Table 25. Screening of MnO_2 Based Catalysts for Higher Alcohols Synthesis

Catalyst Catalyst Number	Run	Conversion (%) MeOH	 EtOH	Selectivity (mole%) iC_4OH	 CO_x	Productivity (g/kg cat/hr) iC_4OH
Commercial MnO_2						
Chemetals CIR-189						
None 8265-42	254	7	6	3	8	2
2% Pt 8265-61	265	49	80	4	64	28
2% Pd 8265-60	264	42	81	3	48	20
250ppm Co 8265-52	259	5	9	4	13	4
Chemetals ODC-924						
None 8265-44	255	7	-6	4	14	2
2% Pt 8265-65	267	57	79	1	78	11
2% Pd 8265-66	268	16	36	2	50	6
Laboratory MnO_2						
Cryptomelane 8265-46	256	7	-7	3	21	2
Pharmacosiderite 8265-48	257	6	-15	0	4	0

Conditions: 350°C, 30 psig, 2 hr^{-1} MeOH WHSV, 1/0.1/2 MeOH/EtOH/N_2

Table 26. Characterization of 2% Pt on Zn/Mn/Zr Oxide Supports and Catalysts

CATALYST NUMBER	DESCRIPTION OF CATALYST/SUPPORT (Targets)	ELEMENTAL ANALYSES (Wt.%)							ABD	N2 BET ANALYSIS			Plant 700 RUN NUMBERS
		Pt	Pd	Zn	Mn	Zr	Na, ppm	K, ppm	g/cc	SA (m2/g)	PV (cc/g)	PD (A)	
8265-72	60/20/20 Zn/Mn/Zr Oxide Support			42.2	10.2	19.9							
8265-76	Impregnated with 2% Pt	1.9		41.2	10.0	19.5	90	2100	1.06	59	0.16	112	272/274/275/276/277/291
8265-86	Impregnated with 0.5% Pt	0.6							1.11	88	0.15	68	284
8265-87	Impregnated with 2% Pt	2.0								45	0.15	136	285/286
8265-88	Impregnated with 5% Pt	6.4								48	0.16	134	
8265-94	Impregnated with 2% Pt	2.0								42	0.16	150	295
8265-95	Impregnated with 0.5% Pt	0.5					125	2100	1.17	73	0.15	86	296/297/299/300
8265-96	60/20/20 Zn/Mn/Zr Oxide Support			41.3	9.8	19.4				100	0.22	86	
8265-97	Impregnated with 2% Pt	1.8					44	5300	1.00	79	0.20	102	301
8265-98	Impregnated with 2% Pt	1.9		40.6	9.8	19.4	100	6800	0.98	58	0.17	118	302-319/321-323
8265-28	45/45/10 Zn/Mn/Zr Oxide Support			18.1	13.1	5.7				44	0.15	134	
8295-36	Impregnated with 2% Pt	1.9		33.7	26.2	11.1			0.73	36	0.13	144	252
8265-34	Impregnated with 2% Pd		2.0						0.73	39	0.13	132	251
8265-30	45/10/45 Zn/Mn/Zr Oxide Support			27.2	5.6	39.1				96	0.17	70	
8265-77	Impregnated with 2% Pt	1.9		27.2	5.6	39.4			1.26	84	0.17	84	273
8265-56	Impregnated with 2% Pd		1.9							85	0.14	86	263
8265-20	33/33/33 Zn/Mn/Zr Oxide Support			21.8	18.2	28.7				129	0.20	62	
8265-50	Impregnated with 2% Pt	2.0		21.3	17.8	28.5			0.71	84	0.21	98	258
8265-22	Impregnated with 2% Pd		2.1						0.73	116	0.19	62	247
8265-78	20/20/60 Zn/Mn/Zr Oxide Support												
8265-80	Impregnated with 2% Pt	2.0		11.3	8.1	48.6				152	0.35	92	263
8265-81	Impregnated with 2% Pd		2.1						1.10	167	0.32	76	
8265-62	20/60/20 Zn/Mn/Zr Oxide Support			17.1	29.1	24.0				107	0.25	96	
8265-90	Impregnated with 2% Pt	1.9		16.6	28.4	23.2			1.23	87	0.25	114	268
8265-65	Impregnated with 2% Pd		1.9						1.04	77	0.15	78	262
8265-58B	10/45/45 Zn/Mn/Zr Oxide Support			6.2	16.2	43.3				185	0.37	80	
8265-82	Impregnated with 2% Pt	1.8							0.63				278/279/290/292
8265-83	Impregnated with 2% Pd		2.0						0.55	178	0.36	82	280

Table 27. Effect of Support Composition on Performance - 2% Pt on Zn/Mn/Zr Oxide Catalysts

Catalyst Number	8265-76	8265-36	8265-77	8265-50	8265-80	8265-90	8265-82
Description	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	2.0% Pt on Zn/Mn/Zr Oxide (45/45/10)	2.0% Pt on Zn/Mn/Zr Oxide (45/10/45)	2.0% Pt on Zn/Mn/Zr Oxide (33/33/33)	2.0% Pt on Zn/Mn/Zr Oxide (20/20/60)	2.0% Pt on Zn/Mn/Zr Oxide (20/60/20)	2.0% Pt on Zn/Mn/Zr Oxide (10/45/45)
Run	272	260	273	258	279	288	278
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N2 (molar)						
Conversion (%)							
MeOH	58.7	63.6	68.3	57.3	59.0	69.9	73.3
EtOH	100.0	100.0	100.0	99.8	99.4	100.0	100.0
Selectivity (C%)							
nC3OH	0.0	0.0	0.0	0.2	0.3	0.0	0.0
nC4OH	0.0	0.0	0.0	0.0	0.1	0.1	0.0
iC4OH	11.1	10.4	8.0	10.8	8.9	8.2	8.9
iC4 Aldehyde	17.7	16.5	11.3	15.6	11.7	12.1	12.0
Me iButyrate	5.3	3.6	6.8	4.9	4.8	6.3	7.3
MeiBu Ether	0.0	0.1	0.3	0.0	0.0	0.0	0.1
C5+OH	0.9	0.9	0.9	1.1	1.5	1.3	1.0
Other Ald/Ketone	0.8	0.9	0.7	0.9	1.2	0.8	0.8
Other Esters	0.3	0.8	1.4	0.4	0.5	0.5	0.9
Others	5.3	7.6	5.2	9.8	18.8	13.1	4.9
DiME Ether	1.1	0.6	3.6	1.3	2.4	1.4	1.0
MeEt Ether	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Me Formate	2.5	4.2	3.3	2.7	1.5	1.7	0.6
Me Acetate	1.8	1.6	2.6	2.2	2.2	1.2	0.2
C1	0.8	1.4	2.2	0.9	0.8	1.3	0.6
C2+s	1.1	2.8	1.5	2.1	2.4	1.6	0.8
CO	25.4	22.5	24.2	21.0	15.5	24.5	38.6
CO2	26.0	27.4	26.4	26.2	27.0	25.9	22.3

