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FEB 16 1999

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Novel Approaches To The Production of Higher Alcohols From Synthesis Gas

**Quarterly Report
October 1 - December 31, 1995**

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Work Performed Under Contract No.: DE-AC22-90PC90043

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report
October 1, 1995 to December 31, 1995

CONTRACT OBJECTIVES

- Task 1. Program Management.
- Task 2. Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.
- Task 3. Novel Catalysts for Synthesis of Higher Alcohols. (Complete)
- Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis. (Complete)
- Task 5. Technology Evaluation. (Complete)

A three-day thermal stability test was carried out with tetralin (tetrahydronaphthalene) at 425°C and 1000 psig H₂ pressure. About 90 wt % of the original charge of liquid was recovered at the end of the run. However, the liquid exhibited some evidence of instability, as determined by gas chromatography/mass spectroscopy (GC/MS) analysis.

Two series of experiments were carried out in the continuous stirred autoclave reactor using Engelhard Zn-0312T 1/8 "zinc chromite" catalyst. In one series, tetralin (tetrahydronaphthalene) was used as the slurry medium; the other series was carried out with tetrahydroquinoline (THQ). The methanol productivity was substantially higher with THQ over a range of operating conditions.

TECHNICAL DETAILS

A. Thermal Stability Test

Tetralin (tetrahydronaphthalene) thermal stability test at 425°C.

This test was carried out at the conditions shown in Table 1. Note that the reactor temperature was 425°C instead of 375°C, as used in the standard thermal stability test.

Table 2 shows the data on gas production rates and overall liquid loss, along with comparative data for tetralin, Decalin[®] (decahydronaphthalene) and Drakeol[®] 34 at 375°C. The overall liquid loss, 10 wt. % of the original charge, was quite good. Both gas production rates were substantially greater than for tetralin at 375°C, and the steady-state rate was greater than that of Decalin at 375°C.

Nuclear Magnetic Resonance (NMR) and gas chromatography/mass spectroscopy (GC/MS) analyses indicated some changes of the liquid composition over the course of the test, as shown in Table 3. The measured concentration of tetralin in the final liquid was 42 mol %. The majority (53.3 mol %) of the remaining components were isomers with the same molecular weight (132 gr/mol) as tetralin. Due to this fact, the average molecular weight at the end of the test was not significantly different from that of pure tetralin.

Table 1

Conditions of Thermal Stability Test

Reactor Temperature:	425°C
Reactor Pressure:	1000 psig
Length of Test:	72 hours after reaching 375°C*
Gas/Liquid Separator Temperature:	25°C
H ₂ Flowrate:	3.5 sL/min.
No Catalyst Present	

Table 2

Summary of the Results of Thermal Stability Tests

Liquid	Rate of C ₁ -C ₄ gas production (% initial charge/hr)		Weight of liquid lost via C ₁ -C ₄ gases (% of initial charge)	Total weight liquid lost (% of initial charge)
	Maximum	Steady State		
Drakeol 34	1.2	0.10	-	59
Decalin	0.095	0.0040	-	26
Tetralin	0.012	0.002	0.12	13
Tetralin @ 425°C	0.041	0.015	1.6	10

Table 3

Composition of "Spent" Tetralin Based on GC/MS Results

Sample: Tetralin from Thermal Stability Test @ 425°C (72 hrs)

Component	Retention time (min)	Probability (% accuracy)	Peak Area	Molecular Formula	MW (gr/mol)	mole %
Toluene	4.16	94	533343	C ₇ H ₈	92	1.4
Ethylbenzene	5.94	94	853464	C ₈ H ₁₀	106	2.3
Benzene, (1-methylpropyl)- or Benzene, (1-methyl-2-propyl)-	8.86	44 42	291630	C ₁₀ H ₁₄	134	0.8
Benzene, butyl	9.90-9.95	84	6491858	C ₁₀ H ₁₄	134	17.5
1H-Indene, 2,3-dihydro-1-methyl-	10.32-10.53	75	12072132	C ₁₀ H ₁₂	132	32.5
∞ TETRALIN	11.88-12.11	95	15713676	C ₁₀ H ₁₂	132	42.2
Naphthalene	12.73	97	1238501	C ₁₀ H ₈	128	3.3
Total area			37194604			100
Average MW (gr/mol)					131.1	

B. Catalyst Performance in Various Liquids

1. Tetralin

a. Run #1 (November, 1995)

The slurry reactor operated continuously for 8 days. Table 4 is a summary of the operating conditions that had been planned. Table 5 contains a summary of the experimental results.

