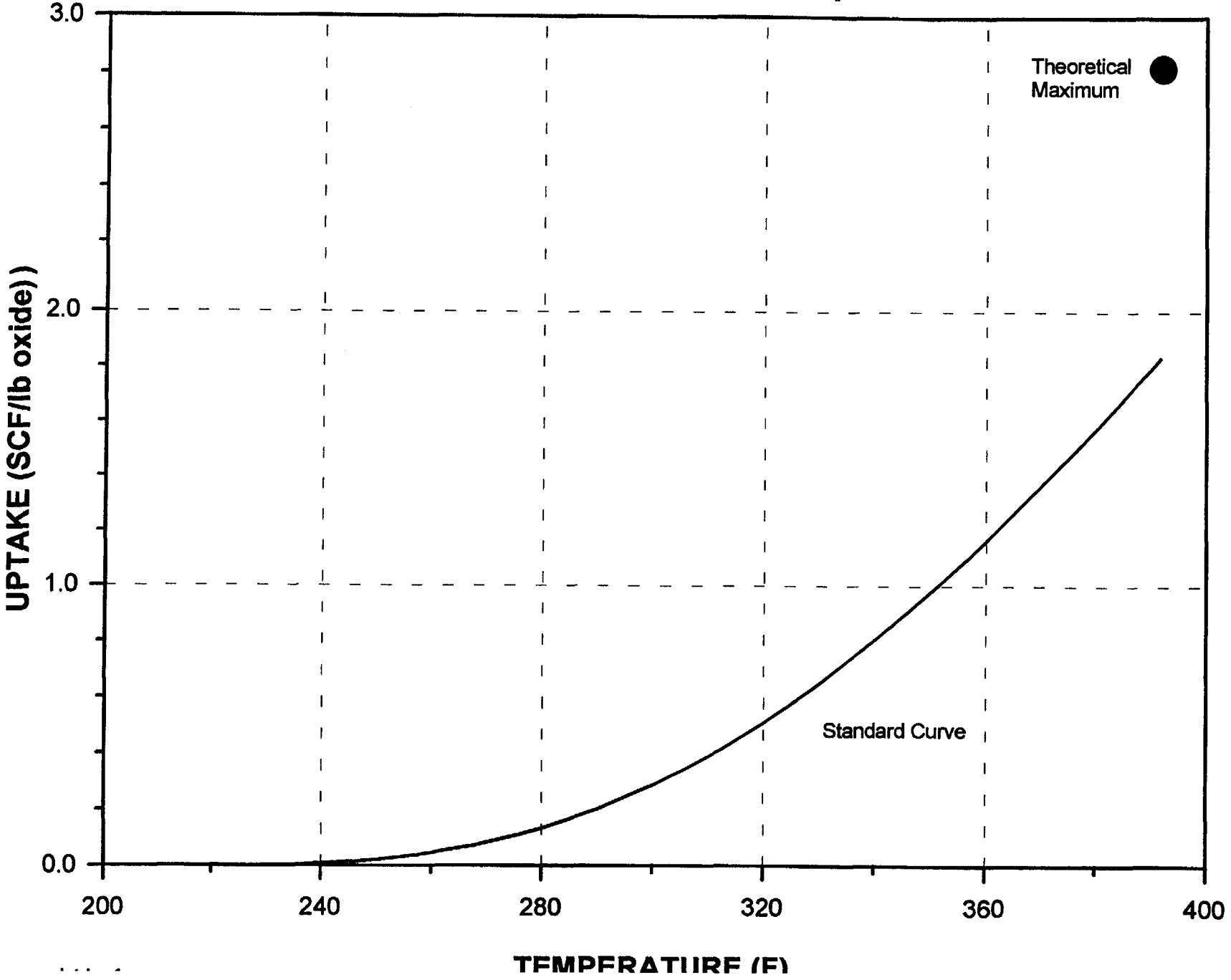
RUN				AF-R9.1	AF-R9.2
Description	---	---	Reduction	MEOH-1	MEOH-2
Duration	---	days	2	2	2
Syngas	---	---	---	TEXACO	KINGSPORT
Inlet Space Velocity	---	sL/kg-hr	1,200	6,700	4,000
Reactor Pressure	PIC-1247	psig	100	750	735
REACTOR					
Pressure	PIC-1247	psig	100	750	735
Temperature	TI-1233	F	---	482	482
Heat Duty		MM BTU/hr	---	1.14	1.21
Inlet Superficial Velocity	---	ft/sec	0.730	0.842	0.514
Outlet Superficial Velocity	---	ft/sec	---	0.644	0.348
Liquid Level	LI-2142	% span	90 - 95%	100%	100%
Catalyst Load	---	lb	1,250	1,250	1,250
Cat Weight Fraction	---	%	40.0%	42.4%	40.0%
Cat Weight Fraction	---	%	40.0%	42.4%	40.0%
Vapor Void Fraction	---	%	23 - 30%	42.9%	34.5%
FEED FLOWS					
LP H2	FIC-101	scfh	311	17,970	20,770
CO	FIC-104	scfh	466	15,581	12,694
CO2	FIC-107	scfh	130	1,192	1,065
N2	FIC-111	scfh	25,003	57	271
01.10 Total Flow	FI-726	scfh	25,910	34,800	34,800
HP H2	FIC-1200	scfh	0	8,665	4,937
01.20 Recycle	FIC-246	scfh	0	101,984	46,578
10.95 PUMP INJECTION					
Total Flow	FI-1221	gpm	zero	zero	zero
MEOH	---	wt%	---	---	---
C2OH	---	wt%	---	---	---
C3OH	---	wt%	---	---	---
REACTOR FEED					
Target Feed Temp	TI-1253	F	---	362.2	390.7
Feed Dewpoint	---	F	---	89.0	78.2
Total Dry Flow	FI-1216	scfh	25,910	145,449	86,316
H2	---	mol%	1.20%	34.71%	60.91%
CO	---	mol%	1.80%	50.57%	24.49%
N2	---	mol%	96.50%	1.00%	3.90%
CO2	---	mol%	0.50%	12.89%	10.03%
MEOH	---	mol%	0.00%	0.71%	0.42%
ETOH	---	mol%	0.00%	0.00%	0.00%
PROH	---	mol%	0.00%	0.00%	0.00%
C1	---	mol%	0.00%	0.03%	0.08%
			100.00%	*99.91%*	*99.83%*

