

GAS PHASE TESTING: CONVENTIONAL CATALYSTS

<u>Catalyst</u>	<u>Comment</u>	<u>Quarterly Report No.</u>	<u>Ref.</u>
Fused Fe <sub>2</sub> O <sub>3</sub>	Baseline catalyst; standard Schulz-Flory.	2	9
Fe/Cu/K	Precipitated catalysts; best uncalcined; deviation from Schulz-Flory noted.	2,3	9,10
Fe/Mn/K	Precipitated catalysts; calcined: very active, nonselective; uncalcined: deviation from Schulz-Flory.	3,4	10,11
Fe/Aluminosilicate	Fe exchanged aluminosilicate, impregnated with Fe; very high methane yields.	4,5	11,12
Ru/Al <sub>2</sub> O <sub>3</sub>	Supported catalysts; generally high methane yields; RuCl <sub>3</sub> precursor gave best hydrocarbon production.	4,6,7,8	11,13,14,15
Ru/NaY	Series of zeolite (NaY)-impregnated catalysts; all produced large amounts of methane.	5	12
Ru/CeY		5	12
Fe/Mn/NaY		5	12
Fe/Ru/NaY		6	13
FeCu/Al <sub>2</sub> O <sub>3</sub>	Alumina impregnated with mixed Fe and Cu salts; poor activity; high methane selectivities.	3,5,8	9,11,15
Ru/Zr(OPr) <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	Ru salt supported on Zr-promoted Al <sub>2</sub> O <sub>3</sub> ; good activity, apparent deviation from Schulz-Flory distribution.	5	11
Fe/Zr/Ti (K)	Precipitated catalysts from co-precipitation of Fe, Zr and Ti salts; standard distributions; added potassium enhanced olefin selectivity.	8,9	15,16
Fe/ZrO <sub>2</sub> .TiO <sub>2</sub>	ZrO <sub>2</sub> .TiO <sub>2</sub> impregnated with iron salt; possible deviation from Schulz-Flory distribution above C <sub>15</sub> .	9,10	16,17
Fe/Cu/Al <sub>2</sub> O <sub>3</sub> (K)	Cu and Fe salts successively impregnated on Al <sub>2</sub> O <sub>3</sub> , largely light products; K added as promoter; K enhanced higher molecular weight products.	9	16

TABLE 2  
(continued)

GAS PHASE TESTING: CONVENTIONAL CATALYSIS

<u>Catalyst</u>	<u>Comment</u>	<u>Quarterly Report No.</u>	<u>Ref.</u>
Fe/Zr (OPr) <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	Fe salt supported on Zr-promoted Al <sub>2</sub> O <sub>3</sub> ; Schulz-Flory distributions with low ; high CH <sub>4</sub> selectivity; high oxygenate selectivity.	10	17
Fe/Mn/Al <sub>2</sub> O <sub>3</sub>	Alumina impregnated with Fe and Mn salts; standard Schulz-Flory distributions.	10,11	17,18
Fe/Offretite	Fe exchanged and impregnated ammonium offretite; K promotion enhanced selectivity to hydrocarbons.	11,12	18,19
Fe-Y	Iron-exchanged Y zeolite; high Fe loading detrimental; K promotion gave apparent non-Schulz-Flory behavior.	12	19
Ru-Y	Ru-exchanged and impregnated Y-zeolite; high CH <sub>4</sub> selectivity; hydrocarbon oil cracking under some conditions; RuCl <sub>3</sub> -derived catalyst had apparent Schulz-Flory deviation.	12,13	19,20
Fe/Co/K	Series of coprecipitated Fe/Co catalysts with K promoters; very good activity; standard Schulz-Flory distributions.	12,13,14	19,20, 21
Fe/Nb/Cs	Coprecipitated catalysts; standard Schulz-Flory distribution.	13,15	20,22

