Section 7

POISONING STUDIES

Commercial methanol catalyst was deliberately subjected to feeds containing certain contaminants present in unpurified synthesis gas produced by the gasification of coal. These tests were run in a dry reaction system as shown on Figure 7-1.

Two parallel units were mounted side by side with reactors immersed in a common salt bath. Both reactors have a center thermowell fitted with a sliding thermocouple so that a center line axial temperature profile could be measured. Thirty cm^3 of catalyst were loaded into the reactor with 10 cm^3 of glass beads above and below.

Each reactor could be fed from two gas cylinder banks. One bank contained a "Lurgi Gas" feed containing 50 percent H_2, 25 percent CO, 10 percent CO_2 and 15 percent CH_4. The second bank contained nitrogen doped with various impurities. The feed gas rotameters were calibrated against dry test meters prior to operation.

On-line GC analysis of the feed and product gases were used to calculate conversion levels. Methane served as an internal standard in making this calculation.

The contaminants tested and their level of contamination (in a Lurgi synthesis gas) are listed below:

	Contaminant	Level
1.	Ethylene	0.5%
2.	NO_2	10 ppmv
3.	Sulfur, as H_2S	1 ppmv, 5 ppmv
4.	Chlorine as CH_3Cl	10 ppmv

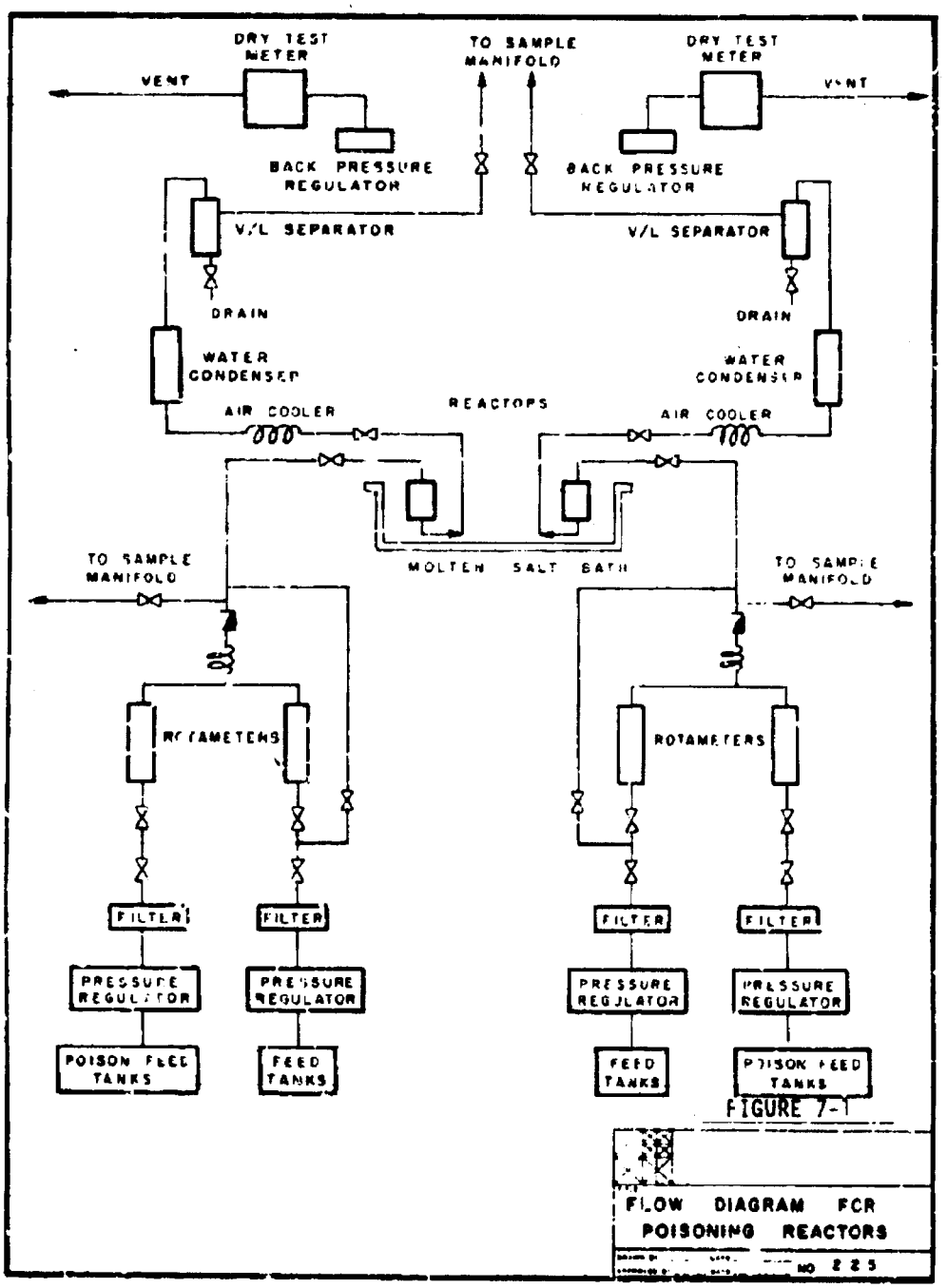

FIGURE 7-1

FLOW DIAGRAM FOR POISONING REACTORS

NO 225

Prior to starting the poisoning tests, the two fixed bed reactors were put on-stream, operating on an uncontaminated Lurgi synthesis gas in order to determine the normal operating behavior for these small reactors. Each reactor contained approximately 30 cm^3 of 3/16" Ø tablets. Salt bath temperature was maintained at 225°C. The conversion was limited in order to maintain the hot spot temperature at less than 240°C. By starting the reaction at atmospheric pressure and slowly increasing the pressure, in 50 psi increments, an operating pressure of 500 psig was found to give a hot spot temperature of 235°C, with a CO conversion to methanol of 20 percent at a VHSV of 2000 hr^{-1}. Equilibrium conversion at these reaction conditions is about 25 percent.

The pair of reactors were run side by side for the entire program. One reactor (Reactor A) was run on uncontaminated gas as a control for approximately seven months. The second reactor (Reactor B) was subjected to ethylene, NO_2, and H_2S contamination in that order. Finally, the control Reactor A was subjected to chlorine poisoning.

The schedule for the two reactors was as follows:

Reactor A		Reactor B	
Feed	Hours	Feed	Hours
Uncontaminated	0-5019	Uncontaminated	0-430
Uncontaminated Lurgi/N_2 Blend	5019-5355	0.7% Ethylene	430-1237
10 ppm Cl (as CH_3Cl)	5355-6243	Uncontaminated	1247-1463
		10 ppmv NO_2	1463-2447
		Uncontaminated	2447-2759
		1 ppmv H_2S	2759-3695
		5 ppmv H_2S	3695-4943