Table 28. Effect of Support Composition on Performance - 2% Pd on Zn/Mn/Zr Oxide Catalysts

Catalyst Number	8265-34	8265-56	8265-22	8265-81	8265-85	8265-83
Description	2.0% Pd on Zn/Mn/Zr Oxide (45/45/10)	2.0% Pd on Zn/Mn/Zr Oxide (45/10/45)	2.0% Pd on Zn/Mn/Zr Oxide (33/33/33)	2.0% Pd on Zn/Mn/Zr Oxide (20/20/60)	2.0% Pd on Zn/Mn/Zr Oxide (20/60/20)	2.0% Pd on Zn/Mn/Zr Oxide (10/45/45)
Run	251	263	247	283	282	280
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N2 (molar)					
Conversion (%)						
MeOH	44.4	70.0	45.0	53.5	33.2	50.9
EtOH	96.4	98.7	97.3	97.0	66.5	96.4
Selectivity (C%)						
nC3OH	1.3	0.3	1.2	1.5	2.7	1.5
nC4OH	0.3	0.1	0.2	0.3	0.1	0.1
iC4OH	5.9	7.0	7.3	5.1	1.0	7.4
iC4 Aldehyde	12.1	8.7	11.8	7.3	4.1	9.6
Me iButyrate	1.8	3.5	2.2	1.5	1.3	2.9
MeiBu Ether	0.1	0.1	0.0	0.1	0.0	0.0
C5+OH	1.2	1.0	1.1	0.4	0.7	1.0
Other Ald/Ketone	4.1	1.2	3.2	3.8	11.7	4.0
Other Esters	0.3	1.2	0.4	0.5	0.2	0.3
Others	14.4	23.1	12.0	25.5	18.9	19.7
DiME Ether	0.5	2.2	1.6	2.6	0.4	0.7
MeEt Ether	0.0	0.1	0.0	0.1	0.0	0.0
Me Formate	7.0	3.6	2.1	2.0	0.3	0.9
Me Acetate	4.1	3.2	3.0	2.9	0.9	1.7
C1	1.1	0.9	1.2	1.1	0.7	0.5
C2+s	5.4	4.3	5.2	6.0	1.4	2.8
CO	13.6	13.5	21.7	14.4	40.4	21.7
CO2	27.0	25.9	26.0	24.8	15.1	25.2

Table 29. Effect of Noble Metal Loading on Performance - Pt on Zn/Mn/Zr Oxide Catalysts

Catalyst Number	8265-86	8265-87	8265-76	8265-88
Description	0.5% Pt on Zn/Mn/Zr Oxide (60/20/20)	1.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	5.0% Pt on Zn/Mn/Zr Oxide (60/20/20)
Run	284	285	272	286
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N2 (molar)			
Conversion (%)				
MeOH	68.5	71.6	58.7	67.6
EtOH	100.0	100.0	100.0	99.8
Selectivity (C%)				
nC3OH	0.0	0.0	0.0	0.1
nC4OH	0.1	0.0	0.0	0.1
iC4OH	8.5	9.2	11.1	8.2
iC4 Aldehyde	12.1	12.1	17.7	10.9
Me iButyrate	6.5	6.2	5.3	3.0
MeiBu Ether	0.1	0.1	0.0	0.1
C5+OH	1.3	1.1	0.9	0.9
Other Ald/Ketone	0.8	0.7	0.8	0.8
Other Esters	0.6	0.4	0.3	0.7
Others	6.2	8.5	5.3	15.3
DiME Ether	2.1	1.3	1.1	0.6
MeEt Ether	0.0	0.0	0.0	0.1
Me Formate	1.0	1.2	2.5	3.3
Me Acetate	0.9	0.5	1.8	1.8
C1	1.0	1.2	0.8	1.3
C2+s	1.0	1.1	1.5	3.2
CO	32.9	31.6	25.4	22.6
CO2	24.8	24.7	26.0	27.2

Table 30. Effect of Noble Metal Loading on Performance - 0.5% and 2% Pt on Zn/Mn/Zr Oxide Catalysts

Catalyst Number	8265-94			8265-95		
Description	0.5% Pt on Zn/Mn/Zr Oxide (60/20/20)			2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)		
Run	295			297		
Conditions	350 C, 30 psig, 10/0.1/2/ MeOH/EtOH/N2					
MeOH WHSV (hr-1)	2	3	4	2	3	4
Conversion (%)						
MeOH	51.8	35.0	25.6	50.2	41.0	31.0
EtOH	99.9	93.7	86.6	99.0	94.3	90.7
Selectivity (C%)						
nC3OH	0.1	2.5	4.1	0.5	2.1	3.1
nC4OH	0.1	0.2	0.2	0.1	0.2	0.3
iC4OH	11.8	8.0	3.7	13.0	12.0	8.0
iC4 Aldehyde	17.8	16.5	11.1	16.2	18.6	18.1
Me iButyrate	4.8	1.6	0.9	5.4	3.9	2.9
MeiBu Ether	0.0	0.1	0.0	0.0	0.0	0.0
C5+OH	0.7	0.8	0.8	1.2	1.2	1.4
Other Ald/Ketone	0.7	6.0	11.4	1.8	5.0	7.5
Other Esters	0.3	0.1	0.1	0.1	0.0	0.0
Others	5.6	8.8	10.9	5.7	5.8	8.0
DiME Ether	0.9	0.4	0.4	1.2	0.8	0.6
MeEt Ether	0.0	0.0	0.0	0.1	0.1	0.1
Me Formate	2.6	2.3	3.7	0.8	0.7	0.7
Me Acetate	1.9	3.2	3.2	2.4	4.0	4.5
Hydrocarbons	1.7	1.1	1.1	2.2	1.9	1.7
CO	24.5	25.0	27.3	23.2	21.6	22.3
CO2	26.5	23.4	21.2	25.9	22.1	20.8

Table 31. Pilot Plant Performance of Large Scale Preparation of 2% Pt on Zn/Mn/Zr Oxide Catalyst

Catalyst	8265-76	8265-95	8265-98
	2% Pt on Zn/Mn/Zr (60/20/20) Oxide		
	Screening Preparation	Support Certification	Final 200 g Preparation
Plant 700 Run Number	272	297	308
Conditions	350°C, 30 psig, 2 hr^{-1} MeOH WHSV, 1/0.1/2 MeOH/EtOH/N_2 (molar)		
Conversion (%)			
MeOH	58.7	50.2	53.4
EtOH	100.0	99.0	99.1
Selectivities (mole %)			
nC_3OH	0.0	0.5	0.4
nC_4OH	0.0	0.1	0.1
iC_4OH	11.1	13.0	11.6
iC_4 Aldehyde	17.7	16.2	18.0
Me iButyrate	5.3	5.4	4.3
Other Oxygenates	2.0	3.2	1.5
Others (No ID)	5.3	5.7	7.3
C_1-C_2 Oxygenates	5.4	4.5	4.1
C_1-C_4 Hydrocarbons	1.9	2.2	1.4
CO	25.4	23.2	22.3
CO_2	26.0	25.9	28.0
Productivities (g/kg/hr)			
iC_4OH	96	102	94
iC_{4+} Oxygenates	360	340	348