GAS PHASE TESTING: SUPPORTED CLUSTER CATALYSTS

<u>Cluster</u>	<u>Support</u>	<u>Comment</u>	<u>Quarterly Report No.</u>	<u>Ref.</u>
Ru <sub>3</sub> (CO) <sub>12</sub>	MgO	Low activity; Schulz-Flory distribution; predominantly CH <sub>4</sub> and CH <sub>3</sub> OH.	2	9
	Al <sub>2</sub> O <sub>3</sub>	Average to poor activity; apparent deviation from Schulz-Flory distribution; deactivated rapidly; high methanation activity.	2	9
	CeO <sub>2</sub>	High olefin selectivity; Schulz-Flory distribution.	3	10
	Zr (OPr) <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	Poor activity.	3	10
	Poly(styrene)	Inactive.	4	11
	TiO <sub>2</sub>	Inactive below 300°C.	7	14
Na(HRu <sub>3</sub> (CO) <sub>11</sub> )J	MgO	Low activity; Schulz-Flory distribution.	2	9
HCoRu <sub>3</sub> (CO) <sub>13</sub>	MgO	Low activity.	3	10
	Al <sub>2</sub> O <sub>3</sub>	High CH <sub>4</sub> selectivity.	3	10
	CeO <sub>2</sub>	Good activity; ~35% CH <sub>4</sub> .	5	12
H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub>	Al <sub>2</sub> O <sub>3</sub>	Poor activity; major product was dimethyl ether.	3	10
	MgO	Good activity; Schulz-Flory distributions.	3	10
	Zr(OPr) <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	CH <sub>4</sub> and CH <sub>3</sub> OCH <sub>3</sub> predominant products.	4	11

TABLE 3

## GAS PHASE TESTING: SUPPORTED CLUSTER CATALYSTS

(continued)

<u>Cluster</u>	<u>Support</u>	<u>Comment</u>	<u>Quarterly Report No.</u>	<u>Ref.</u>
	Poly(styrene)	Inactive.	4	11
	TiO <sub>2</sub>	Predominantly CH <sub>4</sub> produced.	7	14
H <sub>2</sub> FeRu <sub>3</sub> (CO) <sub>13</sub>	Al <sub>2</sub> O <sub>3</sub>	Low activity; high CH <sub>4</sub> selectivity.	3	10
	Zr(OPr) <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	Low activity; good selectivities to methane and dimethyl ether.	4	11
	CeO <sub>2</sub>	High yields of methane and oxygenates.	4	11
	MgO	Inactive up to 290°C.	5	12
Ru <sub>6</sub> C(CO) <sub>17</sub>	MgO	Hydrocarbon products; moderate activity; apparent Schulz-Flory deviation; deactivated rapidly.	4	11
	Al <sub>2</sub> O <sub>3</sub>	Low activity; high CH <sub>4</sub> selectivity.	4	11
H <sub>2</sub> FeOs <sub>3</sub> (CO) <sub>13</sub>	MgO	Inactive.	4	11
	Al <sub>2</sub> O <sub>3</sub>	Low activity; produced only light hydrocarbons.	4	11
Fe <sub>3</sub> (CO) <sub>12</sub>	CeO <sub>2</sub>	Good activity; apparent deviation from Schulz-Flory distribution; deactivated with time on-stream.	4	11
	Zr(OPr) <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	Low activity; high dimethyl ether selectivity.	5	12
HOs <sub>3</sub> (CO) <sub>11</sub>	Al <sub>2</sub> O <sub>3</sub>	High methane selectivity (>60%).	5	12
	MgO	High methane selectivity (>50%).	5	12

GAS PHASE TESTING: SUPPORTED CLUSTER CATALYSTS

(continued)

<u>Cluster</u>	<u>Support</u>	<u>Comment</u>	<u>Quarterly Report No.</u>	<u>Ref.</u>
$\text{Ir}_2\text{Cu}_4$ (C=CPh) $_8$ (PPh $_3$ ) $_2$	Al $_2$ O $_3$	>50% methane.	5	12
[Rh $_2$ Pt(CO) $_x$ ] $_n$	CeO $_2$	Low activity, high methane selectivity.	5	12
	Zr(OPr) $_4$ /Al $_2$ O $_3$	Low activity.	5	12
	Al $_2$ O $_3$	Primary product methane.	6	13
	MgO	CH $_4$ and CH $_3$ OH predominant products.	6	13
	MgO	Inactive.	6, 7	13, 14
	Al $_2$ O $_3$	High methane selectivity.	6	13
	Zr(OPr) $_4$ /Al $_2$ O $_3$	Saturated hydrocarbons, predominantly C $_{10}+$ .	6	13
	MgO	Schulz-Flory distribution.	6	13
	Al $_2$ O $_3$	Schulz-Flory distribution; high CH $_4$ .	8	15
	MgO	Predominantly oxygenates.	8	15
	Zr(OPr) $_4$ /Al $_2$ O $_3$	Very active; high molecular weight product.	8	15

