APPENDIX F :
ANALYTICAL DATA / LIQUID PRODUCTION / CATALYST RECONCILIATION

Most of the run data was recorded by the data acquisition computer and can be retrieved from tape in the future, if necessary. Some of the data, however, is not. This section documents such data as well as "corrected" data.

Liquid Samples

Liquid samples were taken from the bottom of the 22.11 flash pot. During methanol-only operation, this sample is representative of the methanol collected in the day tank. Table F1 present the analysis of individual samples taken roughly 12 hours apart during the AF-R1 series.

Table F2 contains the analysis of 22.11 liquid samples taken during the AF-R2 and AF-R3 series. Note that an additional component, called Volatiles, has been added. When significant quantities of DME are produced and a sample is taken from the 22.11, gasses are evolved. A method of determining the quantity of gases evolved was developed (based on weight differences) and applied to correct the GC analysis of the remaining liquid. Based on thermodynamic equilibrium calculations it is estimated that the volatiles contain 60% DME, 20% CO_2, 20% MeOH (by mole).

Table F3 contains some miscellaneous liquid samples taken during the course of operations.

Vapor Samples

During the DME runs, the vapors from the 22.11 flash pot and 22.18 DME degasser were taken at discreet times and not continuously. Table F4 contains the composition data for the 22.11; Table F5 contains the composition data for the 22.18.

The reactor effluent composition is key to developing accurate mass balances. Unfortunately, the Karle GCs are nonlinear in the response to methanol. This means that response factors determined for one methanol composition is not the same for either higher or lower concentration. The solution to this shortcoming in the GCs is to develop response factors charts to correct the analyses reported by the GCs.

Procedurally, a 3.82 mole% MeOH standard is used to calibrate the GCs and correction factors are applied when the measured composition is deviates from 3.82 mole %. The GC correction curves were developed based on available 1.22 mole% and 3.82 mole% standards and previously determined curves. A comparison of the previous correction curves and the "new" correction curves is presented in Figure F1.

The correction curves presented in Figure F1 were applied to the GC-reported data to correct the MeOH composition. The actual MeOH and DME concentrations in the reactor effluent are presented in Figures F2, F4, and F5 for runs AF-R1, R2, and R3, respectively.

Liquid Production

The liquid production is measured by tracking level rise in the 22.16 day tank with time. A plot of accumulated production with time is presented in Figure F5. The production rate is calculated from the slope of the production curve (as is reported on the figure).

Catalyst Reconciliation

Establishing the quantity of catalyst and catalyst proportion within the reactor was complicated by the fact that catalyst was withdrawn and added on two occasions and by the occurrence of catalyst settling. Fortunately, the catalyst "material balance" could be closed with reasonable certainty.

The quantities of catalyst added to the system are easily determined since catalyst was added by measured weight. The methanol catalyst was added once (489 lb). Alumina was added on two occasions (32 lb and 67.5 lb). When the methanol catalyst is activated there is a 25% weight loss; when the alumina is dried there is a 4% weight loss. From this the net weight of catalyst added can be calculated. These weights, summarized in Table F6.1, must be accounted for later.

When catalyst was removed from the plant it was drained into 55 gallon drums along with an unknown quantity of oil. The weight and volume of each mix was measured and from this the density of the slurry in each drum could be determined.

There were 12 different lots of catalyst and oil withdrawn from the plant. The weights and density of each lot is summarized in Table F6.2. To summarize, two drums were drained from the reactor during the run (marked S1 and S2), 5 drums were drained from the reactor at the end-of-run (denoted D1-D5), 3 drums of "rinse oil" were drained from plant (marked as R1-R3, these contained very little catalyst), and 2 lots of concentrated slurry were physically removed from the bottom of the reactor following shut-down and rinsing.

The density of the reduced or dried catalyst was known and the density of the oil-alone was measured. These densities are:

Component	Density lb/ft^3
BASF S3-86	357.6
Catapal γ-Alumina	206.5
Oil	53.3

If the proportion of alumina is known then the quantities of oil, methanol catalyst and alumina can be determined for each drum. To determine the alumina proportion the following sequence of events were assumed to occur:

Step	Action
1	489 lb Methanol catalyst was charged to the reactor and fully reduced
2	The 14 lb "lodged in piping" lot settled in the 4" piping in the reactor bottom during activation.
3	Drum S1 was withdrawn from the reactor at the end of AF-R1.
4	32 lb of alumina was dried then added to the remaining methanol catalyst
5	Drum S2 was withdrawn from the reactor at the end of AF-R2
6	67.5 lb of alumina was dried then added to the remaining alumina/methanol catalyst mix
7	The 74 lb "settled in reactor head" lot settled out in the bottom head right before AF-R3 began
8	Following run AF-R3, the slurry in the reactor was drained into drums D1-D5
9	Rinse oil was added to the reactor and drained into drums R1-R3