		Uncontaminated	4943-4991

The following paragraphs review the results of these tests.

REACTOR A - CONTROL RUN

The feed gas was a simulated Lurgi composition of 50 percent H_2, 25 percent CO, 10 percent CO_2, and 15 percent CH_4. Reaction conditions were maintained as follows over a period of 5000 hours:

VHSV	1700 - 2000 hr^{-1}
Salt Bath Temperature	220 - 225°C
Lurgi Gas Partial Pressure	300 - 330 psig

After 5019 hours, the feed gas was switched to a mixture of 2/3 Lurgi gas and 1/3 nitrogen at 450 psig total pressure. This latter mode of operation was used to coincide with the poisoning studies which used a impurity in the nitrogen feed as the source of contaminant.

Data for the control run with Reactor A are contained in Table 7-1. The CO conversion varied 2 percent absolute within a month due to operating conditions drift and analysis variations. The general trend indicated a CO conversion drop of about 1 percent (absolute) per 1000 hours, which was accounted for in the Reactor B tests.

REACTOR B - ETHYLENE

The results of this test are shown in Table 7-2. A Lurgi gas containing 0.7 volume percent ethylene was used. The test ran for 400 hours with no noticeable decline in catalyst activity. The ethylene was quantitatively converted to ethane as measured in the reactor exit gas. Ethylene and ethane were analyzed via gas chromatography.

REACTOR B - NO_2

After subjecting Reactor B to ethylene with no ill effect, the reactor was returned to an uncontaminated Lurgi gas for 225 hours. At 1,463 hours the total pressure was raised to 450 psig to maintain the Lurgi feed gas partial pressure at 300 psig. Nitrogen was co-fed containing 30 ppm of NO_2. The average NO_2 concentration was then 10 ppm. This mode of operation continued for 984 hours, until the 2447 on-stream hour

TABLE 7-1

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR A - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION % BED	VHSV, HR^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
5/27/76[1]	0	224	100	244	Inlet	---	---	---
5/28	22	228	300	243	Inlet	---	---	---
6/1	118	226	300	245	20%	1905.9	26.94	29.43
6/2	142	226	300	245	20%	1955.1	29.99	28.27
6/3	166	226	330	247	20%	2003.3	33.82	26.96
6/4	190	227	330	250	20%	1995.0	28.76	25.88
6/7	262	226	300	245	20%	2055.7	22.53	21.54
6/8	291	226	300	245	20%	1876.0	22.32	21.70
6/9	215	225	300	244	20%	1831.1	21.91	21.28
6/10	340	220	300	242	20%	1924.0	22.63	23.56
6/11	365	220	300	242	33%	2117.5	26.94	25.55
6/14	437	---	---	---	---	---	---	---
6/15	461	220	300	241	20%	1855.0	20.64	18.38
6/16	485	221	300	241	33%	1922.3	23.56	20.95
6/17	509	221	320	242	33%	2041.0	21.57	22.00
6/18	533	220	320	241	33%	1968.4	24.64	27.26
6/21	605	219	320	239	20%	1906.0	21.80	20.30
6/22	629	218	320	239	33%	1921.7	26.80	26.90
6/23	653	222	320	240	20%	1861.4	25.36	24.52

[1]Lurgi Gas: Feed 50% H_2, 25% CO, 15% CH_4, 10% CO_2.