Table 32. Effect of Process Variables on Performance of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion

Catalyst	8265-98 2% Pt on Zn/Mn/Zr (60/20/20) Oxide										
Run Number	309	308	310	308	311	312	308	304	307	306	325
Conditions	2 hr^{-1} MeOH WHSV, 2/1 N_2/MeOH (molar)										1 hr^{-1} WHSV
Temperature (°C)	325	350	375	350	350	350	350	350	350	350	325
Pressure (psig)	30	30	30	30	100	300	30	30	30	30	300
MeOH/EtOH (molar)	10/1	10/1	10/1	10/1	10/1	10/1	10/1	7/1	4/1	1/1	7/1
Conversion (%)											
MeOH	39.7	53.4	64.2	53.4	46.0	56.4	53.4	57.4	58.8	65.5	55.2
EtOH	96.6	99.1	98.1	99.1	95.7	97.6	99.1	97.4	93.4	82.8	97.0
Selectivities (mole %)											
nC_3OH	1.2	0.4	1.1	0.4	0.3	0.8	0.4	1.0	2.9	2.0	1.6
nC_4OH	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.5	1.2	0.1
iC_4OH	15.6	11.6	5.7	11.6	14.4	20.7	11.6	15.3	9.1	0.3	22.2
iC_4 Aldehyde	16.6	18.0	13.4	18.0	11.2	7.2	18.0	19.0	12.9	1.0	4.8
Me iButyrate	4.9	4.3	2.1	4.3	5.1	5.6	4.3	5.4	4.9	0.2	9.1
Other Oxygenates	3.4	1.5	4.4	1.5	1.8	1.4	1.5	3.9	9.7	3.1	6.8
Others (No ID)	8.5	7.3	8.1	7.3	5.8	2.1	7.3	5.5	13.4	14.1	13.0
C_1-C_2 Oxygenates	7.2	4.1	2.2	4.1	3.3	3.0	4.1	4.1	6.9	66.9	5.7
C_1-C_4 Hydrocarbons	0.7	1.4	3.5	1.4	2.7	2.6	1.4	1.3	0.9	0.7	1.0
CO	14.5	22.3	33.9	22.3	26.2	31.2	22.3	18.1	13.0	5.1	14.6
CO_2	27.5	28.0	25.5	28.0	29.2	25.2	28.0	26.2	25.8	5.6	21.1
Productivities (g/kg/hr)											
iC_4OH	102	94	54	94	104	176	94	150	109	7	105
iC_4 Oxygenates	241	276	200	276	220	285	276	388	322	33	192

Table 33. Effect of H_2, CO and CO_2 Co-Feeds on Performance of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion

Catalyst	8265-98 2% Pt on Zn/Mn/Zr (60/20/20) Oxide				
Run Number	308	313	314	318	319
Conditions	325°C, 30 psig, 2 hr^{-1} MeOH WHSV				
MeOH/EtOH	10	10	10	10	10
N_2/MeOH	2	2	2	2	2
Other/MeOH	None	2 H_2	2 CO	1.5 CO_2	2.8 CO_2
Conversion (%)					
MeOH	53.4	58.3	29.3	53.3	55.4
EtOH	99.1	99.5	90.5	99.6	98.9
Selectivities (mole %)					
nC_3OH	0.4	0.2	2.9	0.2	0.5
nC_4OH	0.1	0.0	0.2	0.0	0.0
iC_4OH	11.6	14.0	1.6	9.6	7.7
iC_4 Aldehyde	18.0	11.6	7.5	18.0	15.9
Me iButyrate	4.3	7.3	0.9	6.5	4.9
Other Oxygenates	1.5	3.2	12.8	2.2	2.4
Others (No ID)	7.3	6.4	12.5	4.4	3.3
C_1-C_2 Oxygenates	4.1	3.9	4.9	2.4	1.5
C_1-C_4 Hydrocarbons	1.4	2.6	1.6	1.1	0.6
CO	22.3	24.4	28.1	32.6	36.1
CO_2	28.0	26.4	27.2	23.0	27.3
Productivities (g/kg/hr)					
iC_4OH	94	122	9	78	63
iC_4 Oxygenates	276	287	57	276	233

Table 34. Conversion of Methanol Only Using Pt on Zn/Mn/Zr Oxide Catalysts

Catalyst Number	8265-76		8265-50		8265-82	
Description	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)		2.0% Pt on Zn/Mn/Zr Oxide (33/33/33)		2.0% Pt on Zn/Mn/Zr Oxide (10/45/45)	
Run	272	291	258	293	278	292
Feed	MeOH/EtOH	MeOH	MeOH/EtOH	MeOH	MeOH/EtOH	MeOH
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, N2 Inert					
Conversion (%)						
MeOH	58.7	49.6	57.3	49.1	73.3	60.1
EtOH	100.0	-	99.8	-	100.0	-
Selectivity (C%)						
nC3OH	0.0	0.0	0.2	0.0	0.4	0.0
nC4OH	0.0	0.0	0.0	0.0	0.0	0.0
iC4OH	11.1	0.2	10.8	0.2	8.9	0.2
iC4 Aldehyde	17.7	0.3	15.6	0.3	12.0	0.2
Me iButyrate	5.3	0.1	4.9	0.1	7.3	0.1
MeiBu Ether	0.0	0.0	0.0	0.0	0.1	0.0
C5+OH	0.9	0.2	1.1	0.3	1.0	0.1
Other Ald/Ketone	0.8	0.3	0.9	0.3	0.8	0.1
Other Esters	0.3	0.2	0.4	0.2	0.9	0.2
Others	5.3	0.9	9.8	0.8	4.9	0.8
DiME Ether	1.1	7.9	1.3	8.4	1.0	8.9
MeEt Ether	0.0	0.0	0.0	0.0	0.0	0.0
Me Formate	2.5	10.3	2.7	7.3	0.6	3.3
Me Acetate	1.8	0.0	2.2	0.0	0.2	0.0
C1	0.8	6.6	0.9	6.9	0.6	3.1
C2+s	1.1	0.7	2.1	1.2	0.8	0.4
CO	25.4	61.3	21.0	63.6	38.6	72.9
CO2	26.0	11.0	26.2	11.3	22.3	10.0