Given this sequence of events it was possible to calculate the proportion of alumina in the reactor at any point during the run. With this information the quantities of S3-86, alumina and oil were determined for each lot as summarized in Table F6.2. The weight of alumina and S3-86 was then summed for all the lots as indicated by "TOTAL" (in Table F6.2). These totals must agree with the "TOTAL" from Table F6.1. As can be seen, agreement is within 1% which is excellent.

As a check on the consistency of this method, elemental analysis of selected lots was performed as summarized in Table F7. As shown the agreement is reasonable.

To summarize, the quantity and proportion of catalyst in the reactor for each of the runs is presented below:

RUN	Mass of Catalyst (lb, As-Charged Basis)			Weight % Alumina
	BASF S3-86	Alumina	Total	
AF-A2	489.0	0.0	489.9	0.0
AF-R1	479.4	0.0	479.4	0.0
AF-R2	452.6	32.0	484.6	6.6
AF-R3	362.6	86.7	449.3	19.3

TABLE F1

LIQUID SAMPLES FROM 22.11 - RUN AF-R1

Date	5/2/91	5/3/91	5/3/91	5/3/91	5/4/91	5/4/91	5/5/91	5/6/91	5/6/91	5/6/91	Average
Time	12:20	0:55	14:45	23:55	12:00	23:58	12:00	0:10	12:30	23:50	wt%
Methanol	96.706	96.669	96.79	96.697	96.748	96.785	96.713	95.776	96.06	96.819	96.800
Ethanol	0.603	0.576	0.611	0.645	0.63	0.602	0.61	0.892	0.832	0.593	0.645
n-Propanol	0.213	0.211	0.217	0.233	0.229	0.217	0.221	0.334	0.294	0.209	0.232
IsoPropanol	0.01	0.012	0.013	0.013	0.013	0.013	0.013	0.017	0.008	0.012	0.012
n-Butanol	0.097	0.098	0.105	0.109	0.108	0.107	0.108	0.108	0.139	0.101	0.107
sec Butanol	0.036	0.028	0.034	0.04	0.034	0.036	0.033	0.043	0.042	0.034	0.036
IsoButanol	0.032	0.028	0.029	0.025	0.034	0.03	0.032	0.053	0.049	0.031	0.033
n-Pentanol	0.056	0.053	0.055	0.063	0.074	0.059	0.056	0.086	0.08	0.058	0.063
IsoPentanol	0.045	0.043	0.04	0.047	0.038	0.046	0.046	0.063	0.028	0.034	0.043
2,3-Pentanol	0.029	0.025		0.027	0.024	0.03	0.026	0.038	0.035	0.028	0.026
Methyl Formate	1.161	1.052	1.051	1.014	0.998	1.043	1.03	1.299	1.279	1.042	1.084
Methyl Acetate	0.156	0.132	0.141	0.151	0.145	0.137	0.135	0.279	0.248	0.136	0.159
Dimethyl Ether	0.034	0.031	0.029	0.027	0.028	0.027	0.026	0.036	0.036	0.027	0.030
Water	0.496	0.499	0.507	0.524	0.506	0.529	0.524	0.425	0.421	0.535	0.504
Mineral Oil	0.281	0.386	0.215	0.188	0.231	0.19	0.227	0.173	0.165	0.182	0.226
SUM	99.958	99.843	99.837	99.803	99.84	99.851	99.8	99.629	99.723	99.841	100