(Continued)
TABLE 7-1

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR A - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
6/24	677	225	320	242	20%	2084.0	26.10	21.66
6/25	701	224	320	242	20%	2108	24.42	25.36
6/28	773	---	---	---	---	---	---	---
6/29	797	224	330	243	20%	1927.7	25.8	25.8
6/30	821	224	330	241	20%	1831.3	20.01	19.83
7/1	844	224	300	239	20%	1780.0	24.35	24.4
7/2	868	224	300	239	20%	1790.4	20.67	19.73
7/5	940	---	---	---	---	---	---	---
7/6	964	224	300	241	20%	1834.3	21.6	16.2
7/7	988	223	300	239	20%	1909.0	23.87	22.59
7/8	1012	223	300	239	33%	1835.5	24.75	23.85
7/9	1036	223	300	239	33%	1807.2	16.66	14.88
7/12	1108	223	300	239	20%	2033.1	23.69	24.56
7/13	1132	224	300	241	20%	1873.5	24.62	24.16
7/14	1156	223	300	239	20%	2003.0	25.98	23.84
7/15	1180	223	300	240	20%	2030.1	26.61	22.96
7/16	1204	223	300	240	20%	2003.0	24.61	24.90
7/19	1275	225	300	241	20%	2032.5	23.98	22.36
7/20	1300	224	300	240	20%	1957.8	27.00	26.18
7/21	1324	224	300	240	20%	1922.3	22.97	22.10

(Continued)

TABLE 7-1

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR A - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
7/26	1349	224	300	240	20%	1924.1	25.48	22.47
7/27	1468	224	300	241	20%	1929.2	22.43	19.75
/28	1492	224	300	240	20%	1771.1	17.85	15.48
7/29	1516	224	300	239	20%	1873.5	23.5	20.76
7/30	1540	223	300	238	33%	1845.2	25.18	22.33
8/2	1611	223	300	238	33%	1778.9	21.25	19.9
8/3	1635	223	300	238	33%	1900.6	21.62	20.71
8/4	1659	223	300	238	33%	1814.8	23.28	21.69
8/5	1683	223	300	238	33%	1873.5	21.82	19.88
8/6	1707	223	300	238	33%	1828.3	22.6	21.04
8/10	1803	224	300	239	33%	1677.7	24.85	23.96
8/11	1827	225	300	241	33%	---	---	---
8/12	1851	224	300	239	33%	---	---	---
8/13	1875	222	300	239	33%	---	---	---
8/19	2019	225	300	240	33%	1858.0	26.29	24.45
8/20	2043	222	300	239	33%	1795.8	21.51	21.05
8/23	2115	225	300	242	33%	1743.9	22.19	21.95
8/24	2139	226	300	242	33%	1760.2	20.68	20.56
8/25	2163	226	300	243	33%	1733.1	21.67	20.64
8/26	2187	225	300	241	33%	1828.3	23.0	24.5

(Continued)

TABLE 7-1

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR A - COMMERCIAL CATALYST A (3/16" Ø x 3 16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
8/30	2283	225	300	240	33%	1762.0	22.0	22.81
8/31	2307	---	---	---	---	---	---	---
9/1	2331	---	---	---	---	---	---	---
9/2	2355	224	300	240	33%	1775.3	18.73	19.36
9/7	2475	225	300	240	33%	1700.9	19.64	21.59
9/8	2499	224	300	238	33%	1733.4	19.97	21.61
9/9	2523	224	300	238	33%	1834.3	19.57	20.29
9/10	2547	225	300	238	33%	1686.7	19.93	20.17
9/13	2619	224	300	238	33%	1719.9	21.42	22.19
9/14	2643	224	300	237	33%	1731.9	18.43	20.17
9/15	2667	224	300	239	33%	1827.1	18.99	20.50
9/16	2691	222	300	236	33%	1716.9	19.29	21.00
9/17	2715	221	300	235	33%	1694.9	18.82	20.30
9/20	2787	222	300	235	33%	1843.4	24.70	26.0
		222	300	235	33%	1746.9	18.57	20.17
9/21	2811	---	---	---	---	---	---	---
9/22	2835	222	300	235	33%	1737.9	15.1	17.19
9/23	2859	221	300	235	33%	1858.4	20.92	22.69
9/24	2883	221	300	236	33%	1837.3	21.23	20.88
9/27	2955	221	300	236	33%	1810.2	17.58	19.29
9/28	2979	222	300	235	33%	1750.0	19.83	19.61

(Continued)