Some operational problems occurred, and some incorrect operating procedures were used during the test. The metering pump, which returns liquid from the gas/liquid separator to the reactor, leaked continuously during most of the test. The loss of slurry liquid was compensated by adding more liquid make up. However, liquid make up was fed at too high a rate during the first five runs, causing a loss of catalyst from the reactor and causing the slurry concentration to change from the initial level (20 wt. % catalyst) to approximately 8 to 15 wt. % after run 5. From run 6 until the end of the test, operation was stable and the slurry concentration was approximately 15% wt., based on the weight of catalyst in the reactor at the end of the run. The gas hourly space velocity (GHSV) for runs 6 to 12 was recalculated using the final amount of catalyst remaining in the reactor (48% of the initial amount). The actual GHSV was about 9,000 cat-hr.

The data can be used to establish some preliminary, qualitative conclusions. Runs 1 and 5 were carried out at the same operating conditions: $T=325^{\circ}\text{C}$, $P=2000$ psig, H_2/CO feed ratio=2, and $\text{GHSV}=4400$ sl/kg cat-hr (average). Due to the problems noted above, the slurry concentrations of runs 1 and 5 were estimated to be 20 and about 8 wt. %, respectively. Nevertheless, H_2 and CO conversion, as well as methanol productivity, were not significantly different, as shown in Table 5. Additionally, a comparison of runs 1 and 2, where pressure was changed from 2000 to 1000 psig., shows a reduction of methanol productivity with total pressure, as expected.

Table 4.

November 1995

Planned Kinetic Studies for Alcohol Synthesis (Tetralin, Run #1)

Run	H ₂ /CO Ratio	Temp. (°C)	Total Pressure (psig)	P _{H2} (psig)	P _{CO} (psig)	G _{SV} (sl/kg- hr)
1	2	325	2000	1333	667	5000
2	"	325	1000	667	333	"
5	2	325	2000	1333	667	5000
6	"	375	2000	1333	667	5000
7	"	375	1000	667	333	5000
10	2	325	2000	1333	667	5000
11	2	400	2000	1333	667	5000
12	"	400	1000	1667	333	5000

Stirrer speed = 1750 rpm

Engelhard "zinc chromite" catalyst, Zn-0312T 1/8

Liquid medium = tetralin

Table 5

SUMMARY OF RESULTS

RUN: Engellhard 03122T 1/8" (Ground to -90u) Reduced & Stabilized ZnCrO Catalyst Run
 RUN DATE: Nov-95 Tetralin as liquid media

Run	T(°C)	P (psig)	I12/CO	GIISV (sl/kg-hr)	Conversions I12 CO	Average Rm (mol/kg-hr)	Normal Rm (mol/kg-hr)	Normal Rm+DME (mol/kg-hr)
1	325	2017	1.9	4426	11.3 14.3	8.00	8.04	8.18
2	325	1052	2.0	4615	11.7 12.9	5.78	5.77	5.83
5	325	1991	2.0	4409	11.2 12.5	8.50	8.62	8.77
6	375	1980	2.0	~9000	8.9 11.7	6.03	6.17	7.20
7	375	1099	2.0	~9000	5.3 6.8	5.65	5.70	6.27
10	325	1974	1.9	~9000	6.8 7.8	4.53	4.61	5.05
11	400	2033	1.9	~9000	11.6 11.3	3.01	2.98	4.28
12	400	2040	1.9	~9000	6.6 4.3	2.41	2.42	2.82
10	325	2027	1.9	~9000	5.1 7.2	6.85	6.90	7.54

Runs 11 and 12 were carried out at 400°C in order to study the effect of temperature on methanol and higher alcohols productivity. Methanol productivity was very low at this temperature due to the unfavorable equilibrium. Significant amounts of methane, ethane and CO₂ were produced (see Appendix 1). Hydrocarbons and CO₂ accounted for over half of the carbon selectivity. There was no significant production of higher alcohols.

Table 6 presents a comparison with earlier data obtained using Decalin as the liquid medium. Because of the problems in this test with tetralin, the present data cannot be used for quantitative purposes.