JMRepasky 3/3/94

RUN PLAN FOR SPRING ..94 IBOH DEMONSTRATION

RUN				AF-R9.1	AF-R9.2
Description	---	---	Reduction	MEOH-1	MEOH-2
21.11 Feed/Product Exchanger					
Feed Inlet Temp	TI-1257	F	---	172.2	209.3
Feed Outlet Temp	TI-1263	F	---	402.3	401.6
Total Feed to 02.63 Temp	TI-1216	F	---	362.3	390.7
Reactor Eff. Inlet Temp	TI-1262	F	---	482.0	482.0
Reactor Eff. Outlet Temp	TIC-1260	F	---	280.0	280.0
Reactor Eff. Dew Temp	---	F	---	226.9	267.8
REACTOR EFFLUENT					
Total Flow	FI-196	scfh	---	119,495	62,776
H2	---	mol%	---	20.75%	46.48%
CO	---	mol%	---	50.50%	14.66%
N2	---	mol%	---	1.21%	5.36%
CO2	---	mol%	---	15.85%	14.02%
MEOH	---	mol%	---	11.20%	17.88%
ETOH	---	mol%	---	0.08%	0.24%
ETOH	---	mol%	---	0.08%	0.24%
PROH	---	mol%	---	0.02%	0.08%
C4OH	---	mol%	---	0.01%	0.03%
IBOH	---	mol%	---	0.00%	0.01%
C5OH+	---	mol%	---	0.01%	0.02%
C1	---	mol%	---	0.05%	0.16%
			---	*99.66%*	*98.95%*
PRODUCT RECOVERY					
Syngas to Backend Flow	FI-682	scfh	---	None	None
22.11 to Flare Flow	FI-237	scfh	---	875	667
Main Flare Flow	FI-245	scfh	---	3,867	3,867
Product Flow	---	gpd	---	3,697	3,527
BACK-END					
MEOH Circulation	FIC-814	gpm	None	None	None
MEOH to 07.10 Temp	TI-814	F	---	---	---
07.10 OH Temp	TI-1275	F	---	---	---
07.20 OH to Flare Flow	FI-7291	scfh	---	---	---
07.20 Reboiler Temp	TIC-7339	F	---	---	---
07.22 Steam Pressure	PIC-7338	psig	---	---	---
07.22 Steam Usage	FI-7338	lb/hr	---	---	---
21.80 CO2 Usage	---	TPD	---	---	---
Total CO2 Usage	Fd+21.80	TPD	0.18	1.63	1.45
RECYCLE FEED					
H2	---	mol%	---	23.38%	57.67%
CO	---	mol%	---	56.85%	18.13%
N2	---	mol%	---	1.36%	6.65%
CO2	---	mol%	---	17.22%	16.30%
MEOH	---	mol%	---	1.01%	0.78%
C1	---	mol%	---	0.04%	0.16%
			---	*99.85%*	*99.69%*