TABLE 4

SLURRY PHASE TESTING: CONVENTIONAL CATALYSTS

<u>Catalyst</u>	<u>Comment</u>	<u>Quarterly Report No.</u>	<u>Ref.</u>
Fused Fe <sub>2</sub> O <sub>3</sub>	Baseline tests; Schulz-Flory distribution; conversion not significantly affected by mass transfer; potential S poisoning of catalyst.	5	12
Fe/Mn/K	Apparent Schulz-Flory deviation in gas phase; poor slurry activation; standard Schulz-Flory distribution; severe deactivation at high CO ratios.	5	12
Fe/Cu/K	Maximum conversion of 15%; apparent deviation from Schulz-Flory distribution; deactivation as temperature increased above 260°C.	6	13
Ru/Al <sub>2</sub> O <sub>3</sub>	Very low conversions.	6	13
Fe/Cu/K/Al <sub>2</sub> O <sub>3</sub>	Lower activity than in gas phase; standard Schulz-Flory distribution.	10	17
Fe/Zr/Ti/K	Lower activity than in gas phase; apparent deviation from Schulz-Flory distribution.	10	17
Fe/ZrO <sub>2</sub> /TiO <sub>2</sub>	Much lower activity than gas phase; high methane selectivity.	11	18
Fe/Zr/Al <sub>2</sub> O <sub>3</sub>	Poor activity; high methane selectivity.	11	18
Fe/Mn/Al <sub>2</sub> O <sub>3</sub>	Extremely low activity.	11	18
Fe-Y	More active than in gas phase; high methane selectivity; low selectivity to liquid hydrocarbons.	12	19
Fe-Offretite	Moderate activity; poor selectivity.	13	20
Fe/Co/K	Good activity; poor selectivity; high CH <sub>4</sub> yield.	14	21
Fe/Nb/Cs	Low activity at 240°C; good activity at 300°C, but produces light products.	15	22

SLURRY PHASE TESTING: SUPPORTED CLUSIER CATALYSTS

<u>Catalyst</u>	<u>Comment</u>	<u>Quarterly Report No.</u>	<u>Ref.</u>
$\text{Ru}_3(\text{CO})_{12}/\text{Zr}(\text{OPr})_4/\text{Al}_2\text{O}_3$	Very low conversions (2-6 wt %); apparent Schulz-Flory deviation.	6	13
$\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$	Low activity; maximum 6.5% conversion.	7	14
$\text{Fe}_3(\text{CO})_{12}/\text{CeO}_2$	Loss of metal to slurry oil; low activity.	7	14
$\text{Ru}_3(\text{CO})_{12}/\text{Zr}(\text{OPr})_4/\text{Al}_2\text{O}_3$	Gas phase activated; improved activity; $\text{CH}_4$ selectivity approaching 30%.	8	15
$\text{Ru}_3(\text{CO})_{12}/\text{CeO}_2$	Activity comparable to gas phase; high selectivity to methane and 1-alkenes.	8	15
$\text{Fe}_3(\text{CO})_{12}/\text{Zr}(\text{OPr})_4/\text{Al}_2\text{O}_3$	Very low activity; Fe loss from support.	8	15
$\text{Co}_2(\text{CO})_8/\text{Zr}(\text{OPr})_4/\text{Al}_2\text{O}_3$	Good activity; low methane; apparent Schulz-Flory deviation.	8	15
$\text{Co}_2(\text{CO})_8/\text{TiO}_2$	Catalyst loss from reactor; poor selectivity.	9	16

TABLE 6

ANALYSIS OF UNREDUCED COPRECIPITATED Fe/Cu/K

<u>Run No.</u>	<u>Wt. Fraction</u>	<u>Batch No.</u>	<u>Wt%</u>		
			<u>Fe</u>	<u>Cu</u>	<u>K</u>
7165-66-1.2	1.00	5868-32-1.2	66.20	0.47	0.18
7002-1-1.2	1.00	5868-6-1.2	67.2 ±1.3	0.1 ±0.1	0.08 ±0.01
7165-30-1.2	0.626	5868-25-1.2	69.11	0.43	0.09
	0.374	5868-28-1.2	65.02	0.43	0.14