Table 35. Conversion of Methanol Only at High Temperature and Pressure

Catalyst	Glass Beads (Blank)			8265-98 2% Pt on Zn/Mn/Zr Oxide					
Run Number	324			322			323		
Hours on Stream	9-16	25-32	41-48	9-16	25-32	41-48	9-16	25-32	41-48
Conditions	2 hr^{-1} MeOH WHSV, 2/1 N_2/MeOH (molar)								
Temperature (°C)	350	400	450	350	400	450	350	400	450
Pressure (psig)	30	30	30	30	30	30	300	300	300
Conversion (%)									
MeOH	0.2	2.1	8.8	45.9	95.6	95.7	46.7	95.4	96.3
Selectivities (mole %)									
nC_3OH	0.0	1.8	1.2	0.0	0.0	0.0	0.0	0.0	0.0
nC_4OH	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
iC_4OH	0.0	0.0	0.0	0.1	0.1	0.0	0.2	0.2	0.1
iC_4 Aldehyde	0.0	0.6	0.0	0.2	0.3	0.2	0.1	0.1	0.1
Me iButyrate	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Other Oxygenates	7.8	1.2	0.3	0.4	0.6	0.8	0.3	0.3	0.3
Others (No ID)	4.7	1.0	0.0	0.2	1.3	0.7	0.2	0.9	0.2
C_1-C_2 Oxygenates	87.5	54.6	35.0	17.6	0.1	0.1	12.4	0.0	0.1
C_1-C_4 Hydrocarbons	0.0	4.2	5.0	5.2	6.9	7.6	2.4	2.6	3.4
CO	0.0	30.9	51.7	67.3	81.2	80.6	76.5	90.9	90.7
CO_2	0.0	5.0	6.8	9.0	9.6	9.9	7.9	5.1	5.1
Productivities (g/kg/hr)									
iC_4OH	0	0	0	0	2	0	2	2	0

Table 36. Evaluation of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion at High H_2 Partial Pressures - Plant 700, Run 326

Catalyst	8265-98 2% Pt on Zn/Mn/Zr (60/20/20) Oxide				
Period HOS	5 33-40	7 49-56	10 73-80	13 97-104	18 137-144
Conditions	325°C, 7/1 MeOH/EtOH (molar), 3/1 N_2/MeOH (molar)				
Pressure (psig)	1200	300	50	50	300
MeOH WHSV (hr^{-1})	1.0	1.0	0.5	0.5	1.0
H_2/MeOH (molar)	15	15	15	0	0
Conversion (%)					
MeOH	15.3	26.3	53.3	61.6	43.9
EtOH	18.9	36.8	78.7	82.8	64.7
Selectivities (mole %)					
nC_3OH	0.2	0.2	0.1	2.0	0.0
nC_4OH	0.1	1.1	1.3	0.8	1.4
iC_4OH	1.1	1.3	3.4	1.9	2.6
iC_4 Aldehyde	9.1	6.6	3.4	1.7	5.2
Me iButyrate	0.1	0.4	0.4	2.5	1.7
Other Oxygenates	13.2	16.8	13.5	6.6	9.2
Others (No ID)	0.3	2.4	11.9	16.2	12.7
C_1-C_2 Oxygenates	4.1	5.1	1.5	9.2	12.4
C_1-C_4 Hydrocarbons	1.4	0.5	0.4	0.5	0.4
CO	32.0	18.6	14.7	16.3	10.3
CO_2	38.4	47.0	49.4	42.3	44.0
Productivities (g/kg/hr)					
iC_4OH	2	4	7	6	9
iC_4 Oxygenates	13	19	15	13	35

Table 37. Modelling of Higher Alcohol Synthesis Process

Temperature, °C	325
Pressure, psig	300
MeOH LHSV, hr-1	1
MeOH/EtOH, molar	7
MeOH/N2 (H2), molar	0.5
Methanol Conv, %	55.18
Ethanol Conv, %	96.95

Assumptions:

1. C5+ Alcohols are treated as C5's
2. "Other" Aldehydes and Ketones are treated as C5's
3. "Other" Esters are treated as C6's
4. "Other" Hydrocarbons are treated as C6's

	% Methanol Conversion	100% Conv Basis	% Ethanol Conversion	100% Conv Basis
Unconverted	44.82		3.05	
CO	12.09	21.91		
CO2	17.48	31.68		
n-C3OH	0.44	0.80	3.07	3.17
n-C4OH			0.40	0.41
i-C4OH	7.29	13.21	38.96	40.19
C5+ OH	0.67	1.21	9.40	9.70
DME	0.87	1.58		
MeBuEther	0.01	0.02	0.16	0.17
i-C4 Aldehyde	1.55	2.81	8.47	8.74
"Other" Ald + Ketone	0.19	0.34	2.60	2.68
MeFormate	0.32	0.58		
MeAcetate	1.18	2.14	8.26	8.52
Me i-Butyrate	1.50	2.72	21.01	21.67
"Other" Esters			4.62	4.77
C2	0.61	1.11		
C3	0.20	0.36		
C5	0.01	0.02		
Other HC	10.77	19.52		
Total	100.00	100.00	100.00	100.00

	C	H	O
Methanol	1	4	1
Ethanol	2	6	1
CO	1		1
CO2	1		2
n-C3OH	3	8	1
n-C4OH	4	10	1
i-C4OH	4	10	1
C5+ OH	5	12	1
DME	2	6	1
MeBuEther	5	12	1
i-C4 Aldehyde	4	8	1
i-Pentanal	5	10	1
MeFormate	2	4	2
MeAcetate	3	6	2
Me i-Butyrate	5	10	2
Et i-Butyrate	6	12	2
C2	2	6	
C3	3	8	
C5	5	12	
C6	6	14	

Reaction Coefficients for HYSIM Simulation:

Methanol	-100	
Ethanol		-100
CO	21.91	
CO2	31.68	
n-C3OH	0.27	2.11
n-C4OH		0.21
i-C4OH	3.30	20.09
C5+ OH	0.24	3.88
DME	0.79	
MeBuEther	0.00	0.07
i-C4 Aldehyde	0.70	4.37
i-Pentanal	0.07	1.07
MeFormate	0.29	
MeAcetate	0.71	5.68
Me i-Butyrate	0.54	8.67
Et i-Butyrate		1.59
C2	0.55	
C3	0.12	
C5	0.00	
C6	3.25	
H2	138.8	37.27
H2O	6.26	36.32
C Balance:	100.00	100.02
H Balance:	100.00	100.00
O Balance:	100.00	100.00

Table 38. Isobutanol Process - Performance vs. Separator Temperature

Operating Conditions		"Best" Pilot Plant Results	Capital Cost Estimate Basis	Process Simulation →					
Fresh Feed,	BPSD		5300	4980	5050	5090	5220	7120	8580
Combined Feed,	BPSD		20300	20300	20300	20300	20300	20300	20300
Fresh MeOH,	BPSD			3700	3750	3780	3870	5300	6500
Combined MeOH,	BPSD			6430	6550	6640	6840	9140	10580
Fresh MeOH,	KG-MOLES/HR			608	617	622	637	872	1069
Combined MeOH,	KG-MOLES/HR			1057	1078	1092	1124	1504	1740
Total Carbon In	KG-MOLES/HR			900	913	921	943	1290	1540
HPS Temp,	°F			59	80	100	120	150	180
Recycle Gas/Comb Feed,	MOLAR			0.12	0.12	0.12	0.12	0.12	0.12
Recycle Gas/Fresh Feed,	MOLAR		1.0	0.33	0.33	0.33	0.33	0.28	0.24
Methanol/Ethanol,	MOLAR	7.0		7.0	7.1	7.1	7.1	7.0	7.1
H2 Partial Pressure,	PSIA	<29		26	26	25	25	25	24
Performance Data									
Carbon Conversion,	%			97.0	97.5	97.8	98.3	96.7	92.8
Isobutanol Selectivity,	%			22.1	22.2	22.1	22.1	22.2	22.1
Isobutanol Yield*,	%			21.5	21.6	21.6	21.5	21.2	19.7
Feed and Product Losses, Carbon % of Fresh Feed									
VENT LOSSES									
Methanol				0.3	0.5	0.8	1.3	3.2	7.1
Ethanol				0.0	0.0	0.0	0.0	0.1	0.1
Isobutanol				0.0	0.0	0.0	0.1	0.3	0.8
LIQUID PURGE LOSSES									
Methanol				2.6	1.9	1.3	0.4	0.0	0.0
Ethanol				0.0	0.0	0.0	0.0	0.0	0.0
Isobutanol				0.0	0.0	0.0	0.0	0.0	0.0
TOTAL				2.9	2.4	2.1	1.8	3.6	8.0