TABLE 7-1

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR A - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
9/24	3003	222	300	235	33%	1792.2	20.24	20.66
9/30	3027	223	300	235	33%	1819.3	20.15	22.35
10/4	3123	222	300	235	33%	1876.5	22.74	25.07
10/5	3147	224	300	238	33%	--	---	---
10/6	317.	225	300	241	33%	1760.5	15.04	17.78
10/7	3195	224	300	237	33%	1750.0	18.80	19.36
10/8	3219	225	300	240	33%	1743.9	17.94	19.02
10/11	3291	223	300	238	33%	1803.6	17.70	18.08
10/12	3315	225	300	242	33%	1785.1	18.09	18.49
10/13	3339	223	300	238	33%	1774.1	19.03	19.94
10/14	3363	224	300	238	33%	1867.5	20.7	21.7
10/15	3387	223	300	238	33%	1840.3	18.59	20.58
		222	300	236	33%	1759.0	17.64	17.68
10/18	3459	222	300	236	33%	---	---	---
10/19	3483	223	300	236	33%	1706.0	14.52	14.62
10/20	3507	223	300	240	33%	1732.8	16.34	17.49
10/21	3531	224	300	241	33%	1758.1	19.17	19.55
10/22	3555	223	300	236	33%	1788.9	18.89	19.62
10/25	3627	223	300	234	33%	1704.2	14.07	16.23
10/26	3651	225	300	239	33%	1810.2	19.90	21.78

(Continued)

TABLE 7-1

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR A - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
10/27	3675	224	300	238	33%	1795.2	20.12	21.41
10/28	3699	224	300	238	33%	---	---	---
10/29	3723	224	300	238	33%	---	---	---
11/1	3745	224	300	238	33%	---	---	---
11/2	3819	224	300	238	33%	---	---	---
11/3	3843	223	300	239	33%	---	---	---
11/4	3867	224	300	238	33%	---	---	---
11/5	3891	224	300	238	33%	---	---	---
11/8	3965	222	300	238	33%	1751.5	18.25	18.64
11/9	3987	224	300	240	33%	1751.8	19.15	19.74
11/10	4011	224	300	238	33%	1746.9	17.99	18.20
11/17	4071	225	300	---	---	1827.1	---	---
11/18	4203	226	300	241	33%	1709.1	17.62	17.15
11/19	4227	225	300	239	33%	1782.8	19.15	19.16
11/22	4249	224	300	239	33%	---	---	---
11/23	4323	225	300	239	33%	1694.3	14.80	15.40
11/25	4347	223	300	238	33%	1719.3	20.12	20.08
11/29	44 7	224	300	240	33%	1587.9	16.74	14.97
11/30	4491	---	300	---	---	---	---	---
12/1	4515	225		238	33%	1675.4	14.73	13.39

(Continued)

TABLE 7-1

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR A - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
12/2	4539	225	300	238	33%	1716.9	17.07	16.56
12/3	4563	224	300	237	33%	1689.5	16.20	13.89
12/6	4615	225	300	239	33%	1745.8	17.77	19.33
12/7	4694	225	300	238	33%	1756.0	19.57	19.38
12/8	4683	225	300	238	33%	1753.3	19.27	18.34
12/9	4707	224	300	236	33%	1710.8	17.26	16.30
12/13	4803	223	300	236	33%	1727.4	17.03	17.03
12/14	4827	224	300	236	33%	1721.7	17.06	17.06
12/15	4851	224	300	237	33%	1729.8	17.97	17.24
12/16	4875	224	300	237	33%	1749.1	17.96	19.29
12/17	4819	223	300	237	33%	1725.9	18.07	17.79
12/20	4971	224	300	237	33%	1725.9	18.07	17.79
12/20	4971	224	300	237	33%	1722.9	17.28	17.00
12/21	4995	224	300	237	33%	1728.0	16.08	18.12
12/22	5019	223	300	236	33%	1682.8	17.93	13.25
12/29[1]	5185	---	---	---	---	---	---	---
12/30	5211	224	450	236	33%	3000.0	13.7	14.6
1/3	5307	224	450	236	33%	3050	15.8	14.0
1/4	5331	223	450	237	33%	3040	15.8	16.2

[1] 2/3 Lurgi-1/3 N_2 @ 450 psig

(Continued)

TABLE 7-1

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR A - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
1/5[1]	5355	---	---	---	---	---	---	---
1/7	5403	223	450	235	33%	3140	17.6	18.1
1/8	5427	224	450	236	33%	2980	15.8	16.2
1/9	5451	225	450	235	33%	3110	15.1	16.8
1/13	5547	223	450	234	33%	3030	13.9	14/7
1/18	5667	222	450	235	33%	3040	11.8	12.8
1/28	5907	223	450	233	33%	2960	10.4	10.8
1/5[2]	---	---	---	---	---	---	---	---
2/3	6051	221	450	231	33%	2980	8.79	8.13
2/4	6075	222	450	230	33%	2875	8.73	6.15
2/7	6099	223	450	230	33%	2840	6.96	6.09
2/8	6123	223	450	230	33%	2845	5.94	6.15
2/10	6147	222	450	229	33%	2825	4.32	6.22
2/14	6243	222	450	229	33%	2780	4.57	3.77
2/15[3]	---	---	---	---	---	---	---	---

(1) 3/4 Lurgi-1/3 CH_3Cl Doped (30ppmv) N_2

(2) 2/3 Lurgi-1/3 CH_3Cl Doped (30 ppmv) N_2

(3) Cooled reactor under N_2- removed catalyst for testing.