EXTENDED SLURRY TEST SUMMARY

Fe/Cu/K

Phases 1 and 2

Total Run Time Days	Sample #	Time on Steam h	P psig	T °C	GHSV h <sup>-1</sup>	V min <sup>-1</sup>	X <sub>CO + N<sub>2</sub></sub>	X <sub>CO</sub>	X <sub>H<sub>2</sub></sub>	S	U	Bulk Activity mol syngas/kg cat/h	Selectivity wt%					
													C <sub>1</sub>	C <sub>5-C<sub>11</sub></sub>	C <sub>2-C<sub>4</sub></sub>			
7165-30-1.2 - 19.2 wt% of Fe/Cu/K (batch nos. 5868-25-1.2, 5868-28-1.2)																		
9	23	173.9	320	237.2	307.3	1200	0.194	0.154	0.235	0.968	1.48	13.85	6.2	9.8	46.1	26.8		
16	40	308.9	162	237.9	303.2	1200	0.191	0.185	0.198	0.958	1.07	13.58	4.3	11.0	33.1	37.0		
17	43	331.9	160	240.7	302.7	1200	0.160	0.156	0.164	0.996	1.05	11.34	4.0	25.1	35.9	27.8		
20	51	403.3	167	238.7	298.4	1200	0.130	0.137	0.123	1.032	0.928	9.07	4.0	18.5	43.6	29.5		
21	54	427.3	168	241.2	297.1	1200	0.148	0.175	0.121	1.043	0.722	10.26	6.4	25.1	43.9	18.4		
22	60	451.4	152	240.6	297.2	1200	0.159	0.166	0.153	1.043	0.958	11.08	4.3	23.7	44.5	23.4		
23	64	475.9	165	240.5	297.6	1200	0.162	0.174	0.150	1.042	0.895	11.26	5.1	23.0	46.2	24.8		
7165-66-1.2 - 16.9 wt% slurry of Fe/Cu/K (batch no. 5868-32-1.2) Reactor dismantled to change slurry																		
37	12	141.8	300	210.1	295.7	1200	0.197	0.166	0.228	1.00	1.37	16.43	12.2	15.1	37.6	27.3		
38	15	165.6	300	241.8	296.3	1200	0.200	0.188	0.212	1.00	1.11	16.73	10.6	21.6	42.8	22.4		
39	19	185.8	300	242.0	296.1	1200	0.186	0.160	0.212	1.00	1.26	15.53	8.4	25.1	43.7	19.1		
42	25	260.7	300	241.7	294.4	1200	0.190	0.165	0.215	1.00	1.24	15.74	5.7	11.0	47.5	26.5		
43	28	285.6	300	239.5	297.3	1200	0.189	0.174	0.204	1.00	1.15	15.86	3.3	21.4	43.4	25.8		
44	32	311.1	297	238.3	297.4	1200	0.196	0.167	0.224	1.00	1.29	16.40	4.1	17.5	42.6	27.3		
46	36	357.7	297	240.6	300.1	1200	0.228	0.217	0.239	1.01	1.11	19.32	6.8	15.7	45.1	23.3		
49	38	428.1	300	233.0	298.8	1200	0.186	0.174	0.199	1.01	1.13	15.68	2.9	11.5	49.8	30.5		
50	42	451.0	300	237.0	299.1	1200	0.183	0.176	0.190	1.00	1.08	15.44	4.1	8.5	47.8	30.2		
52-60	N <sub>2</sub> purge	478.2	300	237.8	12.0	1200	reactor under N <sub>2</sub> purge after wax blockage in outlet line											

Table 7 (Cont'd.)