METHANOL CATALYST REDUCTION
Reduction Gas Uptake vs. Temperature



TEST AUTHORIZATION # 38

LaPorte Alternative Fuels Development Unit (AFDU)

Date : 03/02/94
By: ESS

RUN NUMBER: AF-R9
APPROX. START DATE: 15 March, 1994

TITLE: METHANOL SYNTHEESIS WITH BASF S3-86 CATALYST

OBJECTIVE:
To study the performance of S3-86 methanol catalyst in the 27.20 reactor train.

SUMMARY:
Upon completion of the activation steep (AF-A5), 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, 6,700 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). The objective is to condition the oil, allow the hyper-activity of the catalyst to decline, break-in the new DCS controls, and ultimately line-out at a steady rate of methanol production while collecting data for H2-rich reactor feed gas.

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 lineae will be in use during run AF-R9. 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-R9.2.

AUTHORIZATIONS:

E. C. Heydorn, Plant Mgr

E. S. Schaub, Process Engr

TEST DETAILS:

1. Upon completion of the catalylyst activation (AF-A5), switch from reduction gas to Texaco-type gas by following the standard proocedure. The CO2 removal section should NOT be operating during this run (V-2001,V-2003,V-20004,V-2006 shut; V-2000 open). In the event of a premature shut-down, consult TA #20 (RUN EE-05) for appropriate standby conditions.

2. Increase the reactor pressuree to 750 psig and control the slurry temperature at 482°F. Slowly increase the reactor feed ratee to 25,000 SCFH while maintaining slurry level at 95% of NDG span. When the plant has lined out, t, the reactor feed composition should correspond closely to case AF-R9.1 (refer to Table). Once ththe compositions are lined out, slowly introduce recycle flow and back off the fresh feed flowrates unintil they match the targets outlined in the Table for case AF-R9.1. Note that the HP hydrogen pipipeline is in service during cases AF-R9.1 and AF-R9.2.

3. When the target feed rate hasas been achieved, put LIC-1242 in automatic to control slurry level at 95%. Adjust the fresh feed flflow to achieve an initial purge flow rate of approximately 3,000 SCFH. Maintain reactor feed flow anond reactor temperature and pressure at the case AF-R9.1 values for a nominal 24 hour period.

4. During the first 24 hours, the s syngas conversion across the reactor will fall as the catalyst loses it's hyperactivity. The purge flowv will increase and the reactor feed composition will be changing during this period. When theese rates of change diminish, fine tune the fresh feed flow to reach the desired reactor feed compositition as specified for case AF-R9.1. The ultimate purge rate should be around 3,900 SCFH.

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

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

7. Maintain conditions for approxximately 2 days. After conferring with the process engineer or plant manager, switch to AF-R9.2 rrun conditions (Kingsport gas). Run this data period for approximately 3 days.