TABLE F2

LIQUID SAMPLES FROM 22.11 - RUN AF-R2 & AF-R3

Date	5/9/91	5/9/91	5/10/91	5/10/91	5/11/91	5/11/91	5/12/91	5/12/91	5/14/91	5/15/91	5/15/91	5/16/91	5/16/91	5/17/91
Time	3:45 *	14:20	0:10 *	12:00 *	1:00	13:00	0:15	12:05	12:05	0:30	12:56	0:15	18:00	6:20
Methanol	77.795	79.015	78.5124	84.0897	83.723	84.05	79.548	77.36	73.138	65.76	75.914	75.316	74.822	71.243
Ethanol	0.347	0.388	0.342	0.2826	0.298	0.307	0.385	0.394	0.062	0.049	0.048	0.049	0.058	0.056
n-Propanol	0.123	0.14	0.1224	0.1017	0.122	0.109	0.136	0.146	0.035	0.028	0.026	0.027	0.028	0.028
IsoPropanol	0.009	0.009	0.0081	0.0081	0.008	0.008	0.011	0.009	0	0	0	0	0.003	0
n-Butanol	0.052	0.057	0.0531	0.0549	0.046	0.049	0.061	0.061	0.045	0.01	0.012	0.008	0.009	0.01
sec Butanol	0.024	0.027	0.0252	0.0306	0.028	0.023	0.032	0.029	0.006	0.007	0.007	0.007	0.007	0.008
IsoButanol	0.025	0.034	0.0243	0.0324	0.019	0.017	0.025	0.028	0.008	0.008	0.006	0.006	0.008	0.008
n-Pentanol	0.022	0.025	0.0207	0.0189	0.021	0.02	0.02	0.026	0.005	0	0	0	0.006	0
IsoPentanol	0	0	0.0216	0	0	0	0	0	0	0	0	0	0	0
2,3-Pentanol	0.021	0.021	0.0207	0.0216	0.016	0.018	0.024	0.023	0	0	0	0	0	0
Methyl Formate	0.456	0.5	0.495	0.4329	0.449	0.447	0.506	0.503	0.639	0	0.57	0	0.348	0
Methyl Acetate	0.061	0.068	0.0549	0.0396	0.041	0.043	0.072	0.071	0	0	0	0	0	0
Dimethyl Ether	8.597	5.93	8.0505	3.1968	4.118	3.601	6.144	4.544	4.758	7.689	5.042	8.135	3.05	8.685
Water	1.074	1.053	1.0152	1.0386	1.186	1.039	0.908	0.887	4.087	4.228	3.871	3.989	4.061	3.719
Mineral Oil	0.781	0.661	0.7956	0.3375	0.463	0.36	0.362	0.4	0.948	0.622	0.522	0.762	0.841	1.08
Volatiles	10	11.5	10	10	9.1	9.6	11.25	14.92	16.13	21.51	13.93	11.639	16.67	15.04
SUM	99.388	99.428	99.5617	99.6859	99.638	99.691	99.484	99.401	99.861	99.911	99.948	99.938	99.911	99.877

* The volatile content was not measured for these samples. Volatile content shown is estimated.

TABLE F3

VARIOUS LIQUID SAMPLES FROM OTHER VESSELS

	22.18			22.16			28.10
Date	5/11/91	5/12/91	5/14/91	5/11/91	5/16/91	5/17/91	5/20/91
Time	8:00	5:00	12:00	13:00	0:30	7:45	-
Methanol	86.37	86.972	89.008	90.47	85.367	86.449	91.313
Ethanol	0.225	0.242	0.206	0.382	0.061	0.049	0.425
n-Propanol	0.043	0.054	0.05	0.136	0.034	0.031	0.165
IsoPropanol	0.006	0.007	0.006	0.01	0	0	0.009
n-Butanol	0.012	0.011	0.009	0.059	0.012	0.011	0.071
sec Butanol	0.009	0.008	0.01	0.031	0.007	0.008	0.028
IsoButanol	0.008	0	0.008	0.026	0.008	0.009	0.028
n-Pentanol	0	0	0	0	0	0	0.033
IsoPentanol	0	0	0	0.026	0	0	0
2,3-Pentanol	0	0	0	0.023	0	0	0.022
Methyl Formate	1.153	0.931	0.581	0.52	0.787	0.557	0.608
Methyl Acetate	0.088	0.099	0.067	0.065			0.092
Dimethyl Ether	8.702	8.472	8.162	6.046	8.491	8.485	5.432
Water	2.893	2.633	1.515	1.117	4.372	4.318	1.463
Mineral Oil				0.61	0.762		
Volatiles							
SUM	99.509	99.429	99.622	99.521	99.901	99.917	99.689