EXTENDED SLURRY TEST SUMMARY

Fe/Cu/K

Phases 1 and 2

Total Run Time Days	Sample	Time on Stream h	P psig	T °C	GHSV h <sup>-1</sup>	V min <sup>-1</sup>	F <sub>CO + H<sub>2</sub></sub>	F <sub>CO</sub>	F <sub>H<sub>2</sub></sub>	S	U	Bulk Activity mol syngas/kg cat/h	Selectivity wt%				
													C <sub>1</sub>	C <sub>2-C<sub>11</sub></sub>	C <sub>12-C<sub>21</sub></sub>		
66	49	506.6	303	240.2	284.8	1200	0.173	0.189	0.158	1.00	0.84	13.93	2.5	13.0	43.2	34.1	
67	52	529.4	302	239.3	284.7	1200	0.168	0.176	0.161	1.00	0.92	13.52	2.5	14.5	47.2	30.9	
71	62	625.8	300	242.5	285.4	1200	0.183	0.191	0.176	1.00	0.93	14.75	4.6	19.1	50.3	21.2	
73	66	659.6	305	239.0	298.2	1200	0.187	0.203	0.162	0.64	0.51	15.72	3.1	9.5	55.4	29.4	
74	70	683.8	303	240.0	297.9	1200	0.188	0.201	0.169	0.64	0.54	15.83	4.9	10.3	56.1	25.6	
79	75	803.6	308	237.4	298.7	1200	0.187	0.204	0.162	0.65	0.51	15.79	2.5	12.3	45.1	37.1	
80	79	838.0	307	238.1	299.1	1200	0.176	0.187	0.158	0.65	0.54	14.83	2.6	7.5	50.5	30.3	
84-100	N <sub>2</sub> purge	925.6	305	227.1	29.0	1200	reactor under N <sub>2</sub> purge after wax blockage in product outlet line and leak in slurry removal line										
101	85	958.0	320	240.7	419.2	1200	0.270	0.229	0.333	0.65	0.94	22.74	11.5	41.1	34.1	5.2	
106	91	1000.1	310	238.2	422.5	1200	0.098	0.080	0.126	0.65	1.02	8.35	5.9	25.0	37.6	16.6	
107	95	1023.9	310	240.2	421.2	1200	0.118	0.104	0.139	0.65	0.87	9.97	3.6	22.8	48.7	15.7	
108	99	1047.8	302	242.5	423.0	1200	0.129	0.105	0.167	0.65	1.03	10.39	6.3	22.6	49.3	13.6	
109	102	1071.3	307	240.9	423.3	1200	0.118	0.095	0.154	0.65	1.05	10.08	4.2	23.6	48.5	15.0	
113	113	1122.7	300	261.2	652.4	1200	0.216	0.193	0.251	0.66	0.86	25.24	6.0	20.2	42.2	21.0	
114	117	1146.1	300	261.8	653.6	1200	0.192	0.162	0.238	0.66	0.97	22.51	5.5	29.2	44.2	15.9	
115	121	1170.4	292	260.7	653.4	1200	0.200	0.172	0.243	0.66	0.94	23.43	5.6	37.7	38.2	17.3	
116	125	1194.4	295	262.0	653.7	1200	0.200	0.188	0.240	0.66	0.85	24.40	4.1	34.6	37.5	16.4	
118-119	N <sub>2</sub> purge	1238.3	295	253.5	74.0	1200	reactor under N <sub>2</sub> purge after gas in line plugged										

Table (cont'd.)

## EXTENDED SLURRY TEST SUMMARY

Fe/Cu/K

Phases 1 and 2

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHV $\frac{\text{Btu}}{\text{h}}$	V $\frac{\text{m}^3}{\text{min}}$	$\text{H}_2\text{O} + \text{N}_2$	$\text{H}_2\text{CO}$	$\text{H}_2$	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													$\text{C}_1$	$\text{C}_2-\text{C}_3$	$\text{C}_4-\text{C}_5$	
121	135	1285.8	307	261.0	647.0	1200	0.203	0.178	0.241	0.65	0.88	24.95	8.6	32.3	38.1	7.2
122	138	1308.9	313	260.3	649.2	1200	0.227	0.171	0.230	0.65	0.83	27.99	10.6	25.7	32.9	6.4
123	142	1332.0	313	261.1	650.2	1200	0.231	0.208	0.267	0.65	0.83	28.54	9.5	27.6	36.3	6.8
126	150	1405.9	320	261.1	653.8	1200	0.243	0.222	0.277	0.65	0.81	33.30	9.6	32.3	34.4	5.7
127	155	1429.6	299	261.7	652.9	1200	0.236	0.213	0.273	0.65	0.83	32.26	9.2	30.4	36.3	5.4
128	159	1453.7	297	261.6	652.1	1200	0.257	0.236	0.290	0.65	0.79	35.09	9.5	32.1	33.3	4.9
129	163	1477.9	300	259.7	652.8	1200	0.276	0.258	0.304	0.65	0.76	37.70	9.1	32.2	34.3	4.9
133	172	1548.8	298	255.9	332.3	1200	0.335	0.324	0.353	0.64	0.70	28.53	6.8	22.3	43.6	11.9
134	176	1572.4	303	254.7	331.9	1200	0.312	0.283	0.341	0.65	0.75	26.49	6.0	25.7	48.6	10.0
135	179	1596.2	303	260.2	331.9	1200	0.335	0.326	0.349	0.64	0.69	28.43	6.7	31.5	43.4	7.8
142	187	1661.1	310	260.1	371.1	1200	0.381	0.376	0.390	0.65	0.67	32.51	6.9	30.9	47.4	7.8
143	191	1685.3	307	259.4	371.9	1200	0.334	0.315	0.363	0.65	0.75	28.48	7.7	34.4	39.0	8.2
148	193	1710.4	310	259.4	183.4	1200	0.421	0.428	0.469	0.54	0.51	17.74	7.6	31.4	37.4	13.0
150	198	1758.3	305	257.4	184.5	1200	0.513	0.505	0.536	0.55	0.57	21.75	6.5	40.0	37.5	10.5
156	210	1866.5	313	257.1	185.0	1200	Reactor Shutdown									

Table 7 (Cont'd.)