Table 6

Comparison of Tetralin with Decalin

(T=325°C, P=1000 psig, H₂/CO=2, GHSV=4600-5000 sl/kg-hr)

	<u>Tetralin</u>	<u>Decalin</u>
Methanol Productivity (mol/kg-hr)	5.8	4.3
Carbon Selectivity:		
Methanol	91.5	86.7
DME	2.0	5.6
CO ₂	5.2	5.2
Hydrocarbons	1.3	2.4

b. Run #2 (December, 1995)

This run was also carried out with Engelhard "zinc chromite" catalyst, Zn-0312T 1/8. Tables 7 and 8 present a summary of the operating conditions and the main results obtained in this test. Temperature and H_2/CO feed ratio were varied between 325 and 425°C, and 0.5 and 2, respectively. Total pressure and gas hourly space velocity (GHSV) were constant at 2000 psig and 4400 sl/kg cat-hr (average) for all experiments. Stirrer speed was 1750 rpm for all experiments. These runs were carried out during a period of continuous slurry reactor operation that lasted for 8 days. Appendix 2 presents detailed data for this run. The results are discussed in Section 3 below.

2. Tetrahydroquinoline (THQ)

The purpose of this test was to compare the effect of slurry liquid composition on catalyst performance. Five experiments from the previous test were repeated. Tables 9 and 10 present a summary of the operating conditions and the main results obtained. The maximum temperature in this test was 375°C since no significant production of higher alcohols was obtained in the previous test at higher temperatures (i.e., up to 425°C). This run required 5 days of continuous reactor operation. Appendix 3 presents detailed data.

Table 7

December 1995Kinetic Studies for Alcohol Synthesis (Tetralin, Run #2)

Run	H ₂ /CO Ratio	Temp. (°C)	Total Pressure (psig)	P _{H2} (psig)	P _{CO} (psig)	GHSV (sl/kg- hr)	Stirrer Speed (rpm)
1	2	325(*)	2000	1333	667	4400	1750
2	0.5	325	"	667	333	"	"
3	0.5	375	"	667	667	"	"
4	2	375	"	1333	667	"	"
5	2	325(*)	"	1333	333	"	"
6	2	425	"	1333	667	"	"
7	0.5	425	"	667	667	"	"
8	0.5	325(*)	"	1333	333	"	"

(*)Baseline condition

Stirrer speed = 1750 rpm

Engelhard "zinc chromite" catalyst, Zn-0312T 1/8

Liquid medium = tetralin

Table 8

SUMMARY OF RESULTS

RUN: Engelhard 0312T 1/8" (Ground to -90u) Reduced & Stabilized ZnCrO Catalyst Run
 RUN DATE: Nov/Dec95 Tetralin as liquid media

Run	T(°C)	P (psig)	H ₂ /CO	GIHSV (sl/kg-hr)	Conversions H ₂ CO	Average Rm (mol/kg-hr)	Normal Rm (mol/kg-hr)	Normal Rm+DME (mol/kg-hr)
1	325	2006	2.0	4463	8.5 14.4	3.64	3.72	3.92
2	325	2044	0.5	4382	23.3 16.3	1.49	1.50	1.51
3	375	2059	0.5	4410	35.8 21.4	1.61	1.62	1.65
4	375	2032	1.9	4415	20.6 33.7	3.71	3.84	3.91
5	325	2036	1.9	4399	11.4 19.3	1.76	1.81	1.82
6	425	2055	1.9	4506	26.0 45.7	1.29	1.32	1.34
7	425	2042	0.5	4476	44.5 27.9	0.93	0.92	0.93
8	325	2048	2.0	4215	9.8 12.5	2.10	2.17	2.17

Table 9

December 1995Kinetic Studies for Alcohol Synthesis (THQ)

Run	H ₂ /CO Ratio	Temp. (°C)	Total Pressure (psig)	P _{H2} (psig)	P _{CO} (psig)	GHSV (sl/kg- hr)	Stirrer Speed (rpm)
1	2	325(*)	2000	1333	667	4400	1750
2	0.5	325	"	667	1333	"	"
3	0.5	375	"	667	1333	"	"
4	2	375	"	1333	667	"	"
5	2	325(*)	"	1333	667	"	"

(*)Baseline condition

Stirrer speed = 1750 rpm

Engelhard "zinc chromite" catalyst, Zn-0312T 1/8

Liquid medium = tetrahydroquinoline

Table 10

SUMMARY OF RESULTS

RUN: Engelhard 0312T 1/8" (Ground to -90u) Reduced & Stabilized ZnCrO Catalyst Run
 RUN DATE: Dec95 THQ as liquid media