TABLE F4

VAPOR SAMPLES FROM 22.11 - RUN AF-R2 & AF-R3

Date	5/10/91	5/10/91	5/11/91	5/11/91	5/11/91	5/11/91	5/12/91	5/12/91	5/14/91	5/14/91	5/14/91	5/17/91	5/17/91
Time	19:22	20:28	3:16	4:26	19:00	20:07	5:51	6:57	5:35	6:42	7:48	4:26	5:32
Hydrogen	3.285	3.166	3.206	3.22	2.381	2.409	2.456	2.502	2.012	1.884	1.864	2.048	2.059
Nitrogen	0.154	0.154	0.132	0.131	0.095	0.097	0.101	0.102	0.383	0.506	0.161	0.067	0.064
Methane	0.078	0.079	0.095	0.095	0.071	0.069	0.084	0.095	0	0.048	0.051	0	0
Carbon Monoxide	14.199	14.218	14.164	14.25	11.622	11.655	11.762	11.813	7.996	7.881	7.515	8.166	8.136
Carbon Dioxide	47.938	47.784	47.98	48	46.724	46.311	48.012	48.181	39.04	38.035	37.139	40.621	40.395
Water	0.084	0.094	0.075	0.083	0.088	0.076	0.071	0.06	0.156	0.185	0.204	0.238	0.187
Methanol	4.776	4.659	4.77	4.717	4.051	3.911	3.816	3.669	3.14	3.306	3.147	3.014	3.051
Dimethyl Ether	27.173	27.082	27.608	27.514	31.936	31.303	31.977	31.653	47.734	47.235	48.65	45.362	45.36
SUM	97.687	97.236	98.03	98.01	96.968	95.831	98.279	98.075	100.461	99.08	98.731	99.516	99.252

TABLE F5

VAPOR SAMPLES FROM 22.18 - RUN AF-R2 & AF-R3

Date	5/10/91	5/10/91	5/11/91	5/11/91	5/11/91	5/12/91	5/12/91	5/14/91	5/14/91	5/16/91	5/16/91	5/16/91
Time	17:09	18:16	5:33	6:39	21:14	8:04	9:10	8:55	10:00	6:58	8:04	5:51
Hydrogen	0.759	0.783	0.755	0.744	0.7	0.582	0.725	0.777	0.619	0.819	0.774	0.711
Nitrogen	0.052	0.052	0	0.041	0.041	0.042	0.043	0.069	0.067	0	0	0
Methane	0	0	0	0	0	0	0	0	0	0	0	0
Carbon Monoxide	4.695	4.74	4.864	4.543	4.754	4.886	4.866	4.738	4.65	4.048	3.81	3.38
Carbon Dioxide	40.91	40.88	40.913	41.029	41.609	43.303	43.245	43.422	43.159	35.836	33.973	31.869
Water	0.099	0.082	0.088	0.106	0.094	0.072	0.088	0.189	0.266	0.201	0.162	0.185
Methanol	5.713	5.251	6.625	6.626	6.726	7.17	7.542	5.089	5.067	7.793	7.638	6.502
Dimethyl Ether	46.433	45.877	45.025	45.973	42.073	42.5	42.57	45.608	45.65	55.306	52.998	57.617
SUM	98.661	97.665	98.27	99.062	95.997	98.555	99.079	99.892	99.478	104.003	99.355	100.264

Date	5/16/91	5/16/91	5/17/91	5/17/91
Time	19:12	21:33	6:39	7:45
Hydrogen	0.844	0.857	0.818	0.929
Nitrogen	0	0	0	0
Methane	0	0	0	0
Carbon Monoxide	4.746	4.73	4.674	4.631
Carbon Dioxide	42.239	42.704	42.218	42.036
Water	0.161	0.173	0.2	0.221
Methanol	4.637	4.758	5.436	5.553
Dimethyl Ether	46.265	46.357	46.088	45.846
SUM	98.892	99.579	99.434	99.216

TABLE F6
CATALYST INVENTORY RECONCILIATION

6.1 Catalyst Added

Date		Weight As Charged (lb) S3-86	Al2O3	Total		After Activation/Drying (lb) S3-86	Al2O3	Total
4/29/91	Initial Charge	489	0	489		367	0	367
5/6/91	1st Alumina Addition		32	32			31	31
5/12/91	2nd Alumina Addition		67.5	68			65	65
					TOTAL	366.8	95.7	462.4

6.2 Catalyst Recovered (Catalyst Data on Post Activation/Drying Basis)

Date		Total Wt Oil+Cat. (lb)	Density (lb/ft3)	Weight Fraction Catalyst	Wt % Al2O3	Catalyst Mass (lb) S3-86	Al2O3	Total
5/7/91	S1 - 1st Drain	78	68.56	0.2615	0	20.4	0	20.4
5/13/91	S2 - 2nd Drain	150	70.32	0.2874	8.31	39.5	3.6	43.1
5/17/91	D1 - Post Run Drain	348	63.72	0.1982	23.47	52.8	16.2	69.0
	D2 - Post Run Drain	388	63.15	0.1890	23.47	56.1	17.2	73.3
	D3 - Post Run Drain	378	63.43	0.1936	23.47	56.0	17.2	73.2
	D4 - Post Run Drain	402	62.74	0.1824	23.47	56.1	17.2	73.3
	D5 - Post Run Drain	323	62.61	0.1802	23.47	44.5	13.7	58.2
5/20/91	R1 - Post Run Rinse	386	54.17	0.0196	23.47	5.8	1.8	7.6
	R2 - Post Run Rinse	380	53.98	0.0152	23.47	4.4	1.4	5.8
	R3 - Post Run Rinse	286	53.48	0.0042	23.47	0.9	0.3	1.2
5/21/91	Lodged in Piping	14	-	-	0	7.4	0	7.4
	Settled in Reactor Head	74	92.82	0.5158	23.47	26.0	8.0	34.0
					TOTAL	369.9	96.4	466.4