8. Liquid samples of the methannol product will be collected in special sample bombs and shipped to Allentown for detailed analysisis during case AF-R9.2. The samples will be collected downstream of the 22.11 separator. Consisult with the process engineer and analytical representative for the frequency and manner of takiking the samples.

9. When notified by the plant manager that case AF-R9.2 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 #39.

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 PROCEDUURES FOR MeOH-ONLY OPERATION

RUN PLAN FOR SPRING 1994 IBOH DEMONSTRATION

RUN				AF-R9.1	AF-R9.2
Description	---	---	Reduction	MEOH-1	MEOH-2
Duration	---	days	2	2	2
Syngas	---	---	---	TEXACO	KINGSPORT
Inlet Space Velocity	---	sL/kg-hr	1,200	6,700	4,000
Reactor Pressure	PIC-1247	psig	100	750	735
REACTOR					
Pressure	PIC-1247	psig	100	750	735
Temperature	TI-1233	F	---	482	482
Heat Duty		MM BTU/hr	---	1.14	1.21
Inlet Superficial Velocity	---	ft/sec	0.730	0.842	0.514
Outlet Superficial Velocity	---	ft/sec	---	0.644	0.348
Liquid Level	LI-2142	% span	90 - 95%	100%	100%
Catalyst Load	---	lb	1,250	1,250	1,250
Cat Weight Fraction Cat Weight Fraction	--- ---	% %	40.0% 40.0%	42.4% 42.4%	40.0% 40.0%
Vapor Void Fraction	---	%	23 - 30%	42.9%	34.5%
FEED FLOWS					
LP H2	FIC-101	scfh	311	17,970	20,770
CO	FIC-104	scfh	466	15,581	12,694
CO2	FIC-107	scfh	130	1,192	1,065
N2	FIC-111	scfh	25,003	57	271
01.10 Total Flow	FI-726	scfh	25,910	34,800	34,800
HP H2	FIC-1200	scfh	0	8,665	4,937
01.20 Recycle	FIC-246	scfh	0	101,984	46,578
10.95 PUMP INJECTION					
Total Flow	FI-1221	gpm	zero	zero	zero
MEOH	---	wt%	---	---	---
C2OH	---	wt%	---	---	---
C3OH	---	wt%	---	---	---
REACTOR FEED					
Target Feed Temp	TI-1253	F	---	362.2	390.7
Feed Dewpoint	---	F	---	89.0	78.2
Total Dry Flow	FI-1216	scfh	25,910	145,449	86,316
H2	---	mol%	1.20%	34.71%	60.91%
CO	---	mol%	1.80%	50.57%	24.49%
N2	---	mol%	96.50%	1.00%	3.90%
CO2	---	mol%	0.50%	12.89%	10.03%
MEOH	---	mol%	0.00%	0.71%	0.42%
ETOH	---	mol%	0.00%	0.00%	0.00%
PROH	---	mol%	0.00%	0.00%	0.00%
C1	---	mol%	0.00%	0.03%	0.08%
			100.00%	*99.91%*	*99.83%*