Run	T(°C)	P (psig)	H ₂ /CO	GHSV (sl/kg-hr)	Conversions H ₂ CO	Average R _m (mol/kg-hr)	Normal R _m (mol/kg-hr)	Normal R _m +DME (mol/kg-hr)
1	325	2036	1.9	4393	21.9 26.0	13.08	13.29	13.59
2	325	2055	0.5	4541	25.9 10.9	7.23	7.23	7.51
3	375	2059	0.5	4379	23.8 9.9	2.57	2.60	3.08
4	375	2042	1.9	4477	20.0 28.8	9.15	9.65	10.18
5	325	2048	1.9	4417	22.2 25.6	12.38	12.82	13.10

3. Comparison between tetralin and tetrahydroquinoline

Table 11 presents a preliminary comparison of the main results from the run with THQ and the second run with tetralin. Significant differences in catalyst performance were observed between liquids. In general, the best results were obtained using THQ. For all five sets of operating conditions, the methanol productivity (moles methanol/kg cat-hr) was higher with THQ than tetralin. At 325°C, the methanol catalyst productivity was 3 to 7 fold higher in THQ than in tetralin. At 375°C, the THQ/tetralin activity ratio was 1.5 to 2.4. This decrease was probably the result of a closer approach to equilibrium at 375°C.

A significant increase in dimethyl ether (DME) formation was also observed with THQ. Almost no DME was formed with tetralin as the slurry medium, whereas concentrations of 0.15 to 0.29 mole % were formed with THQ.

Table 11. Comparison of data for Tetralin and THQ

	<u>Tetralin</u>	<u>THQ</u>	<u>THQ/TETRALIN</u>
<u>Run 1, T=325°C, H₂/CO=2 (baseline)</u>			
Average Rm (mol MeOH/kg-hr)	3.64	13.08	3.6
% DME	0.10	0.17	1.7
% MeOH	1.96	7.84	4.0
<u>Run 2, T=325°C, H₂/CO=0.5</u>			
Average Rm (mol MeOH/kg-hr)	1.49	7.23	4.9
% DME	0.01	0.15	15.0
% MeOH	0.85	3.99	4.7
<u>Run 3, T=375°C, H₂/CO=0.5</u>			
Average Rm (mol MeOH/kg-hr)	1.61	2.57	1.6
% DME	0.02	0.26	13.0
% MeOH	0.95	1.42	1.5
<u>Run 4, T=375°C, H₂/CO=2</u>			
Average Rm (mol MeOH/kg-hr)	3.71	9.15	2.5
% DME	0.04	0.29	7.3
% MeOH	2.20	5.28	2.4
<u>Run 5, T=325°C, H₂/CO=2 (baseline)</u>			
Average Rm (mol MeOH/kg-hr)	1.76	12.38	7.0
% DME	0.00	0.16	-
% MeOH	0.99	7.44	7.5
<u>Run 6, T=425°C, H₂/CO=2</u>			
Average Rm (mol MeOH/kg-hr)	1.29	-	-
% DME	0.01	-	-
% MeOH	0.77	-	-
<u>Run 7, T=425°C, H₂/CO=0.5</u>			
Average Rm (mol MeOH/kg-hr)	0.93	-	-
% DME	0.00	-	-
% MeOH	0.57	-	-
<u>Run 8, T=325°C, H₂/CO=2 (baseline)</u>			
Average Rm (mol MeOH/kg-hr)	2.10	-	-
% DME	0.00	-	-
% MeOH	1.20	-	-

APPENDIX 1

(Tetralin, Run #1: November, 1995)