## EXTENDED SLURRY TEST SUMMARY

Fe/Cu/K

Phase 3

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	CHSY h <sup>-1</sup>	v min <sup>-1</sup>	I <sub>CO + H<sub>2</sub></sub>	I <sub>CO</sub>	H <sub>2</sub>	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													C <sub>1</sub>	C <sub>2</sub> -C <sub>11</sub>		
7516-30-1.2 - 19.8 wt% slurry of Fe/Cu/K (batch 5868-37-1.2). Reactor dismantled to change slurry.																
157-172																
178	8	77.9	300	260.2	282.9	1200	0.269	0.303	0.289	1.01	0.97	19.21	7.3	21.0	35.6	19.9
179	12	100.7	298	259.2	282.6	1200	0.326	0.326	0.325	1.01	1.01	21.13	7.2	22.4	39.6	16.6
183	21	197.4	303	259.6	281.9	1200	0.449	0.500	0.400	1.01	0.81	29.11	6.8	26.3	41.9	15.4
184	25	221.2	303	259.3	294.5	1200	0.448	0.445	0.448	0.65	0.65	30.30	5.0	25.4	48.1	16.0
185	30	245.9	308	260.0	294.8	1200	0.460	0.455	0.467	0.65	0.66	31.15	4.3	22.0	47.5	20.6
186-191	N <sub>2</sub> purge	272.2	305	260.0	150.0	1200	Reactor exposed to excess CO after wax blockage in outlet line.									
192	39	295.8	305	261.0	295.9	1200	0.252	0.218	0.303	0.65	0.90	17.11	3.9	12.7	31.0	30.8
193	43	320.3	298	259.9	295.2	1200	0.296	0.269	0.338	0.65	0.81	20.11	3.5	17.4	37.8	32.2
197-206	N <sub>2</sub> purge	400.5	305	260.0	150.0	1200	Reactor under N <sub>2</sub> purge after wax blockage in outlet line. Exposed to excess CO for 8 hours.									
210	57	503.4	290	261.6	128.2	1200	0.325	0.334	0.310	0.65	0.60	9.66	4.5	16.4	39.7	26.8
210			Reactor shutdown													

Table 8

ELEMENTAL ANALYSIS OF (CO<sub>2</sub>(CO)<sub>8</sub>)/Zr/Al<sub>2</sub>O<sub>3</sub>

Run Description	Run No.	Catalyst No.	Batch No.	Before Reaction Wt%			*After Reaction Wt%		
				Co	Zr	H	Co	Zr	C
Fixed bed reactor screening	6930-34-48.2	1	7045-11-48.3	1.99	13.0				
Slurry 21 day test	7077-75-C48.4	2	7045-43-48.4	6.22	11.9	6.53 ±0.07	5.3 ±0.2	9.72	1.68
Extended slurry test	7516-72-C48.4	3	7054-78-48.4	6.72	4.51				

\*Slurry extracted under N<sub>2</sub> with (a) toluene for 72 h, (b) hexane for 24 h