*NOTE: ISOBUTANOL LOST TO VENT IS SUBTRACTED FROM THE TOTAL YIELD

Weight Balance = Total MT Out/Total MT In = 100.08%

Table 39. Isobutanol Process - Material Balance

HYSIM (V2.50) - Generated Material Balance for 120 F Separator Case

		Feed Kg-Moles/hr		Product Kg-Moles/hr					
		Methanol	Ethanol	Recy Vent	Liq Purge	Ovd Vapor	Liq Product	Recy Liq	Recy Gas
	Methanol	650		12.4	4.0	0.2		494.7	2.3
	Ethanol		156	0.1				4.8	
	Isobutanol			0.2			52.0	0.5	
	C Conv:	98.3							
	IC4OH Sel:	22.1							
TOTAL IN: PER DAY	Metric Tons	672	TOTAL OUT: PER DAY	Metric Tons	673				
	Kg-Moles C	23095		Kg-Moles C	23121				
	Kg-Moles H	84884		Kg-Moles H	84935				
	Kg-Moles O	19347		Kg-Moles O	19358				

	C	H	O					MOLES C	MOLES H	MOLES O
Methanol	1	4	1	9.55	3.06	0.17	0.00	400	1598	400
Ethanol	2	6	1	0.06	0.04	0.00	0.00	6	17	3
Hydrogen		2		49.49	0.00	0.12		0	49231	0
CO	1		1	32.81	0.00	0.10		1175	0	1175
CO2	1		2	304.09	0.16	2.05		6961	0	13922
n-C3OH	3	8	1	0.92	0.62	0.02	5.89	382	1019	127
n-C4OH	4	10	1	0.01			0.57	31	78	8
I-C4OH	4	10	1	0.39	0.01	0.00	92.48	5015	12538	1254
C5+ OH	5	12	1	0.02			15.96	908	2180	182
DME	2	6	1	5.38	0.10	0.05		240	721	120
MeBuEther	5	12	1	0.24	0.05	0.00	0.01	17	41	3
I-C4 Aldehyde	4	8	1	12.50	3.67	0.18	2.58	1051	2101	263
I-Pentanal	5	10	1	0.01			4.35	253	507	51
MeFormate	2	4	2	2.48	0.15	0.03		89	177	89
MeAcetate	3	6	2	21.37	2.51	0.29	0.00	979	1958	653
Me I-Butyrate	5	10	2	1.06	0.16	0.01	40.61	2049	4099	820
Et I-Butyrate	6	12	2	0.06			6.84	357	714	119
C2	2	6		2.50	0.00	0.01		167	501	0
C3	3	8		0.79	0.00	0.01		55	146	0
C5	5	12		0.05	0.00	0.00		4	9	0
C6	6	14		39.59	2.65	0.56	0.00	2982	6958	0
Water	0	2	1	2.12	0.92	0.04		0	342	171
Total				485.49	14.33	3.64	169.34	23121	84935	19358

Table 40. Isobutanol Process - Summary of Utility Streams

STREAM	DESCRIPTION	UTILITY	QUANTITY
EN1	Feed Pump Power Delta P=325 psig	Electricity	42.3 KW
EN2	Feed Preheater Delta T=280 F End Temp=617 F	Fuel Gas	44.1 MMBtu/hr
EN3-EN5	Reaction Heat	(Assume Adiabatic)	0
EN6	Reactor Effluent Cooler Delta T=43 F End Temp=120 F	Electricity (Air Cooler)	67.1 KW
EN7	Compressor Delta P=40 psig	Electricity	57.1 KW
	Splitter Overhead Condenser Delta T= 144 F End Temp=170 F	Electricity (Air Cooler)	525 KW
EN9	Splitter Reboiler 398 F Bottoms 366 F Feed	MP Steam	199 Mlb/hr
EN10	Liquid Recycle Pump Delta P=115 psig	Electricity	41.8 KW
EN11	Splitter Charge Heater Delta T=175 F End Temp=366 F	MP Steam	74.6 Mlb/hr

Table 41. Calculation of Utility Requirements

#1 Feed Pump — ΔEnthalpy=29.4KW 80% motor eff.
Factor for centrifugal pump=1.15

42.3 KW electric

#2 Feed Preheater

44.1 MM Btu/hr fuel gas

#3 Reactor Effluent Cooler — ΔEnthalpy=9.46 MM Btu/hr

Cooling air ΔT=25°F (95°F inlet, 120°F outlet) 0.453 Btu/ft^3
ΔP=5.4 lb/ft^2, 70% fan eff., 90% motor eff.

67.1 KW electric

#4 Recycle Gas Compressor — ΔEnthalpy=39.7 KW 80% motor eff
Factor for entrifugal pump=1.15

57.1 KW electric

#5 Splitter Overhead Condenser — ΔEnthalpy=221.2 MM Btu/hr

Cooling air ΔT=75°F (95°F inlet, 170°F outlet) 1.36 Btu/ft^3
ΔP=5.4 lb/ft^2, 70% fan eff., 90% motor eff.