RUN PLAN FOR SPRING 1994 IBOH DEMONSTRATION

RUN				AF-R9.1	AF-R9.2
Description	---	---	Reduction	MEOH-1	MEOH-2
21.11 Feed/Product Exchanger					
Feed Inlet Temp	TI-1257	F	---	172.2	209.3
Feed Outlet Temp	TI-1263	F	---	402.3	401.6
Total Feed to 02.63 Temp	TI-1216	F	---	362.3	390.7
Reactor Eff. Inlet Temp	TI-1262	F	---	482.0	482.0
Reactor Eff. Outlet Temp	TIC-1260	F	---	280.0	280.0
Reactor Eff. Dew Temp	---	F	---	226.9	267.8
REACTOR EFFLUENT					
Total Flow	FI-196	scfh	---	119,495	62,776
H2	---	mol%	---	20.75%	46.48%
CO	---	mol%	---	50.50%	14.66%
N2	---	mol%	---	1.21%	5.36%
CO2	---	mol%	---	15.85%	14.02%
MEOH	---	mol%	---	11.20%	17.88%
ETOH	---	mol%	---	0.08%	0.24%
ETOH	---	mol%	---	0.08%	0.24%
PROH	---	mol%	---	0.02%	0.08%
C4OH	---	mol%	---	0.01%	0.03%
IBOH	---	mol%	---	0.00%	0.01%
C5OH+	---	mol%	---	0.01%	0.02%
C1	---	mol%	---	0.05%	0.16%
			---	*99.66%*	*98.95%*
PRODUCT RECOVERY					
Syngas to Backend Flow	FI-682	scfh	---	None	None
22.11 to Flare Flow	FI-237	scfh	---	875	667
Main Flare Flow	FI-245	scfh	---	3,867	3,867
Product Flow	---	gpd	---	3,897	3,527
BACK-END					
MEOH Circulation	FIC-814	gpm	None	None	None
MEOH to 07.10 Temp	TI-814	F	---	---	---
07.10 OH Temp	TI-1275	F	---	---	---
07.20 OH to Flare Flow	FI-7291	scfh	---	---	---
07.20 Reboiler Temp	TIC-7339	F	---	---	---
07.22 Steam Pressure	PIC-7338	psig	---	---	---
07.22 Steam Usage	FI-7338	lb/hr	---	---	---
21.80 CO2 Usage	---	TPD	---	---	---
Total CO2 Usage	Fd+21.80	TPD	0.18	1.63	1.45
RECYCLE FEED					
H2	---	mol%	---	23.38%	57.67%
CO	---	mol%	---	56.85%	18.13%
N2	---	mol%	---	1.36%	6.65%
CO2	---	mol%	---	17.22%	16.30%
MEOH	---	mol%	---	1.01%	0.78%
C1	---	mol%	---	0.04%	0.16%
			---	*99.85%*	*99.69%*

TEST AUTHORIZATION # 39

LaPorte Alternative Fuels Development Unit (AFDU)

Sheet: 1 of 4
Date : 03/02/94
By: ESS

RUN NUMBER: AF-A6
APPROX. START DATE: 24 March, 1994

TITLE: IN-SITU ISOBUTANOL CATALYST ACTIVATION PRIOR TO SPRING 94 RUN USING DILUTE CO-RICH REDUCTION GAS

OBJECTIVE:
To activate the Liquid-Phase Mixed Alcohols synthesis catalyst.

SUMMARY:
Approximately 1106 lbs of CS-doped BASF S3-86 oxide is to be slurried with Drakeol-10 oil, transferred to the 27.20 reactor and activated with dilute CO-Rich syngas (4.0% 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 hydrogen and CO. During the previous similar 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 0.6 lb/hr.

SPECIAL REMARKS:
Hydrogen and CO 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

E. S. Schaub, Process Engr

TEST DETAILS:

1. This reduction procedure follows the successful ER-6 reduction (refer to TEST AUTHORIZATION #23)

2. Charge the 28.30 prep tank with 1659 lb of oil (235 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 228.4 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 1106 lb of isobutanol catalyst (CS-BASF S3-86)). 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: 22-25 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 gallons. Pressure transfer the flush oil to the reactor and verify level with the NDG.

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 1000 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.

13. Establish CO-Rich reduction ggas flow at 22,920 SCFH (on FI-126) and vent the flow through PV-170. Establish the following ccomposition (Note that this composition is slightly different than those used for typical methanol catalalyst reductions.) :

	Composition	Est. Flows (SCFH)
H2	1.4%	321
CO	2.1	481
CO2	0.5	115
N2	96.0	22,003
	100.0	22,920

MW == 27.7, SCF evaluated at 70°F, 14.7 psia
Target space velocity = 1 1200 sL/h-kg; Target starting inlet superficial velocity = 0.64 ft/sec