Table 9

## EXTENDED SLURRY TEST SUMMARY

13.14 Wt% Slurry of (CO<sub>2</sub>(CO)<sub>8</sub>)/Zr(OPr)<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h <sup>-1</sup>	v min <sup>-1</sup>	X <sub>CO + N<sub>2</sub></sub>	X <sub>CO</sub>	X <sub>N<sub>2</sub></sub>	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													C <sub>1</sub>	C <sub>2-C11</sub>	C <sub>12-C<sub>20</sub></sub>	
9	18	174.3	300	219.9	300.5	1200	0.115	0.076	0.173	0.68	1.56	13.13	9.3	42.9	36.9	2.9
13	27	270.5	305	219.0	301.4	1200	0.081	0.050	0.127	0.68	1.72	9.27	9.9	46.4	31.8	3.2
14	31	294.5	303	220.5	301.1	1200	0.122	0.081	0.182	0.68	1.53	13.94	6.2	45.6	36.9	1.5
16	38	340.8	297	220.4	301.4	1200	0.056	0.019	0.110	0.68	3.92	6.41	11.0	44.6	33.3	3.5
21	52	458.6	305	220.6	301.4	1200	0.065	0.014	0.141	0.68	7.08	7.48	11.4	44.3	33.1	3.1
24	57	507.3	300	240.4	300.6	1200	0.206	0.103	0.356	0.68	2.35	23.48	12.2	36.3	44.0	4.8
28	64	578.2	308	239.7	300.9	1200	0.133	0.042	0.267	0.68	4.32	15.19	9.2	40.2	46.9	5.2
30	69	609.8	302	251.6	298.4	1200	0.151	0.041	0.316	0.67	5.14	17.09	17.3	39.6	38.0	3.1
31	73	633.5	303	251.7	297.3	1200	0.157	0.053	0.312	0.67	3.95	17.64	18.3	32.5	40.6	3.4
35	83	727.6	317	251.7	298.5	1200	0.209	0.101	0.369	0.67	2.45	23.62	19.9	34.1	38.9	3.5
36	87	749.6	310	249.4	298.7	1200	0.202	0.091	0.367	0.67	2.69	22.84	17.6	35.7	44.2	2.8
37	91	773.3	320	248.5	298.5	1200	0.195	0.089	0.352	0.67	2.61	22.04	16.9	37.5	44.8	2.0
38	95	796.5	320	248.3	298.4	1200	0.220	0.121	0.368	0.67	2.04	24.87	18.8	32.7	44.5	3.6

EXTENDED SLURRY TEST SUMMARY

13.14 Wt% Slurry of  $(CO_2(CO)_8)/Zr(OPr)_4/Al_2O_3$

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV $h^{-1}$	V $min^{-1}$	$F_{CO + H_2}$	$F_{CO}$	$F_{H_2}$	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													$C_1$	$C_2-C_{11}$	$C_{12}^*$	
42	106	893.2	310	249.1	299.3	1200	0.162	0.052	0.328	0.67	4.23	18.38	17.7	31.7	45.1	5.1
43	110	917.1	315	246.3	298.2	1200	0.138	0.048	0.274	0.67	3.82	15.65	16.7	33.4	46.8	5.2
44	114	940.6	293	250.6	298.9	1200	0.176	0.067	0.339	0.67	3.39	19.90	17.7	33.6	43.9	5.1
45	119	966.4	295	251.2	299.2	1200	0.159	0.037	0.303	0.51	1.76	18.06	16.6	30.0	43.9	6.6
48	126	1037.3	293	248.9	300.5	1200	0.130	0.055	0.275	0.51	2.58	14.81	14.4	31.2	50.3	6.9
49	131	1061.2	292	250.3	301.3	1200	0.135	0.064	0.273	0.51	2.15	15.39	14.9	34.0	45.8	7.1
50	133	1086.4	295	252.2	300.5	1200	0.151	0.088	0.277	0.51	1.60	17.24	19.3	33.8	39.6	5.5
51	134	1134.2	290	251.9	305.0	1200	0.117	0.033	0.283	0.51	4.41	13.53	19.3	26.2	43.6	7.6
56	145	1230.1	290	251.9	300.2	1200	0.107	0.023	0.271	0.51	5.92	12.14	20.5	36.9	34.7	4.1
58	146	1277.9	290	251.9	300.4	1200	0.103	0.017	0.273	0.51	8.33	11.73	14.1	31.8	50.8	6.1
59	150	1301.6	290	251.8	300.2	1200	0.137	0.060	0.287	0.51	2.40	15.55	16.3	31.8	49.4	5.3
62	151	1373.6	290	252.8	300.3	1200	0.113	0.028	0.281	0.51	5.12	12.86	14.7	25.3	49.3	9.3

Table 9 (Cont'd.)