A. Average Gas Compositions - Reactor Outlet

Run	Average Percentages - Reactor Outlet Samples															
	H2	N2	CO	Methane	CO2	Methane	Ethylene	Ethane	C3's	DME	Methanol	Butenes	C5's	C6's	Ethanol	Isobutanol
1	63.22	0.00	31.73	0.02	0.00	0.02	0.00	0.00	0.00	0.00	4.41	0.00	0.00	0.00	0.00	0.00
2	64.43	0.00	32.35	0.00	0.15	0.0163	0.0000	0.0025	0.0002	0.03	3.13	0.0010	0.0000	0.0000	0.0000	0.0000
5	62.52	0.00	31.19	0.02	0.07	0.0476	0.0000	0.0006	0.0027	0.00	4.67	0.0000	0.0017	0.0000	0.0009	0.0000
6	63.47	0.00	31.49	0.06	0.60	0.1694	0.0001	0.0231	0.0062	0.26	1.58	0.0000	0.0022	0.0014	0.0000	0.0040
7	63.53	0.00	32.25	0.00	0.31	0.1239	0.0012	0.0097	0.0034	0.12	1.41	0.0000	0.0020	0.0000	0.0000	0.0013
10	64.03	0.00	32.59	0.00	0.23	0.0634	0.0000	0.0113	0.0017	0.12	1.22	0.0000	0.0102	0.0000	0.0000	0.0000
11	64.10	0.00	33.54	0.00	1.40	0.4499	0.0000	0.0949	0.0147	0.37	0.85	0.0115	0.0124	0.0000	0.0007	0.0000
12	63.84	0.00	33.65	0.00	1.10	0.2601	0.0000	0.0369	0.0006	0.10	0.61	0.0240	0.0129	0.0000	0.0000	0.0000
10	64.20	0.00	32.43	0.00	0.54	0.0527	0.0000	0.0157	0.0060	0.16	1.76	0.0000	0.0236	0.0010	0.0000	0.0000

APPENDIX 1

(Tetralin, Run #1: November, 1995)

B. Average Gas Inlet Compositions

Run	Inlet Average Percentages			
	H2	N2	CO	CO2
1	65.29	0.00	33.92	0.00
2	65.40	0.00	33.27	0.00
5	66.30	0.00	33.56	0.00
6	64.01	0.00	32.80	0.00
7	64.55	0.00	33.10	0.00
10	64.42	0.00	33.04	0.00
11	64.40	0.00	33.26	0.00
12	64.53	0.00	33.13	0.00
10	65.49	0.00	34.29	0.00

APPENDIX 1

(Tetralin, Run #1: November, 1995)

C. Carbon Selectivity

Combined Selectivities

Run	TOTAL Moles C	CO2	Methane	Ethane	Propane	Isobutanol	DME	TOTAL %	Mass Bal Run	TOTAL IY	GI-C2 Paraffins	C2 Olefins + C4-C6	TOTAL Oxy	OXY/IY
1	4.63	0.00	0.50	0.00	0.13	0.06	0.01	3.41	100.00	1.03	0.62	1.21	98.96	54.00
2	3.36	5.23	0.57	0.00	0.19	0.01	0.00	1.05	100.35	1.25	0.76	0.49	93.87	85.65
5	5.05	1.46	0.96	0.00	0.35	0.16	0.00	3.13	99.79	1.46	1.30	0.16	96.88	67.40
6	3.04	20.05	5.70	0.01	1.56	0.62	0.53	17.00	99.36	7.00	7.25	0.63	71.43	9.09
7	2.10	14.58	5.00	0.11	0.91	0.47	0.25	11.00	99.33	7.30	6.72	0.50	77.46	10.73
10	1.91	12.39	3.37	0.00	1.21	0.76	0.00	12.30	95.23	5.34	4.50	0.76	77.50	14.51
11	3.82	38.11	11.71	0.00	4.75	1.16	0.00	19.19	101.59	22.00	16.47	5.54	41.17	1.93
12	2.43	45.74	10.65	0.00	3.02	1.07	0.00	0.13	107.94	29.10	13.60	15.42	33.10	1.15
10	2.00	18.90	1.85	0.00	1.10	0.72	0.00	11.49	95.73	3.67	2.95	0.72	73.16	19.96

APPENDIX 2

(Tetralin, Run #2: December, 1995)

A. Average Gas Composition - Reactor Outlet

Run	Mass Bal	Average Polcentagos - Reactor Outlet Samples																Total
		H2	N2	CO	Methane	CO2	Methane	Ethylene	Ethane	C3's	DME	Methanol	Butenes	C5's	C6's	Ethanol	Isobutanol	
1		62.92	0.00	30.16	0.00	1.69	0.7295	0.0000	0.1309	0.0565	0.10	1.96	0.0000	0.0157	0.0000	0.0022	0.0000	97.76
2		28.55	0.00	62.33	0.00	5.97	1.0439	0.0000	0.2745	0.0972	0.01	0.85	0.1016	0.1020	0.0267	0.1198	0.0435	99.60
3		24.82	0.00	60.87	0.00	8.11	3.6313	0.0000	0.7144	0.0000	0.02	0.95	0.1335	0.0616	0.0135	0.0324	0.0404	99.41
4		59.01	0.00	25.40	0.00	4.99	4.3284	0.0000	0.3035	0.0903	0.04	2.20	0.0338	0.0082	0.0012	0.0344	0.0150	96.54
5		62.50	0.00	29.38	0.00	2.34	1.2596	0.0000	0.2448	0.1268	0.00	0.99	0.0669	0.0133	0.0016	0.0558	0.0154	97.00
6		57.01	0.00	21.46	0.00	8.36	9.0278	0.0000	0.6161	0.1224	0.01	0.77	0.0242	0.0142	0.0004	0.0000	0.0095	97.43
7		22.77	0.00	59.92	0.00	10.28	5.5316	0.0000	0.9627	0.4088	0.00	0.57	0.1252	0.0581	0.0050	0.0000	0.0431	100.68
8		62.75	0.00	30.70	0.00	1.36	0.6962	0.0000	0.1578	0.0943	0.00	1.20	0.0279	0.0093	0.0020	0.0689	0.0198	97.09