TABLE 7-2

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR B - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS On STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
5/27/76[1]	---	224	100	---	---	---	---	---
5/28	0	228	300	226	Inlet	---	---	---
6/1	91	226	300	246	20%	2256.9	20.69	20.83
6/2	115	226	300	244	20%	2158.1	23.67	23.24
6/3	139	226	330	246	33%	2167.2	22.62	22.06
6/4	163	227	330	245	20%	1946.0	23.80	23.74
6/7	235	226	300	243	20%	1518.9	23.73	22.17
6/8	264	226	300	245	20%	1993.0	27.04	25.40
6/9	288	225	300	243	20%	1858.0	25.35	23.80
6/10	312	220	300	243	20%	1786.0	21.92	22.09
6/11	336	220	300	242	20%	2099.4	22.08	23.25
6/14	---	---	---	---	---	---	---	---
6/15	432	220	300	241	20%	1875.6	21.90	21.00
6/16[2]	456	221	300	240	20%	---	---	---
6/17	480	221	320	245	20%	---	---	---
6/18	504	220	320	243	20%	1881.0	22.40	23.3
6/21	575	219	320	242	20%	1972.9	22.99	22.73
6/22	600	218	320	242	20%	1930.7	26.80	27.70

[1] Lurgi Gas Feed 50%, 25% CO, 15% CH_4, 10% CO_2.

[2] Feed now contains 0.704% ethylene.

(Continued)

TABLE 7-2

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR 3 - COMMERCIAL CATALYST A (3/16" ϕ x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
6/23	624	222	320	243	20%	2009.0	24.71	29.63
6/24	648	225	320	245	20%	2042.2	21.02	20.81
6/25	672	224	320	244	20%	2111.4	24.07	25.40
6/28	744	---	---	---	---	---	---	---
6/29	768	224	330	246	20%	2102.0	25.5	23 87
6/30	792	224	330	242	20%	2034.1	20.1	21.21
7/1	815	224	300	241	20%	1813.9	18.81	20.00
7/2	839	224	300	241	20%	---	---	---
7/5	911	111	---	---	---	---	---	---
7/6	935	224	300	242	20%	1930.7	25.7	25.1
7/7	959	223	300	241	20%	1936.7	25.8	24.33
7/8	983	223	300	241	20%	1807.2	19.54	23.96
7/9	1007	223	300	241	20%	1969.9	22.99	25.3
7/12	1079	223	300	241	20%	2054.2	25.3	26.1
7/13	1103	224	300	243	20%	1834.0	21.64	20.56
7/14	1127	223	300	243	20%	1998.8	25.87	17.89
7/15	1151	223	300	241	20%	2006.0	28.08	27.63
7/16[1]	1175	223	300	243	20%	1954.8	23.03	23 44
7/19	1247	225	300	244	20%	2030.1	22.98	20.12

[1]Ethylene stopped. Formal Lurgi started.

(Continued)

TABLE 7-2

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR B - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DSTE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
7/20	1271	224	300	242	20%	1954.8	24.20	21.60
7/21	1295	224	300	242	20%	1963.9	28.26	23.23
7/22	1319	224	300	244	20%	2093.4	27.0	23.61
7/27[1]	1439	224	300	235	20%	3015.1	13.26	14.26
7/28	1463	224	300	241	20%	2871.69	20.00	18.00
7/29	1487	224	450	244	20%	3061.4	22.5	19.5
7/30	1511	223	450	241	33%	2640.7	18.4	19.07
8/2	1583	223	450	240	33%	2873.5	19.60	17.13
8/3	1607	223	450	242	33%	3000.0	20.27	17.77
8/4	1631	223	450	241	33%	3015.1	20.09	14.91
8/5	1655	223	450	239	33%	---	---	---
8/6	1679	223	450	241	33%	2780.0	19.24	17.04
8/10	1775	224	450	241	33%	---	--	---
8/11	1799	225	450	244	33%	---	---	---
8/12	1823	224	450	241	33%	2999.1	19.25	15.52
8/13	1847	222	450	240	33%	---	---	---
8/19	1991	225	450	243	33%	---	---	---
8/20	2015	2015	450	242	33%	3173.8	19.24	19.33
8/23	2087	225	450	244	33%	3081.3	18.28	17.64

(1) On 7/28/76 - 10 ppm NO_2 in Lurgi/H_2 mix started.