14. When the reactor temperaturee reaches 200°F, bring reduction gas to the reactor slowly and close the nitrogen purge (V-2627). I Establish a final flow to the reactor of 22,910 SCFH. Maintain flow and reducing gas compositionn as specified in step 13. The temperature-programmed activation consists of the following stepss:

- Heat the slurry at a targget rate of 10°F/hr (no more than 15°F/hr) until the slurry temperature reaches 392°F (200°C). ı. This ramp rate is slower than methanol reduction procedures. Care should be taken to contrtrol this ramp rate at the beginning of the reduction.
- Hold the slurry temperatature at 392°F for 12 hours.
- Heat the slurry at 10°F/hhr until the slurry temperature reaches 464°F (240°C).
- Hold the slurry temperatature at 464°F for 1 hour (or longer if syngas uptake is still apparent).

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

If the H2+CO concentration inn the effluent falls below 0.1 mole %, increase the inlet H2+CO concentration per the instructitions of the process or research engineer. The objective here is to prevent reduction gas starvatition.

During the 392°F hold period, I, it may become necessary to maintain this temperature beyond 12 hours until the difference betwween inlet and outlet H2+CO concentration falls below 0.05 mole %.

15. The slurry level should be maiaintained between 80 and 90% of NDG range (estimated 35 ft.) by using LIC 1242 to control the ı makeup oil rate. Note that as the reactor is heated up to 464 F, the slurry will expand. At the samme time, some of the oil will be lost in the reactor effluent. If

authorized by the process engineer or 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 the level of the 27.14 should be recorded before and after each addition. Note that the discharge valve of the 10.52.01 and 02 pumps should be used to throttle to the 100 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 heatup and reduction.

17. When reduction has been completed, scan the reactor with the NDG. Record levels in the 21.11 and 27.14. 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.

18. Withdraw a slurry sample.

TA #39 is done, consult TEST AUTHORIZATION #40 for the next step.

ANALYTICAL REQUIREMENTS:

1. Catalyst sampling requirements:

   - slurried oxide catalyst from prep tank before reduction, and,
   - from the reactor, slurried reduced catalyst

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

2. Composition sampling requirements:

   - reactor in and out continuously
   - H2 and CO are critical
   - CO2 and N2 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 SPRING 1994 IBOH DEMONSTRATION