APPENDIX 2

(Tetralin, Run #2: December, 1995)

B. Inlet Gas Composition

Run	Inlet Average Percentages				Total
	H2	N2	CO	CO2	
1	64.12	0.00	32.87	0.00	97.0
2	33.01	0.00	66.05	0.00	99.1
3	33.06	0.00	66.26	0.00	99.3
4	63.13	0.00	32.54	0.00	95.7
5	63.77	0.00	32.93	0.00	96.7
6	64.12	0.00	32.91	0.00	97.0
7	32.71	0.00	66.23	0.00	98.9
8	63.37	0.00	31.93	0.00	95.3

APPENDIX 2

(Tetralin, Run #2: December, 1995)

C. Carbon Selectivity

Combined Selectivities

Run	TOTAL Moles C	CO2	Methane	Ethane	Elhane	Propene	C4-C6's	Methanol	Isobutanol	DME	TOTAL %	Run	Mass Bal	TOTAL HY	C1-C2 Paraffins	C2 Olefins + C4-C6	TOTAL Oxy	OXY/HY
1	5.23	34.25	14.80	0.00	5.62	3.42	0.00	36.18	0.00	4.11	98.38	1		23.84	20.42	3.42	40.29	2.07
2	10.57	56.71	9.92	0.00	5.18	2.75	25.91	8.11	1.65	0.13	110.36	2		43.76	15.10	28.66	9.89	0.23
3	15.41	52.93	23.73	0.00	9.32	0.00	13.00	6.26	1.05	0.20	106.57	3		46.06	33.06	13.00	7.59	0.17
4	13.43	38.53	33.40	0.00	5.92	2.09	3.91	16.90	0.46	0.68	101.97	4		45.32	39.32	6.00	18.12	0.40
5	6.17	39.07	20.95	0.00	8.17	6.38	16.85	16.56	1.04	0.14	109.16	5		52.35	29.12	23.23	17.74	0.34
6	20.50	41.86	45.20	0.00	6.17	1.83	1.80	3.81	0.19	0.10	100.95	6		55.00	51.37	3.63	4.09	0.07
7	20.40	50.04	26.94	0.00	9.38	5.97	9.15	2.79	0.04	0.04	105.15	7		51.43	36.31	15.12	3.67	0.07
8	4.37	32.17	16.45	0.00	7.45	6.68	9.90	28.09	1.03	0.00	102.66	8		40.48	23.90	16.58	30.01	0.75

APPENDIX 2

(Tetralin, Run #2: December, 1995)

D. Mass Balance Calculations

Atomic Flows (slpm) Based on Average Percentages of Gas Inlet

Run	Hydrogen (Average)				Oxygen (Average)				Carbon (Average)				% Conversions	
	Inlet	Outlet	Difference	% Dev	Inlet	Outlet	Difference	% Dev	Inlet	Outlet	Difference	% Dev	H2	CO
1	2.442	2.481	-0.039	-1.6	0.626	0.637	-0.011	-1.8	0.626	0.631	-0.005	-0.8	7.8	13.8
2	1.235	1.195	0.039	3.2	1.235	1.255	-0.020	-1.6	1.235	1.214	0.021	1.7	22.9	15.9
3	1.244	1.212	0.032	2.6	1.247	1.259	-0.012	-1.0	1.247	1.227	0.019	1.5	35.7	21.3
4	2.378	2.392	-0.014	-0.6	0.613	0.608	0.005	0.8	0.613	0.619	-0.006	-1.0	19.9	33.1
5	2.394	2.346	0.048	2.0	0.618	0.598	0.020	3.3	0.618	0.602	0.016	2.6	11.1	19.1
6	2.465	2.544	-0.078	-3.2	0.633	0.626	0.007	1.1	0.633	0.665	-0.033	-5.2	25.7	45.5
7	1.249	1.262	-0.013	-1.0	1.265	1.256	0.009	0.7	1.265	1.246	0.019	1.5	43.5	26.6
8	2.280	2.267	0.013	0.6	0.574	0.579	-0.005	-0.8	0.574	0.583	-0.009	-1.5	8.1	10.8