525 KW electric

#6 Splitter Reboiler Bottoms — ΔEnthalpy=161 MMBtu/hr

199 Mlb/hr medium pressure (300psig) steam

#7 Liquid Recycle Pump — ΔEnthalpy=29.1 KW 80% motor eff
Factor for centrifugal pump = 1.15

41.8 KW electric

#8 Splitter Charge Heater — 60.4 MMBtu/hr

74.6 Mlb/hr medium pressure (300psig) steam

Table 42. Utility Costs Basis

Fuel Oil Value	$0.28 per Gallon =====>	$79 per MT
Fuel Oil Gravity	0.9500	
Fuel Oil Heat of Combustion	17,000 BTU/lb	

HP Steam (Superheated) @600 psig and 700 deg F	1352 BTU/lb
MP Steam (Staurated) @150 psig	1194 BTU/lb
LP Steam (Saturated) @50 psig	1174 BTU/lb
Boiler Feed Water @ 60 deg F	28 BTU/lb
Boiler Feed Water @ 250 deg F	219 BTU/lb
Boiler Efficiency	85%
Boiler Heating Cost as Percent of Total	95%

Utility	Units	Calculated Value		Recommended Value
Electrical Power	$/KWH	$0.04		$0.05
High Pressure Steam	$/MLB	$3.45	*	$3.45
Medium Pressure Steam	$/MLB	$3.03	*	$3.05
Low Pressure Steam	$/MLB	$2.98	*	$3.00
Boiler Feed Water	$/MLB	$0.42	*	$0.40
Condensate (Credit)	$/MLB	$0.42	*	$0.40
Cooling Water	$/MGal	$0.08		$0.10
Fuel Fired	$/MM BTU	$2.10	*	$2.10
Inert Gas	MSCF	$1.32		$1.35

* Calculated from fuel oil value

Table 43. Calculation of Total Annual Utility Costs

Electric Power (#1 + #4 + #3 + #5 + #7) = 733.3 KW x 8000 hr x $0.05/KWH

= 0.293 MM$/yr

Fuel Gas (#2) = 44.1 MMBtu/hr x 8000 hr x $2.10/MMBtu

= 0.741 MM$/yr

Medium Pressure(300psig) Steam (#6 + #8)

274 Mlb/hr x 8000 hr x $3.05/Mlb

= 6.68 MM$/yr

Total Utility Costs = 7.71MM$/year

Table 44. Basis for Economic Calculations

Fixed Costs	
Staffing	4.8 Operators/Position
Operator Salaries	$33,000/yr
Supervision	37% Labor
Direct Overhead	45% Labor/Super
Maintenance	3% ISBL*
Plant Overhead	65% Labor/Maint.
Tax & Insurance	1.5% Fixed Inv*

Capital Expenses	
Interest on Capital	None
Interest on Working Capital	10%/yr

Utility	Units	Value
Electrical Power	$/KWH	$0.05
High Pressure Steam	$/MLB	$3.45
Medium Pressure Steam	$/MLB	$3.05
Low Pressure Steam	$/MLB	$3.00
Boiler Feed Water	$/MLB	$0.40
Condensate (Credit)	$/MLB	$0.40
Cooling Water	$/MGal	$0.10
Fuel Fired	$/MM BTU	$2.10
Inert Gas	MSCF	$1.35

Total Plant Investment	
ISBL Investment	Curve Costs
Offsites	30% ISBL*
Interest During Construction	10%/yr* for 3 years
Royalties	Full UOP Rates
Catalyst/Adsorbent Inventory	Capitalized

Working Capital	
Raw Materials Storage	15 days at Delivered Value
Total Products in Storage	15 Days Cost of Production
Accounts Receivable	30 Days Production (Key Products)
Accounts Payable (Credit)	30 Days Production (Raw Materials)
Cash Kept on Hand	7 Days Gross Profit
Noble Metal Inventory	Full Inventory at Market Value (Pt @ $376/tr oz)
Warehouse Inventory	2% ISBL Investment*
Chemicals Inventory	Full Inventory at Markey Value (Solvent, Desorbent, ect...)

Depreciation	
ISBL Depreciation	10%/yr
Offsite Depreciation	10%/yr
Royalty Depreciation	10%/yr
Inventory Depreciation	10%/yr (Composite Account)
Depreciation Schedule	Straight Line

* Parameters designated by an asterisk should not be considered in economic evaluations where two or more cases are compared to each other.

Table 45. Base Case Economics for Methanol to Isobutanol

Basis: 333.33 days/yr; 8,000 hours/yr

Daily production: 95.1 MT/day

VARIABLE COSTS AND REVENUES

Mass Balance

	Units	Units/yr	$/unit	$MM/yr
Main products				
Isobutanol	MT	31,687	903	28.61
Fuel Gas	MMBtu	120,000	2.00	0.24
Total products	MT	31,687		28.85
Feedstocks				
Methanol	MT	166667	150	25.00
Ethanol	MT	57500	150	8.63
Total feedstocks		224167		33.63

Consumables: catalysts, adsorbents, and chemicals

	$/MT	$MM/yr
Catalysts and chemicals	15.77	0.50
Total consumables		0.50

Utilities

	$/unit	Units/MT	$/MT	$MM/yr
Power, kW-h	0.050	185.1	9.255	0.29
Steam (HP), M-lb	3.45		0.000	0.00
Steam (MP), M-lb	3.00	69.18	210.999	6.69
Steam (LP), M-lb	3.00		0.000	0.00
Boiler feed water, M-lb	0.40		0.000	0.00
Condensate, M-lb	0.40		0.000	0.00
Cooling water, MGal	0.1		0.000	0.00
Fuel fired, MMBtu	2.10	11.13	23.373	0.74
Inert gas, m^3	0.045		0.000	0.00
Total utilities			243.63	7.72

FIXED OPERATING COSTS

				$MM/yr
Labor				
Operators per shift		4.8 @	$33,000 per year	0.76
Supervision	@	37%	of operating labor	0.28
Direct overhead	@	45%	of labor & supervision	0.47
				1.51
Maintenance				
Materials and labor	@	3%	of ISBL investment	0.18
Overhead expenses				
Plant overhead	@	65%	of labor & maintenance	1.10
Taxes and insurance	@	1.5%	of fixed investment	0.14
				1.23
Other expenses				
Interest on capital (debt)	@	0%	per year (100% equity)	
Interest working capital	@	10%	per year	0.21
Product shipping	@	$10	per MT	0.32
Sales and admin	@	0.2%	of sales	0.06
				0.59

CAPITAL CHARGES

Depreciation and amortization				
ISBL	@	10%	per year	0.68
OSBL	@	10%	per year	0.24
Royalties	@	10%	per year	0.00
Capitalized inventories	@	10%	per year	0.00
				0.92

CAPITAL ITEMS

Plant investment	$MM
M & L	4.4
DE & CE	1.5
ISBL	5.9
OSBL @ 35% ISBL	2.07
Interest @ 10% 2 year	1.23
Total fixed investment	9.30
Royalties	
Royalties	0.00
Total royalties	0.00
Capitalized inventories	0.00
Total plant investment	9.30

Working capital		$MM
Feedstock storage	15 days	1.51
Main product storage	15 days	1.29
By-product storage	15 days	0.00
Accts receivable	30 days	2.60
Accts payable	30 days	(3.03)
Cash in hand	7 days	(0.35)
Spares	2% ISBL	0.12
Total working capital		2.14

Cats., adsorbs., and chems. inventory	
Catalysts	
Chemicals	
Total inventory	0.00