(Continued)

TABLE 7-2

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR B - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	WHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
8/24	2111	226	450	245	33%	---	---	---
8/25	2135	226	450	246	33%	3334.3	18.06	17.08
8/26	2159	225	450	244	33%	2786.1	18.31	19.67
8/30	2255	225	450	244	33%	3120.5	17.08	17.46
8/31	2279	---	---	---	---	---	---	---
9/1	2303	224	450	243	33%	3117.5	17.11	18.85
9/2	2327	225	450	243	33%	2951.8	16.79	19.12
9/7[1]	2447	224	300	239	33%	1733.7	20.64	21.52
9/8	2471	224	300	239	33%	1834.3	19.86	19.88
9/9	2495	225	300	239	33%	1827.4	18.78	19.15
9/10	2519	224	300	238	33%	1709.6	20.36	21.12
9/13	2591	224	300	240	33%	1804.2	24.60	25.00
9/14	2615	224	300	240	33%	1837.3	19.69	20.59
9/15	2639	222	300	238	33%	1795.2	19.71	21.3
9/16	2663	221	300	239	33%	1879.5	19.97	20.66
9/17	2687	222	300	238	33%	1786.1	22.0	23.36
9/20	2759	222	300	237	33%	1819.3	20.6	22.09
9/21[2]	2783	222	450	238	33%	3144.6	17.68	18.90

[1] On 9/7/76 NO_2 flow stopped pressure dropped to 300. Pure Lurgi Gas

[2] Switched to 2/3 Lurgi gas, 1/3 N_2 containing 3 ppm H_2S.

(Continued)

TABLE 7-2

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR B - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	WHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
9/22	2807	221	450	238	33%	2084.3	11.69	15.44
9/23	2831	221	450	238	33%	3240.9	18.45	17.30
9/24	2855	221	450	238	33%	2198.8	18.81	17.53
9/27	2927	222	450	238	33%	3054.2	16.15	14.99
9/28	2951	222	450	239	33%	2108.4	18.91	20.41
9/29	2975	223	450	242	33%	[illegible]4.1	17.26	17.86
9/30	2999	222	450	240	33%	3156.6	18.62	20.98
10/4	3095	224	450	238	33%	3087.3	17.28	17.90
10/5	3119	225	450	243	33%	3075.3	15.81	17.48
10/6	3143	224	450	241	33%	3021.1	11.70	17.60
10/7	3167	225	450	243	33%	3114.5	15.22	17.30
10/8	3191	223	450	240	33%	---	---	---
10/11[1]	3263	225	450	244	33%	3102.4	16.54	16.99
10/12	3287	223	450	234	33%	3054.2	14.57	15.20
10/13	3311	224	450	242	33%	3012.0	10.4	16.07
10/14	3335	223	450	241	33%	3150.6	16.28	17.00
10/15	3359	222	450	239	33%	2140.4	17.15	16.69
10/18	3431	222	450	240	33%	---	---	---
10/19	3455	223	450	240	33%	3135.8	17.75	18.44

[1]Pressure in morning at 390.

(Continued)

TABLE 7-2

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR B - COMMERCIAL CATALYST A (3/16" ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
10/20	3479	224	450	243	33%	3142.8	17.98	16.94
10/21	3503	224	450	243	33%	3102.4	18.25	17.06
10/22	3527	223	450	240	33%	3132.5	17.97	17.53
10/25	3599'	223	450	242	33%	3198.8	17.16	19.60
10/26	3623	225	450	243	33%	2159.6	18.06	17.11
10/27	3647	224	450	244	33%	3165.6	16.70	16.63
10/28	3671	224	450	243	33%	3117.5	16.53	15.03
10/29[1]	3695	224	450	243	33%	3250.0	18.49	19.61
11/1	3767	224	450	243	33%	311.4	15.56	18.22
11/2	3791	224	450	242	33%	3094.3	19.54	18.70
11/3	3815	223	450	241	33%	3213.9	15.65	17.90
11/4	3839	224	450	242	33%	3132.6	15.65	16.18
11/5	3863	224	450	242	33%	3093.4	15.86	14.50
11/8	3935	222	450	244	33%	3045.2	14.15	16.19
11/9	3959	224	450	243	33%	3027.1	13.93	14.66
11/10[2]	3983	224	450	243	33%	3015.1	14.16	12.27
11/17	4151	225	450	242	33%	3011.1	11.76	13.86
11/16	4175	226	450	242	33%	3042.2	11.83	12.83

[1] Switched to N_2 tank containing 15 ppm H_2S.

[2] 11/16 - back pressure failed. Reactor B restarted.