APPENDIX 2

(Tetralin, Run #2: November, 1995)

E. Atomic Flows (slpm) Based on Normalized Percentages

Run	Mass Bal	Hydrogen (Normalized)				Oxygen (Normalized)				Carbon (Normalized)				Overall MASS Balance (grams/hour)			
		Inlet	Outlet	Difference	% Dev	Inlet	Outlet	Difference	% Dev	Inlet	Outlet	Difference	% Dev	Inlet	Outlet	Difference	Run
1		2.518	2.532	-0.014	-0.6	0.645	0.651	-0.006	-0.9	0.645	0.644	0.001	0.2	55.148	55.398	-0.2	1
2		1.246	1.139	0.107	8.6	1.247	1.257	-0.010	-0.8	1.247	1.195	0.052	4.1	96.043	95.341	1.5	2
3		1.253	1.186	0.067	5.3	1.255	1.265	-0.010	-0.8	1.255	1.220	0.035	2.8	97.505	96.632	0.9	3
4		2.486	2.465	0.021	0.8	0.641	0.629	0.012	1.8	0.641	0.637	0.004	0.6	54.712	54.033	0.7	4
5		2.476	2.398	0.078	3.1	0.639	0.615	0.024	3.8	0.639	0.614	0.025	4.0	54.577	52.515	2.1	5
6		2.541	2.601	-0.060	-2.4	0.652	0.642	0.010	1.6	0.652	0.600	-0.028	-4.3	55.703	56.338	-0.6	6
7		1.263	1.215	0.048	3.8	1.278	1.247	0.031	2.5	1.278	1.226	0.052	4.1	99.263	96.120	3.1	7
8		2.392	2.316	0.075	3.2	0.603	0.595	0.008	1.3	0.603	0.595	0.008	1.3	51.595	50.818	0.8	8

APPENDIX 3

(THQ: December, 1995)

A. Average Gas Compositions-Reactor Outlet

Average Gas Outlet Composition (mol %) (*)

Run	T (°C)	P (psig)	H ₂ /CO	H ₂	CO	CO ₂	Methane	Ethylene	Ethane	C3's
1	325	2036	1.9	59.71	29.09	1.11	0.2740	0.0000	0.0522	0.0267
2	325	2055	0.5	27.41	66.82	1.23	0.2293	0.0000	0.0527	0.0097
3	375	2059	0.5	27.00	64.35	4.20	1.5242	0.0000	0.2185	0.0000
4	375	2042	1.9	57.68	26.53	2.90	1.8140	0.0000	0.2034	0.0741
5	325	2048	1.9	58.61	29.06	0.88	0.2553	0.0000	0.0624	0.0349

(*) C₃-C₆ are 100 % olefins

Average Gas Outlet Composition (mol %)

Run	T (°C)	P (psig)	H ₂ /CO	DME	Methanol	C4's	C5's	C6's	Ethanol	Iso- butanol	Total
1	325	2036	1.9	0.17	7.84	0.0000	0.0639	0.0000	0.0352	0.0000	98.37
2	325	2055	0.5	0.15	3.99	0.0399	0.0247	0.0010	0.0082	0.0039	99.97
3	375	2059	0.5	0.26	1.42	0.0775	0.0312	0.0052	0.0056	0.0107	99.10
4	375	2042	1.9	0.29	5.28	0.0078	0.0000	0.0000	0.0066	0.0064	94.79
5	325	2048	1.9	0.16	7.44	0.0645	0.0068	0.0000	0.0340	0.0000	96.61

APPENDIX 3

(THQ: December, 1995)

B. Inlet Gas Compositions

Run	Inlet Average Percentages				Total
	H2	N2	CO	CO2	
1	64.07	0.00	32.95	0.00	97.0
2	32.00	0.00	66.49	0.00	99.3
3	33.06	0.00	66.70	0.00	99.8
4	62.30	0.00	32.18	0.00	94.5
5	62.29	0.00	32.27	0.00	94.6