ECONOMIC ANALYSIS

	$MM/yr	$/MT	$/lb	%	cents/gal
Gross margin					
Main product sales	28.85	910.57	0.41		264.98
By-product sales					
Minus feedstock cost	33.63	1,061.16	0.48	72.7	306.80
Gross margin	(4.77)	(150.59)	(0.07)		(43.82)
Variable costs					
Consumables	0.50	15.77	0.01		4.58
Utilities	7.72	243.63	0.11		70.90
Total variable costs	8.22	259.40	0.12	17.8	75.48
Fixed costs					
Labor	1.51	47.67	0.02		13.87
Maintenance	0.18	5.59	0.00		1.63
Overhead expenses	1.23	38.97	0.02		11.34
Other expenses	0.59	18.58	0.01		5.41
Total fixed costs	3.51	110.80	0.05	7.6	32.24
Cash cost of production	45.36	1,431.36	0.65		416.53
Cash cost of production per main product	45.36	1,431.36	0.65		416.53
Cash flow	(16.50)	(520.79)	(0.24)		(151.55)
Capital charges					
Plant depreciation	0.92	29.03	0.01		8.45
Royalty amortization	0.00	0.00	0.00		0.00
Inventory amortization	0.00	0.00	0.00		0.00
Total capital charges	0.92	29.03	0.01	2.0	8.45
Net cost of production	46.28	1,460.39	0.66	100.0	424.97
Net cost of production per main product	46.28	1,460.39	0.66		424.97
Pre-tax income	(17.42)	(549.82)	(0.25)		(160.00)
Simple pre-tax ROI, %	(189.38)				
Simple payback, years	(0.56)				
DCF IRR, %	IRR @ 10 years		IRR @ 20 years		
DCF payback, years	(0.58) @ 20%		(0.57) @ 10%		
Main product sale price, $/MT					
20% IRR	1,493.04 @ 10 years		1,483.41 @ 20 years		
30% IRR	1,517.70 @ 10 years		1,511.35 @ 20 years		
40% IRR	1,544.06 @ 10 years		1,540.06 @ 20 years		

Table 46. Summary of Economic Cases

($9.2 MM Capital Investment is Assumed for 500 MT/day Methanol Consumption in Each Case)

CASE I, BASE CASE

Assume: Best Results from UOP Research Pilot Plant Work are Obtained Commercially, Isobutanal in the Product Stream has the Same Value as Isobutanol

This Implies:

--22.2% Carbon Selectivity to Isobutanol + Isobutanal Gives 31687 MT/yr Product
--H_2, CO, and CO_2 Byproducts Give 120,000 MMBtu/yr Fuel Gas Credit
--Utilities Costs to Fractionate Liquid Byproducts from Main Product are 7.72 MM$/yr

CASE II

Assume: All Isobutanal Produced is a Reaction Intermediate and Therefore Eventually Converted to the Desired Isobutanol Product

This Implies:

--26.1% Carbon Selectivity to Isobutanol Gives 37137 MT/yr Product
--Same Fuel Gas Credit as the Base Case
--Same Utilities Costs as the Base Case

CASE III

Assume: 50% Selectivity to Isobutanol is Achievable Commercially

This Implies:

--50% Carbon Selectivity to Isobutanol Gives 71264 MT/yr Product
-- Fuel Gas Credit is Reduced 30% from the Base Case
--Utilities Costs are Reduced 50% from the Base Case

CASE IV

Assume: 100% Selectivity to Isobutanol is Achievable Commercially

This Implies:

--100% Carbon Selectivity to Isobutanol Gives 142528 MT/yr Product
-- No Fuel Gas Credit
--Utilities Costs are Reduced 75% from the Base Case

Table 47. Basis for Economic Analysis

(500 MT per Day Methanol Feed)

CASE NUMBER		I	II	III	IV
Carbon % Selectivity to Isobutanol		22	26	50	100
Feed (Methanol + Ethanol) Requirement	MT/yr	224000	224000	224000	224000
Product (Isobutanol + Isobutanal) Generation	MT/yr	31700	37100	71300	142500
Feed Cost ($150 per MT for both MeOH and EtOH)	MM$/yr	33.63	33.63	33.63	33.63
Utilities Cost	MM$/yr	7.72	7.72	3.86	1.93
Fixed Capital Investment	MM$	9.20	9.20	9.20	9.20
Product Sale Price Needed for 20% IRR	$/MT	**1490**	**1270**	**620**	**310**

Table 48. Isosynthesis Catalyst List

Catalyst	Description	Surface Area, m^2/g	Calcination Temp, °C
IS-1	ZrO_2 [b]	63	500
IS-2	ZrO_2 [b]	74	450
IS-3	ZrO_2 [b]	28	600
IS-4	ZrO_2 [b]	35	550
IS-5	ZrO_2	45	600
IS-6	1% Y-ZrO_2	71	600
IS-7	3% Si-ZrO_2	120	600
IS-8	Commercial-CeO_2	2.3	-
IS-9	CeO_2 [b]	69.9	500
IS-10	1% Ba-ZrO_2	71.4	550
IS-11	ZrO_2	81.0	500
IS-12	2% Ba-ZrO_2	95.6	500
IS-13	ZrO_2	60	550
IS-14	1% Cs-ZrO_2	64.6	500
IS-16	ZrO_2	73.6	500
IS-17	2% Cs-ZrO_2	110	500
IS-18	50% IS-16 +50% Clay	-	-
IS-19	1% Cu-ZrO_2 [c]	71.9	450
IS-20	1% Co-ZrO_2 [c]	71.9	450
IS-21	ZrO_2	88.0	500
IS-22	5% Y-ZrO_2	123.0	500
IS-23	8% La-ZrO_2	119.0	500
IS-24	15% Zr-SiO_2	514.0	650
IS-25	Bi_2O_3 [b]	-	500
IS-26	ZrO_2	91.0	475
IS-27	10% Zr-SiO_2	253	450
IS-28	10% Zr-SiO_2-Al_2O_3	299	450
IS-29	1% Y-ZrO_2/n-C_7 [a]	-	450
IS-30	1% Cs-ZrO_2/EtOH [a]	-	450
IS-31	1% Cs-ZrO_2/Me_2CO [a]	-	450
IS-32	ZrO_2	95	475
IS-33	ZrO_2	107	450
IS-34	ZrO_2	122	425