(Continued)

TABLE 7-2

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR B - COMMERCIAL CATALYST A (3/16" ϕ x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
11/19	4199	225	450	243	33%	3072.3	---	12.90
11/22	4271	224	450	240	33%	3021.1	10.37	12.93
11/23	4295	225	40	240	33%	2949.7	10.59	8.71
11/24	4319	223	450	239	33%	2962.3	10.36	10.80
11/29	4439	224	450	241	33%	2933.1	8.39	10.74
11/30	4463	---	450	---	---	---	---	---
12/1	4487	225	450	236	33%	2900.6	7.28	8.61
12/2	4511	225	450	236	33%	2888.9	7.61	8.77
12/3	4535	224	450	233	33%	2914.2	8.13	8.79
12/6	4607	225	450	236	33%	2887.7	6.80	8.47
12/7	4631	225	450	237	33%	2845.8	7.58	5.60
12/8	4655	225	450	237	33%	2877.4	6.72	6.92
12/9	4674	224	450	230	33%	2846.1	6.29	6.51
12/13	4775	223	450	232	33%	2839.8	5.21	6.16
12/14	4799	224	450	232	33%	2949.1	5.48	---
12/15	4823	224	450	232	33%	2796.7	4.79	4.71
12/16	4847	224	450	232	33%	2847.9	5.53	6.16
12/17	4871	223	450	230	33%	2842.2	5.53	5.86
12/20	4943	224	450	---	---	---	---	---

(Continued)

TABLE 7-2

METHANOL SYNTHESIS CATALYST POISONING STUDIES

REACTOR B - COMMERCIAL CATALYST A (3/16" Ø x 3/16" PELLETS)

DATE	HOURS ON STREAM	SALT BATH TEMP. (°C)	REACTOR PRESS. (psig)	HOT SPOT TEMP. (°C)	HOT SPOT LOCATION (% BED)	VHSV, Hr^{-1}	CO CONVERSION (%)	H_2 CONVERSION (%)
12/21[1]	4967	224	450	229	33%	2770.8	5.99	5.67
12/22	4981	223	450	228	33%	2747.6	4.09	4.41
12/27	---	224	450	224	---	---	---	---

[1] H_2S stopped . 2/3 Lurgi 1/3 N_2.

point. The decline in CO conversion over the period, over and above that experienced in Reactor A was minimal, perhaps 2 percent absolute at most. This indicates the NO_2 is, at most, a very weak catalyst poison. These data are shown in Table 7-2.

During this run, feed and product gases were sampled and analyzed for NO and NO_2 using infrared techniques by an outside analytical service. The exit gases were a mixture of NO and NO_2 to within ± 25 percent of the feed concentration.

REACTOR B - SULFUR (AS H_2S)

After the NO_2 contaminant test, Reactor B was returned to a standard Lurgi gas for 312 hours. At 2,759 hours, the total system pressure was raised to 450 psig, and the Lurgi gas was joined by a 1/3 volume of nitrogen containing 3 ppmv H_2S. This was continued for 936 hours, after which time the H_2S level was raised to 5 ppmv in the mixed feed for an additional 1,248 hours.

No drop in CO conversion could be noted over the period of feeding 1 ppmv H_2S contaminated feed. This might have been due to absorption effects of the reactor system walls. However, when the H_2S feed level was raised to 5 ppmv the catalyst started showing a marked decline in activity in less than 100 hours. CO conversion levels dropped from an initial level of 16-18 percent to 4-6 percent by the time the run was terminated (see Table 7-2).

In an attempt to present the effect of sulfur (as H_2S) on catalyst activity in a semi-quantitative manner, the following form of activity decay was assumed:

$$A = A_o e^{-K_s W_s}$$

where A_o = initial CO conversion
K_s = constant
W_s = cumulative sulfur fed to catalyst gms/gm
A = CO conversion at Ws

The data are plotted in Figure 7-2, resulting in a value for the constant K_s, of 24. This equation predicts an activity decline at the 5 ppm level that is 150 times (e^5) faster than the activity decline at the 1 ppm level.

The H_2S analysis used for this work involved scrubbing a known volume of gas with a basic $Cd(OAc)_2$ solution in order to precipitate the H_2S as CdS. After the flow is stopped, the solution is acidified with H_3PO_4, releasing the H_2S, and an excess of I_2 solution (≈0.001 N) is added to affect the reaction, $H_2S + I_2 \longrightarrow 2HI + S$. The unreacted I_2 is then back tirated with $Na_2S_2O_3$, using starch solution at the end point indicator. The H_2S concentration in the gas in then calculated by the relationship:

$$\text{ppmv } H_2S = \frac{11.84 \times 10^6 \left[(\text{ml } I_2 \text{ soln.} \times N_{I_2}) - (\text{ml } Na_2S_2O_3 \text{ soln.} \times N_{Na_2S_2O_3})\right]}{\text{cm}^3 \text{ gas scrubbed}}$$

Generally, about 10-15 percent of the feed sulfur was detected in the exit gas.