## EXTENDED SLURRY TEST SUMMARY

13.14 Wt% Slurry of (CO<sub>2</sub>(CO)<sub>8</sub>)/Zr(OPr)<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h <sup>-1</sup>	v ml/min	M <sub>CO + H<sub>2</sub></sub>	I <sub>CO</sub>	I <sub>H<sub>2</sub></sub>	S	U	Bulk Activity mol/syngas/lb cat/h	Selectivity wt%			
													C <sub>1</sub>	C <sub>2-C<sub>11</sub></sub>	C <sub>4-C<sub>23</sub></sub>	
63	154	1398.3	600	250.4	301.9	1200	0.149	0.063	0.322	0.49	2.50	17.04	19.5	26.9	36.7	10.1
64	155	1421.5	600	250.0	300.4	1200	0.155	0.073	0.318	0.51	2.19	17.72	17.9	26.9	38.2	10.6
66	162	1469.5	603	250.8	299.6	1200	0.118	0.041	0.268	0.51	3.32	13.35	18.1	30.2	37.8	7.7
70	168	1566.1	610	248.3	300.6	1200	0.100	0.040	0.218	0.51	2.75	11.39	20.3	38.7	28.9	7.6
71	171	1588.8	613	248.9	300.6	1200	0.089	0.019	0.225	0.51	5.78	10.12	15.7	24.6	48.0	11.7
79	181	1759.1	623	280.1	299.8	1200	0.281	0.179	0.484	0.50	1.36	32.00	25.8	33.0	31.3	2.8
80	184	1782.7	613	280.5	299.9	1200	0.265	0.135	0.522	0.50	1.94	30.11	28.3	32.3	28.0	2.7
83	193	1854.3	620	281.3	300.2	1200	0.293	0.191	0.496	0.50	1.31	33.38	24.7	34.1	30.1	5.1
84	196	1878.0	617	279.5	300.3	1200	0.271	0.174	0.463	0.50	1.34	30.83	24.3	34.8	30.2	5.4
85	197	1900.8	610	278.5	300.1	1200	0.270	0.172	0.463	0.50	1.35	30.68	26.3	30.4	29.7	6.2
87	203	1968.6	620	277.6	300.4	1200	0.245	0.149	0.435	0.50	1.47	27.89	28.2	27.6	27.5	7.3



Table 10

## EXTENDED SLURRY TEST SUMMARY

11.22 Mty Slurry of  $(CO_2(CO)_8)/Zr(OPr)_4/Al_2O_3$ 

Phase 2

Total Run Time Days	Sample #	Time on Screen h	P psig	T °C	GHSV h <sup>-1</sup>	v min <sup>-1</sup>	X <sub>CO + N<sub>2</sub></sub>	X <sub>CO</sub>	X <sub>N<sub>2</sub></sub>	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													C <sub>1</sub>	C <sub>2-C<sub>11</sub></sub>	C <sub>12-C<sub>20</sub></sub>	
3	7	31.2	303	221.2	303.9	1200	0.107	0.057	0.154	1.06	2.83	14.72	18.5	29.5	23.7	3.4
6	11	102.2	307	220.9	302.0	1200	0.064	0.033	0.109	0.67	2.18	8.72	16.6	21.6	25.9	7.9
7	14	126.1	317	249.9	302.7	1200	0.285	0.170	0.455	0.67	1.79	39.08	13.7	33.8	45.8	0.6
9	17	149.9	320	248.9	304.0	1200	0.262	0.143	0.436	0.68	2.07	36.06	12.3	35.7	47.3	1.6
10	20	175.4	313	249.4	303.6	1200	0.245	0.134	0.409	0.67	2.05	33.68	14.6	29.3	43.8	5.2
11	23	230.5	313	249.2	303.2	1200	0.238	0.141	0.382	0.67	1.82	32.69	14.3	27.8	45.8	5.7
14	31	256.5	317	249.4	302.9	1200	0.244	0.157	0.374	0.67	1.61	33.56	14.7	34.2	39.2	4.3
15	34	281.1	293	250.4	303.7	1200	0.236	0.155	0.355	0.68	1.55	32.43	14.7	29.6	44.5	4.5
16	38	305.7	297	251.4	304.1	1200	0.263	0.182	0.383	0.68	1.42	36.27	15.4	33.3	38.7	6.7
17	41	330.5	303	250.2	303.9	1200	0.250	0.176	0.361	0.68	1.39	34.47	15.1	34.8	37.9	4.5
18	43	354.5	303	251.7	303.8	1200	0.292	0.225	0.392	0.68	1.18	40.26	18.5	30.2	34.0	6.1
23	54	474.2	300	248.7	306.2	1200	0.215	0.162	0.319	0.51	1.01	29.84	19.7	28.2	32.7	3.1
24	56	497.5	300	249.4	306.8	1200	0.189	0.121	0.323	0.51	1.37	26.31	23.1	19.4	27.1	4.0
29	62	618.5	300	249.0	306.9	1200	0.228	0.175	0.331	0.51	0.97	31.67	20.3	18.5	21.5	4.1