RUN			AF-A6	AF-R10.1	AF-R10.2	AF-R10.3	AF-R10.4	AF-R10.5	AF-R10.6	AF-R10.7	AF-R10.8	AF-R10.9	AF-R10.10	AF-R10.11
Description	---	---	Reduction	IBOH-1	IBOH-2	IBOH-3	IBOH-4	IBOH-5	IBOH-6	IBOH-7	IBOH-8	IBOH-9	IBOH-10	IBOH-11
Duration	---	days	2	2	1	2	2	2	1	1	1	1	1	2
Syngas	---	---	---	SHELL	SHELL	SHELL	SHELL	SHELL	SHELL	SHELL	SHELL	SHELL	SHELL	TEXACO
Inlet Space Velocity	---	sL/kg-hr	1,200	5,000	3,000	8,200	8,200	8,200	3,000	5,000	5,000	5,000	5,000	3,000
Reactor Pressure	PIC-1247	psig	100	750	750	750	1,300	1,735	1,735	1,300	1,300	1,300	750	1,300
REACTOR														
Pressure	PIC-1247	psig	100	750	750	750	1,300	1,735	1,735	1,300	1,300	1,300	750	1,300
Temperature	TI-1233	F	---	572	572	572	572	572	572	572	572	572	572	572
Heat Duty		MM BTU/hr	---	0.53	0.52	0.59	1.48	1.97	1.01	1.12	0.85	1.03	0.53	0.59
Inlet Superficial Velocity	---	ft/sec	0.640	0.611	0.366	1.002	0.583	0.438	0.160	0.355	0.390	0.366	0.611	0.213
Outlet Superficial Velocity	---	ft/sec	---	0.517	0.348	0.859	0.461	0.329	0.115	0.275	0.327	0.291	0.517	0.168
Liquid Level	LI-2142	% span	80 - 90%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Catalyst Load	---	lb	1,107	1,107	1,107	1,107	1,107	1,107	1,107	1,107	1,107	1,107	1,107	1,107
Cat Weight Fraction	---	%	40.0%	40.2%	39.1%	41.5%	42.0%	42.2%	39.8%	40.7%	41.1%	42.0%	40.2%	39.6%
Cat Weight Fraction	---	%	40.0%	40.2%	39.1%	41.5%	42.0%	42.2%	39.8%	40.7%	41.1%	42.0%	40.2%	39.6%
Vapor Void Fraction	---	%	25 - 30%	40.2%	36.4%	44.3%	46.0%	46.9%	38.7%	41.7%	43.2%	44.4%	40.2%	38.2%
FEED FLOWS														
LP H2	FIC-101	scfh	321	9,440	7,082	13,518	13,936	9,450	12,104	15,799	9,131	13,932	9,440	10,605
CO	FIC-104	scfh	481	10,016	9,086	12,582	20,790	25,311	13,715	15,670	14,682	15,712	10,016	9,476
CO2	FIC-107	scfh	114	31	0	0	0	0	607	0	0	659	31	0
N2	FIC-111	scfh	22,003	49	54	56	74	73	71	60	66	65	49	75
01.10 Total Flow	FI-726	scfh	22,919	19,536	16,222	26,157	34,800	34,835	26,497	31,529	23,879	30,367	19,536	20,156
HP H2	FIC-1200	scfh	0	0	0	0	10,019	20,322	0	0	0	0	0	0
01.20 Recycle	FIC-246	scfh	0	76,849	40,926	131,169	112,966	102,604	31,305	64,926	72,840	66,495	76,849	38,114
10.95 PUMP INJECTION														
Total Flow	FI-1221	gpm	zero	zero	zero	zero	zero	zero	zero	zero	2.14	0.70	zero	zero
MEOH	---	wt%	---	---	---	---	---	---	---	---	83.00%	69.50%	---	---
C2OH	---	wt%	---	---	---	---	---	---	---	---	5.00%	10.50%	---	---
C3OH	---	wt%	---	---	---	---	---	---	---	---	12.00%	20.00%	---	---
											100.00%	*100.00%*		
REACTOR FEED														
Target Feed Temp	TI-1253	F	---	437.8	443.2	431.7	429.8	429.6	429.5	429.4	400.0	400.0	437.8	431.5
Feed Dewpoint	---	F	---	-6.6	-9.3	-5.2	-9.6	-14.3	-15.1	-9.4	239.5	178.4	-6.6	92.9
Total Dry Flow	FI-1216	scfh	22,920	96,375	57,133	157,308	157,750	157,727	57,770	96,434	96,692	96,859	96,375	58,268
H2	---	mol%	1.40%	29.73%	30.05%	29.87%	29.78%	29.79%	29.72%	29.71%	27.03%	28.73%	29.73%	34.37%
CO	---	mol%	2.10%	65.41%	66.11%	65.70%	65.52%	65.53%	65.38%	65.37%	59.46%	63.21%	65.41%	50.09%
N2	---	mol%	96.00%	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%
CO2	---	mol%	0.50%	2.97%	1.91%	2.99%	2.91%	2.98%	2.97%	2.88%	2.68%	2.87%	2.97%	12.77%
MEOH	---	mol%	0.00%	0.04%	0.03%	0.04%	0.04%	0.03%	0.03%	0.03%	7.89%	2.32%	0.04%	0.55%
ETOH	---	mol%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.33%	0.24%	0.00%	0.01%
PROH	---	mol%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.61%	0.35%	0.00%	0.00%
C1	---	mol%	0.00%	0.84%	0.99%	0.53%	1.04%	0.95%	1.15%	1.15%	1.23%	1.15%	0.84%	0.73%
			100.00%	*99.98%*	*100.09%*	*100.13%*	*100.28%*	*100.28%*	*100.25%*	*100.14%*	*100.22%*	*99.87%*	*99.98%*	*99.53%*