TABLE F7
ELEMENTAL ANALYSIS OF CATALYST SAMPLES

Elemental Analysis

		Cu (wt%)	Zn (wt%)	Al (wt%)	Wt% Al2O3 * meas	assumed	Cu/Zn (lb/lb) * meas	vendor
5/13/91	S2 - 2nd Drain	67.81	23.75	8.44	5.9	6.6	2.86	2.6
5/17/91	D1 - Post Run Drain	59.54	20.61	19.85	20.6	19.3	2.89	2.6
	D3 - Post Run Drain	53.18	19.05	27.77	30.3	19.3	2.79	2.6
5/21/91	Settled in Reactor Head	54.25	18.55	27.20	29.5	19.3	2.92	2.6
	Settled in Reactor Head	56.06	19.71	24.23	25.9	19.3	2.84	2.6
	Settled in Reactor Head	55.99	19.56	24.45	26.2	19.3	2.86	2.6

* The "measured" Al2O3 content of the catalyst mix (oxide/wet basis) was calculated from the elemental analysis as was the "measured" Cu/Zn ratio. The "assumed" Al2O3 content was based on material charged and/or settled.

FIGURE F1

GC FACTORS FOR CORRECTING COMPOSITION

(Comparison of old and new factors)

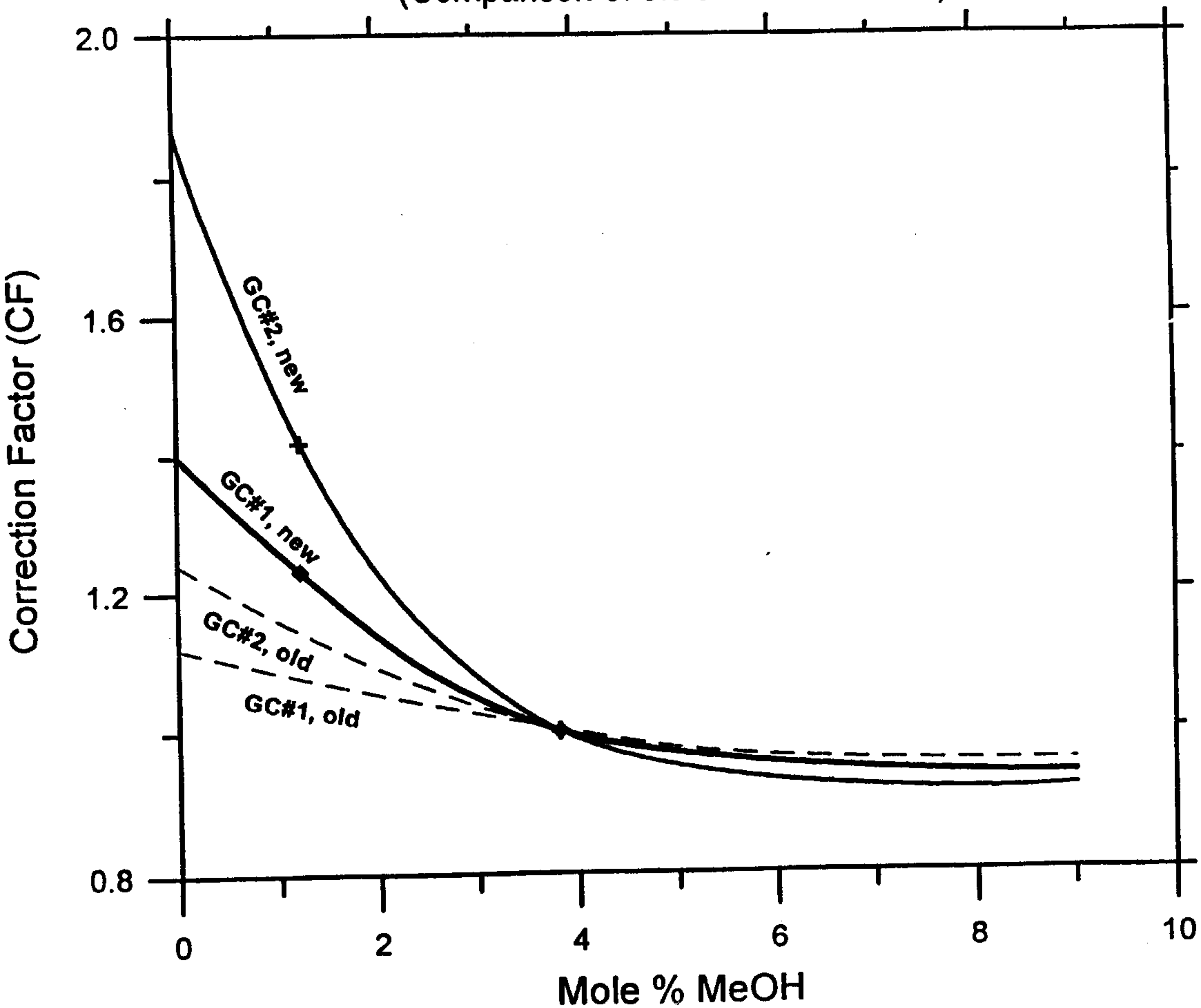

FIGURE F2

COMPOSITION OF MeOH IN REACTOR EFFLUENT

(RUNS AF-R1 : Texaco Gas, 482 F, 750 psig)