[a] Solvent Extracted

[b] Precipitated

[c] Prepared by spray-impregnating nitrate salt onto IS-16

Table 49. Isosynthesis Run Summary

Run	Cat.	Description	Feed H_2:CO Ratio	Feed Additive	CO Conv., %	*i*C4= Yield, %
1	IS-1	ZrO_2	1:1	None	16.7	1.50
5	-	Blank	1:1	None	0.4	0.00
6	IS-3	ZrO_2	1:1	None	4.9	0.79
7	IS-4	ZrO_2	1:1	None	15.3	1.56
8	IS-1	ZrO_2	1:1	None	17.5	1.54
9	IS-5	ZrO_2, sol-gel	1:1	None	23.9	2.21
10	IS-6	1% Y-ZrO_2, sol-gel	1:1	None	26.4	1.69
11	IS-7	3% Si-ZrO_2, sol-gel	1:1	None	18.7	0.77
12	IS-5	ZrO_2, sol-gel	1:1	None	34.9	1.51
13	IS-8	CeO_2	1:1	None	4.6	0.00
14	IS-9	CeO_2	1:1	None	43.2	0.75
15	IS-10	1% Ba-ZrO_2, sol-gel	1:1	None	24.6	1.54
16	IS-11	ZrO_2, sol-gel	1:1	None	30.2	2.23
17	IS-12	2% Ba-ZrO_2, sol-gel	1:1	None	23.0	2.24
18	IS-11	ZrO_2, sol-gel	0.7:1	None	25.2	1.89
19	IS-14	1% Cs-ZrO_2, sol-gel	1:1	None	25.0	2.27
20	IS-15	2% Ba on IS-11	1:1	None	24.4	2.18
21	IS-16	ZrO_2, sol-gel	1:1	None	21.9	2.26
22	IS-17	2% Cs-ZrO_2, sol-gel	1:1	None	23.1	1.76
23	IS-18	50% IS-16 + clay	1:1	None	25.8	2.23
24	IS-17	2% Cs-ZrO_2, sol-gel	0.5:1	None	15.7	1.14
25	IS-17	2% Cs-ZrO_2, sol-gel	0.5:1	None	17.5	1.13
26	IS-17	2% Cs-ZrO_2, sol-gel	0.5:1	None	12.6	1.17
27	IS-14	1% Cs-ZrO_2, sol-gel	0.5:1	None	17.8	1.71
28	IS-17	2% Cs-ZrO_2, sol-gel	0.5:1	None	13.1	0.57
29	IS-19	1% Cu-ZrO_2, sol-gel	1:1	None	27.9	2.17
30	IS-20	1% Co-ZrO_2, sol-gel	1:1	None	28.7	1.43
31	IS-17	2% Cs-ZrO_2, sol-gel	0.5:1	None	17.1	1.16
32	IS-21	ZrO_2, sol-gel	1:1	None	23.9	2.28
33	IS-21	ZrO_2, sol-gel	1:1	None	21.8	1.53

Table 49. (con't.) Isosynthesis Run Summary

Run	Cat.	Description	Feed H_2:CO Ratio	Feed Additive	CO Conv., %	*i*C4= Yield, %
34	IS-21	ZrO_2, sol-gel	2:1	None	21.3	2.33
35	IS-23	8% La-ZrO_2, sol-gel	2:1	None	24.4	1.13
36	IS-22	5% Y-ZrO_2, sol-gel	2:1	None	23.7	1.14
37	IS-24	15% Zr-SiO_2, sol-gel	2:1	None	1.5	0.00
38	IS-25	Bi_2O_3, precip.	2:1	None	2.2	0.00
39	IS-21	ZrO_2, sol-gel	2:1	Ethylene	-	1.39
40	IS-21	ZrO_2, sol-gel	2:1	Propylene	-	1.16
41	IS-21	ZrO_2, sol-gel	2:1	Propylene	-	1.50
42	IS-26	ZrO_2, sol-gel	2:1	Propylene	-	2.14
43	IS-26	ZrO_2, sol-gel	2:1	None	20.99	2.10
44	IS-26	ZrO_2, sol-gel	2:1	None	27.17	2.76
45	IS-27	10% Zr-SiO_2, sol-gel	2:1	None	2.12	0.00
46	IS-28	10% Zr-SiO_2-Al_2O_3, sol-gel	2:1	None	2.35	0.00
47	IS-26	ZrO_2, sol-gel	2:1	Ethanol	19.48	1.72
48	IS-29	1% Y-ZrO_2,extracted	2:1	None	27.0	1.86
49	IS-30	1% Cs-ZrO_2,extracted	2:1	None	29.7	1.76
50	IS-31	1% Cs-ZrO_2,extracted	2:1	None	28.3	1.53
51	IS-13	ZrO_2, sol-gel	2:1	None	19.6	1.70
52	IS-13	ZrO_2, sol-gel	2:1	None	20.5	2.00
53	IS-32	ZrO_2, sol-gel	2:1	None	16.4	2.41
54	IS-33	ZrO_2, sol-gel	2:1	None	28.9	3.70
55	IS-34	ZrO_2, sol-gel	2:1	None	31.7	3.75
56	IS-33	ZrO_2, sol-gel	1:1	None	23.0	2.32
57	IS-21	ZrO_2, sol-gel	2:1	None	33.8	1.24
58	IS-32	ZrO_2, sol-gel	2:1	None	27.8	3.57
59	IS-33	ZrO_2, sol-gel	2:1	None	25.5	3.17

Table 50. Effect of Catalyst Calcination Temperature and Surface Area

Calcination Temperature, °C	Surface Area, m^2/g	Isobutylene Yield, %
550	60	2.00
500	88	2.33
475	95	2.41
450	107	3.70
425	122	3.75

Table 51. Effect of Additives to Zirconia Catalysts on Isobutylene Selectivity

Additive	Isobutene Yield, %
None	2.26
1% Y	1.69
3% Si	0.77
1% Ba	1.54
2% Ba	2.24
1% Cs	2.27
2% Cs	1.76
1% Cu	2.17
1% Co	2.14

Table 52. Non-Zirconia Catalysts

Catalyst	Isobutylene Yield, %
ZrO_2	3.75
CeO_2 - Commercial	0.00
CeO_2 - Precipitated	0.75
Bi_2O_3	0.00

Table 53. Effect of Intermediate Recycle

Intermediate	Major Products
Ethylene	Ethane, *n*-Butene, Heavies
Propylene	Propane, Heavies, Ethylene
Ethanol	Ethylene, Ethane, Propylene, *n*-Butene, Heavies
Methanol	Methane, Dimethyl Ether

Table 54. Effect of Pressure
(450°C, 960 hr^{-1} GHSV, 1/1 H_2/CO)

Pressure (psig)	300	600	1200
CO conversion (%)	6.3	13.6	20.9
Selectivity (%C)			
CO_2	67.7	53.6	54.5
C_1	19.4	17.4	19.1
I-C_4	0	5.8	7.3
I-$C_4^=$	0	5.8	3.6

Table 55. Effect of Temperature
(1200 psig, 960 hr^{-1} GHSV, 1/1 H_2/CO)

Temperature (°C)	353	450	500
CO conversion (%)	1.7	20.9	42.3
Selectivity (%C)			
CO_2	87.5	54.5	45.3
C_1	12.5	19.1	21.3
I-C_4	0	7.3	10.5
I-$C_4^=$	0	3.6	0

Table 56. Effect of Space Velocity
(450°C, 1200 psig, 1/1 H_2/CO)

CO GHSV (cc/cc cat/hr)	540	960	2100
CO conversion (%)	36.8	20.9	16.7
Selectivity (%C)			
CO_2	48.8	54.5	49.4
C_1	17.5	19.1	15.7
I-C_4	11.1	7.3	9.0
I-$C_4^=$	3.7	3.6	9.0

Table 57. Effect of H_2/CO Feed Ratio
(450°C, 1200 psig, 960 hr^{-1} GHSV)

H_2/CO Ratio	Catalyst	CO Conversion, %	Isobutylene Yield, %
0.5	IS-17	15.7	1.14
1.0	IS-17	23.1	1.76
1.0	IS-21	21.8	1.53
2.0	IS-21	21.3	2.33