REACTOR A - CHLORINE (AS CH_3Cl)

After 5200 hours of operation the control Reactor A was adjusted to operate with an uncontaminated mixture of 2/3 Lurgi gas and 1/3 N_2 at 450 psig to establish a base conversion level. A CH_3Cl doped N_2 tank (30 ppmv) was employed resulting in feed gas concentration level of 10 ppmv CH_3Cl. After a short induction period, 5-7 days, the conversion began to fall regularly, dropping from an initial level of 16 percent to 4-5 percent in about 800 hours (see Table 7-1).

These results were treated in a similar semi-quantitative manner using the relationship $A=A_o e^{-K_{Cl}N_{Cl}}$). The data are plotted in Figure 7-3. Due to a lesser reliability of the low conversion analysis, the latter data points were disregarded in establishing the slope. With this assumption the K_{Cl} calculated value was 27.2.

FIGURE 7-2

CUMULATIVE EFFECT OF H_2S POISONING

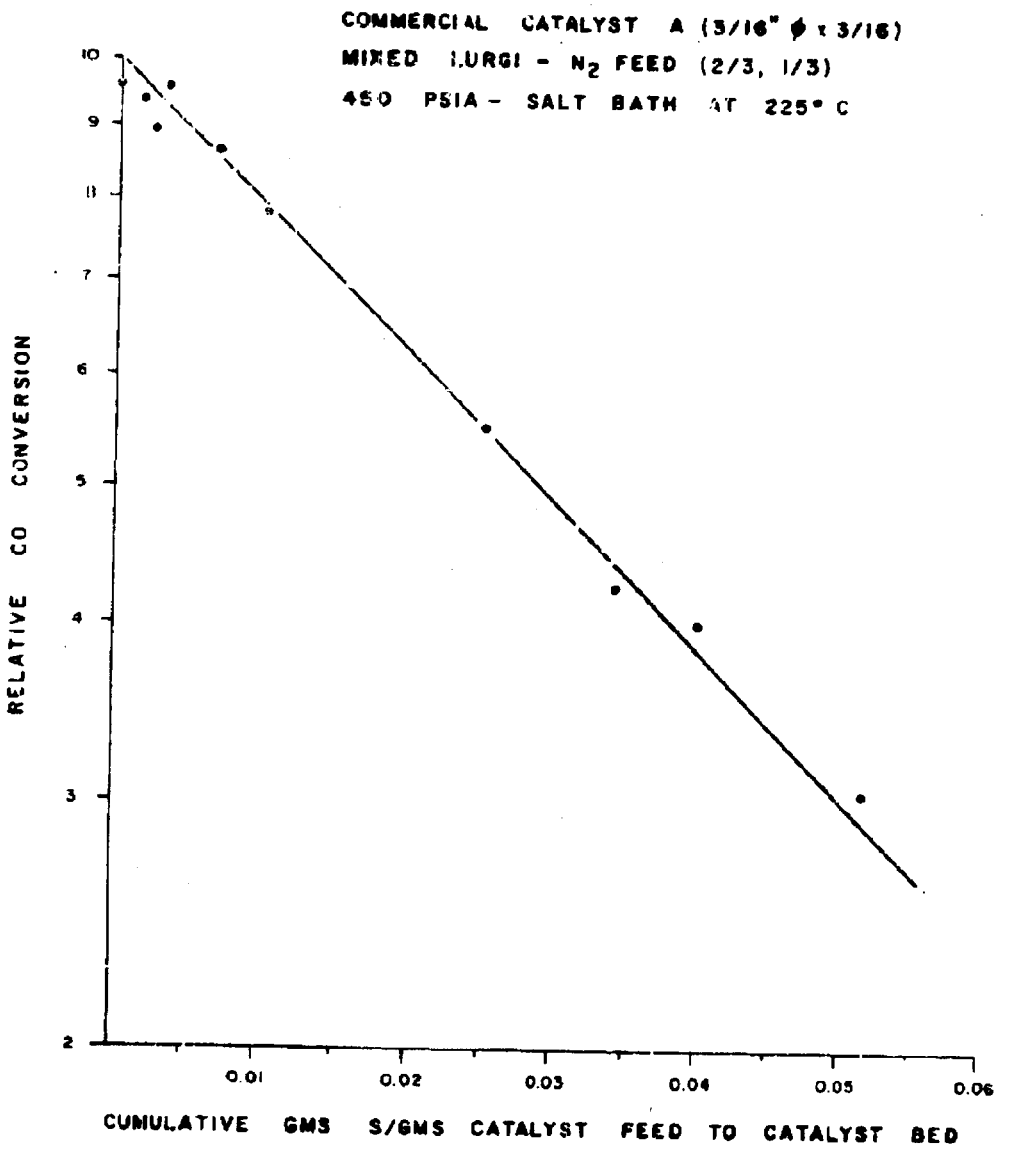

FIGURE 7-3

CUMULATIVE EFFECT OF CH_3CL POISONING