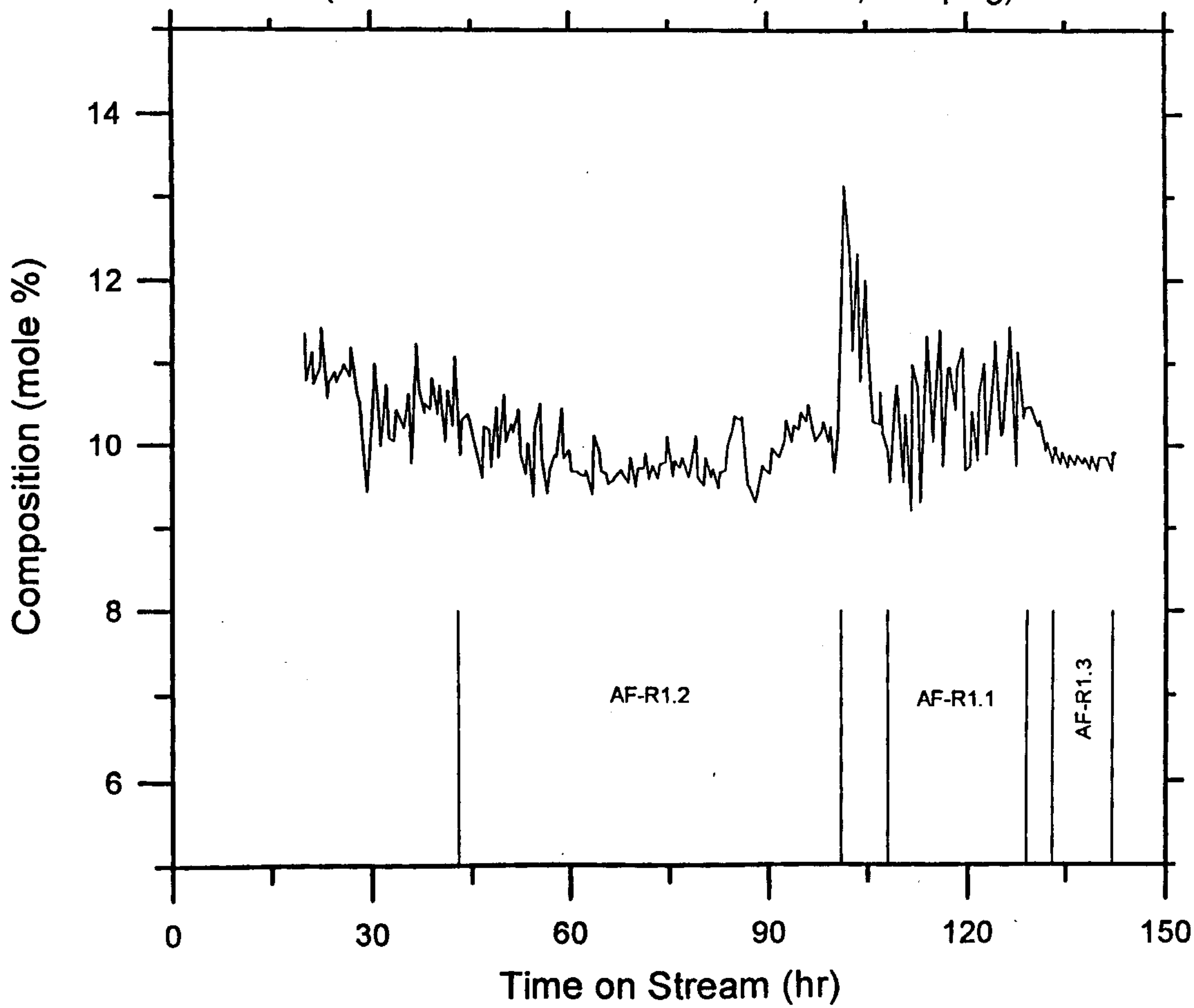

FIGURE F3

COMPOSITION OF DME AND MeOH IN REACTOR EFFLUENT

(RUNS AF-R2 : Texaco Gas, 482 F, 750 psig)