APPENDIX 3

(THQ: December, 1995)

C. Carbon Selectivity

Carbon Selectivities (%)

Run	T (°C)	H ₂ /CO	P (psig)	GHSV (sl/kg hr)	Conversion		CO ₂	Methane	Ethylene	Ethane	C ₃ s	C ₄ -C ₆ s
					H ₂	CO						
1	325	1.9	2036	4393	21.9	26.0	10.93	2.70	0.00	1.03	0.79	10.00
2	325	0.5	2055	4541	25.9	10.9	19.83	3.68	0.00	1.69	0.48	9.42
3	375	0.5	2059	4379	23.8	9.9	48.51	17.61	0.00	5.05	0.00	13.45
4	375	1.9	2042	4477	20.0	28.8	25.75	16.09	0.00	3.61	1.97	1.04
5	325	1.9	2048	4417	22.2	25.6	9.25	2.69	0.00	1.31	1.11	10.19

Carbon Selectivities (%)

Run	T (°C)	H ₂ /CO	P (psig)	GHSV (sl/kg hr)	Methanol	Iso butanol	DME	Total %	Total Hydroc.	Paraffins	Olefins	Total Oxygenat	Ratio Oxyg. Hydroc.
1	325	1.9	2036	4393	77.34	0.00	3.36	106.16	14.52	3.73	10.79	80.70	5.56
2	325	0.5	2055	4541	64.24	0.25	4.96	104.57	15.28	5.37	9.91	69.45	6.08
3	375	0.5	2059	4379	16.43	0.49	6.03	107.57	36.11	22.66	13.45	22.96	0.67
4	375	1.9	2042	4477	46.81	0.23	5.15	100.65	22.71	19.69	3.01	52.19	2.30
5	325	1.9	2048	4417	78.39	0.00	3.47	106.40	15.30	4.01	11.30	81.85	5.35

APPENDIX 3

(THQ: December, 1995)

D. Mass Balance Calculations

Atomic Flows (slpm) Based on Average Percentages of Gas Inlet

Run	Hydrogen (Average)				Oxygen (Average)				Carbon (Average)				% Conversions	
	Inlet	Outlet	Difference	% Dev	Inlet	Outlet	Difference	% Dev	Inlet	Outlet	Difference	% Dev	H ₂	CO
1	2.402	2.460	-0.058	-2.4	0.617	0.627	-0.010	-1.5	0.617	0.625	-0.008	-1.2	20.6	24.0
2	1.271	1.277	-0.006	-0.4	1.286	1.270	0.016	1.4	1.286	1.283	0.003	2.0	25.4	10.3
3	1.235	1.213	0.022	1.8	1.246	1.290	-0.044	-3.5	1.246	1.285	-0.039	-3.1	24.3	10.5
4	2.380	2.442	-0.062	-2.6	0.615	0.626	-0.011	-1.7	0.615	0.626	-0.011	-1.8	19.7	28.5
5	2.348	2.300	0.048	2.1	0.608	0.612	-0.004	-0.6	0.608	0.613	-0.005	-0.8	20.5	24.0

APPENDIX 3

(THQ: December, 1995)

E. Atomic Fluids (slpm) Based on Normalized Percentages

Run Max's Us	Hydrogen (Normalized)			Oxygen (Normalized)			Carbon (Normalized)			Overall Mass Balance (grams/hour)		
	Inlet	Outlet	Difference % Dev	Inlet	Outlet	Difference % Dev	Inlet	Outlet	Difference % Dev	Inlet	Outlet	Difference
1	2.476	2.464	-0.008 -0.3	0.636	0.637	0.000 -0.1	0.636	0.629	0.007 1.2	54.365	54.163	0.2
2	1.280	1.267	0.013 1.0	1.297	1.270	0.027 2.1	1.297	1.259	0.038 3.0	100.738	98.299	2.4
3	1.236	1.200	0.030 2.4	1.249	1.301	-0.052 -4.2	1.240	1.280	-0.020 -1.6	98.999	99.786	-2.8
4	2.510	2.571	-0.052 -2.1	0.651	0.662	-0.012 -1.8	0.651	0.660	-0.009 -1.4	55.545	56.474	-0.9
5	2.483	2.470	0.012 0.5	0.643	0.633	0.010 1.6	0.643	0.631	0.012 1.8	54.855	54.030	0.8