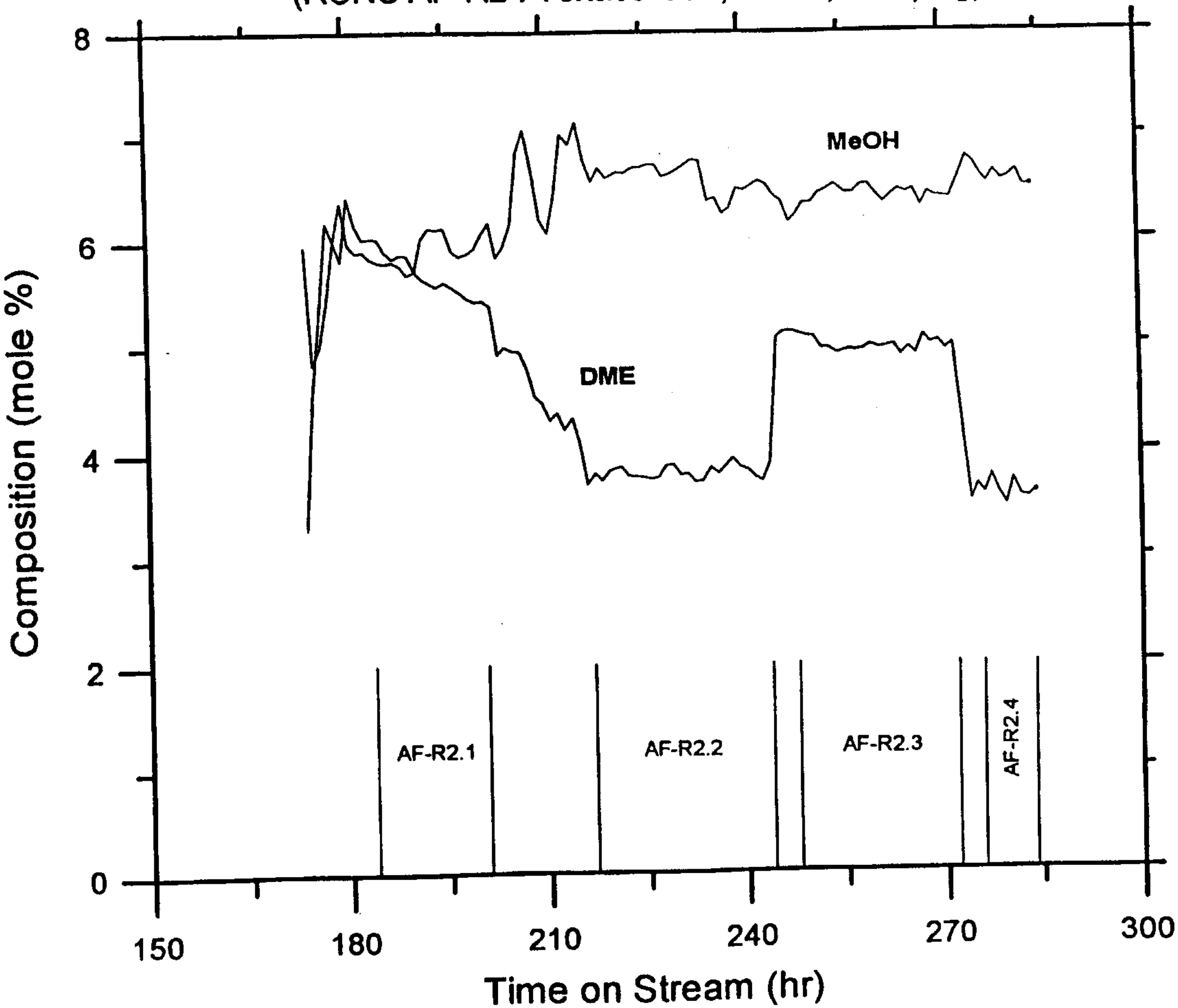

FIGURE F4

COMPOSITION OF DME AND MeOH IN REACTOR EFFLUENT

(RUNS AF-R3 : Texaco Gas, 482 F, 750 psig)

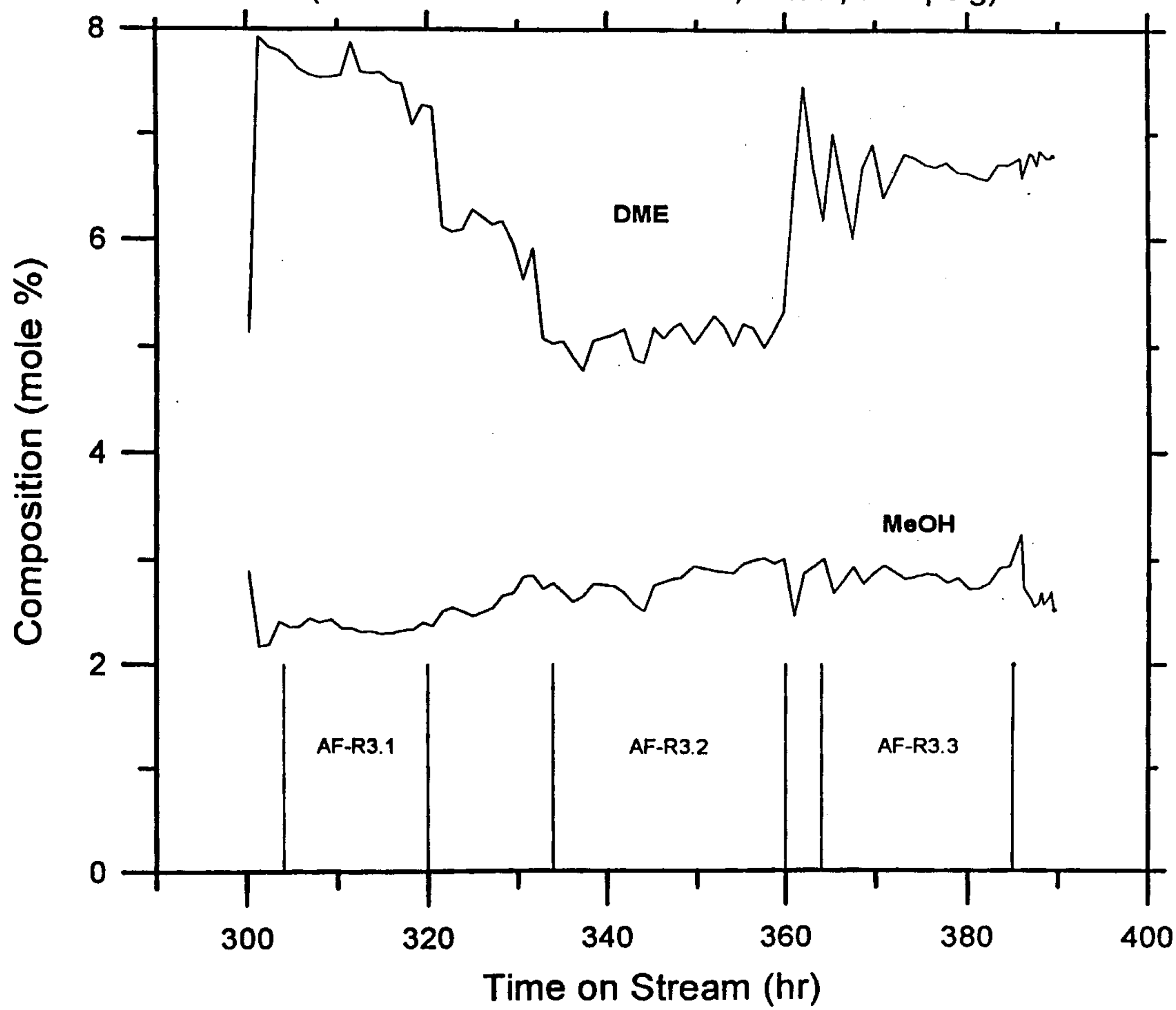

FIGURE F5

LIQUID PRODUCTION AS MEASURED IN DAY TANK

(All Runs)