These attempts to run a designed set of experiments with catalyst 11-DAN-115 to determine the effect of process parameters (temperature, pressure, space velocity and syngas ratio) on catalyst performance were unsuccessful. The catalyst employed, a cousin of 10-DAN-54 (our "best" isobutanol catalyst) prepared via ammonium hydroxide precipitation, was not very selective to total alcohols and showed marked differences from sample to sample. Overall performance also decayed with time. These trends were not observed to the same extent with the same formulation prepared by potassium carbonate precipitation (e.g., 10-DAN-54), indicating that we will have to revisit the catalyst preparation procedure in order to obtain selective and stable materials.

Nonetheless, the design provided useful information: two design points showed that the catalyst can achieve the production of methanol and isobutanol in a 1:1 mole ratio, with an isobutanol activity of > 30 g/kg-hr.

Use of ammonium hydroxide or ammonium carbonate as the precipitating base does not give the desired compositions for the mixed metal oxides, most likely due to the formation of water-soluble ammine complexes.

4.8.2   Tests with 10-DAN-54

We devoted a significant effort to testing a promising isoalcohol catalyst, 10-DAN-54 (a K/Pd promoted Zn/Cr/Mn spinel oxide) under various process conditions. Two separate charges of 10-DAN-54 were tested and produced reasonably consistent numbers under standard test conditions (400°C, 1000 psi, 12000 GHSV and syngas ratio = 1:1). This catalyst produces 200-252 g/kg-hr of total alcohols (total alcohol selectivities of 57-68%) with an isobutanol rate of 94-130 g/kg-hr and a MeOH/i-BuOH product mole ratio of 3. For the second charge, both space velocity (GHSV) and temperature were varied.

Space Velocity: At lower space velocities, productivities fall, but higher alcohols are favored, resulting in a higher proportion of higher alcohols vs. methanol (MeOH/i-BuOH product mole ratio falls from 3.2 to 1.7 on going from 12000 to 3000 GHSV).

Methanol formation is fast with respect to higher alcohol synthesis (HAS), as HAS results from consecutive reactions from methanol. Methanol formation is so fast under reaction conditions that it is essentially controlled by chemical equilibrium. Thus, long residence times favor HAS.

The isobutanol rate is still a respectable 48 g/kg-hr at GHSV = 3000.

Temperature: The rate of HAS increases with increasing temperature because of the more favorable kinetics, whereas the methanol equilibrium is disfavored by thermodynamics. Thus higher temperatures favor isobutanol over methanol. The concern here is that the

syngas that no longer reacts to form methanol can now form hydrocarbons rather than higher alcohols, so a trade-off may exist in manipulating this variable to promote HAS.

At temperatures of 380°C and 400°C, the MeOH/i-BuOH product mole ratio stays constant at 3.6-3.8; in contrast, at 420°C, this ratio becomes 1.0 showing that HAS is favored at the higher temperature. However, selectivity to total alcohols falls from 48-57% down to 34%; hydrocarbon formation is also favored by higher temperatures and this effect appears to outweigh the benefit of increased isobutanol formation vs. methanol.

Catalyst Aging: The catalyst was returned to start-up conditions after 102 hours and showed little deactivation:

	20 hrs on stream	122 hrs on stream
Total ROH activity (g/kg-hr)	200	204
Isobutanol activity (g/kg-hr)	94	89
MeOH/i-BuOH product mole ratio	3.2	3.8
ROH Selectivity	68	48

The catalyst appears to keep a constant alcohol productivity with time, but hydrocarbon production increases, resulting in an overall loss in selectivity.

Conversion: Using temperature and space velocity traverses, we have looked at the effects of conversion on catalyst performance for the 10-DAN-54 catalyst. The data are shown graphically in Figures 4.8-6 – 4.8-11 and the details are given in Tables 4.8-5 – 4.8-8. Increasing conversion (whether by increasing temperature or decreasing space velocity) results in a loss in selectivity to total alcohols and a concurrent increase in hydrocarbon formation, especially methane. It appears that operating the catalyst in the 15-20% conversion range is required to preserve a reasonable selectivity to total alcohols.

Pressure: Results of a pressure traverse with the 10-DAN-54 catalyst show that alcohol activity increases with increasing pressure (see below), with an increase of 11.5 g/kg-hr of isobutanol for every 100 psi increase in the 700 and 1320 psi range. However, the methanol/i-butanol mole ratio increases from 3 to 5 over the same interval, showing that increasing pressure favors methanol formation over higher alcohol synthesis. Overall selectivity to alcohols remains essentially unchanged.

	700 psi	1000 psi	1320 psi
Total ROH activity (g/kg-hr)	106	204	292
Isobutanol activity (g/kg-hr)	49	89	120
MeOH/i-BuOH product mole ratio	3.1	3.8	4.8
ROH Selectivity (%)	40	48	39

Pressure is thus a good handle for raising the overall reaction rate, but at the price of losing some selectivity to higher alcohols.

Syngas Ratio: The catalyst 10-DAN-54 was tested with syngas feeds varying from (a) 2:1 H_2/CO, (b) our standard 1:1 and (c) 1:2. The results are summarized below:

	$H_2/CO = 2$	$H_2/CO = 1$	$H_2/CO = 0.5$
Total ROH activity (g/kg-hr)	328	213	663
ROH Selectivity (%)	11.6	10.6	29
Isobutanol activity (g/kg-hr)	23	25	213
MeOH/i-BuOH product mole ratio	3.8	2.2	0.38

Methanol formation is favored at high syngas ratio, as expected. The results for the low syngas ratio ($H_2/CO = 0.5$) were encouraging, but the catalyst quickly plugged. Repeated attempts to run the catalyst at a syngas ratio of 0.5 resulted in reactor plugging each time. Examination of the catalyst revealed a wax deposit on the surface, which was analyzed by mass spectrometry. The wax consists of a clean hydrocarbon mixture, with a range (C_{24}-C_{48}) of high molecular weight, linear products. The distribution is egg-shaped, peaking at C_{28} and tailing away at higher molecular weights. Carbon deposition also occurs at the reactor *inlet* (prior to the catalyst) and this is responsible for reactor plugging. This last observation made us suspect that the reactor tube itself is catalyzing syngas conversion at the low syngas ratios. Tests with empty tubes confirmed this.

Detailed analysis of the data obtained from the syngas ratio traverse on our Pd-promoted spinel oxide catalysts 10-DAN-54 revealed an unusual alcohol product distribution, with maxima in alcohol productivity in the C_1 and C_3 ranges; the expected maxima usually occur in the C_1 and C_4 ranges. The selectivity to total alcohols was also low (10-30%). These anomalies suggested that some change had occurred in the surface composition of the catalyst.

Analysis of the carbon deposited in the reactor inlet revealed the presence of significant quantities of iron and nickel, probably carried into the reaction system by carburization of the reactor tube and consequent metal dusting. The metals provide sites for Fischer-Tropsch (F-T) chemistry to occur, as was observed—recall the isolation of a C_{24}-C_{48} molecular weight linear hydrocarbon wax on the catalyst after discharge from the reactor.

73

To ensure that carbonyls were not being introduced to the reactor from the feed gas, an activated carbon bed (to remove iron and nickel carbonyls) was inserted upstream of the catalyst bed. A molecular sieve bed to remove any entrained water from the feed cylinders was also added.

Figure 4.8-6. Plot of Selectivity to Alcohols vs. Conversion with Changing Space Velocity,
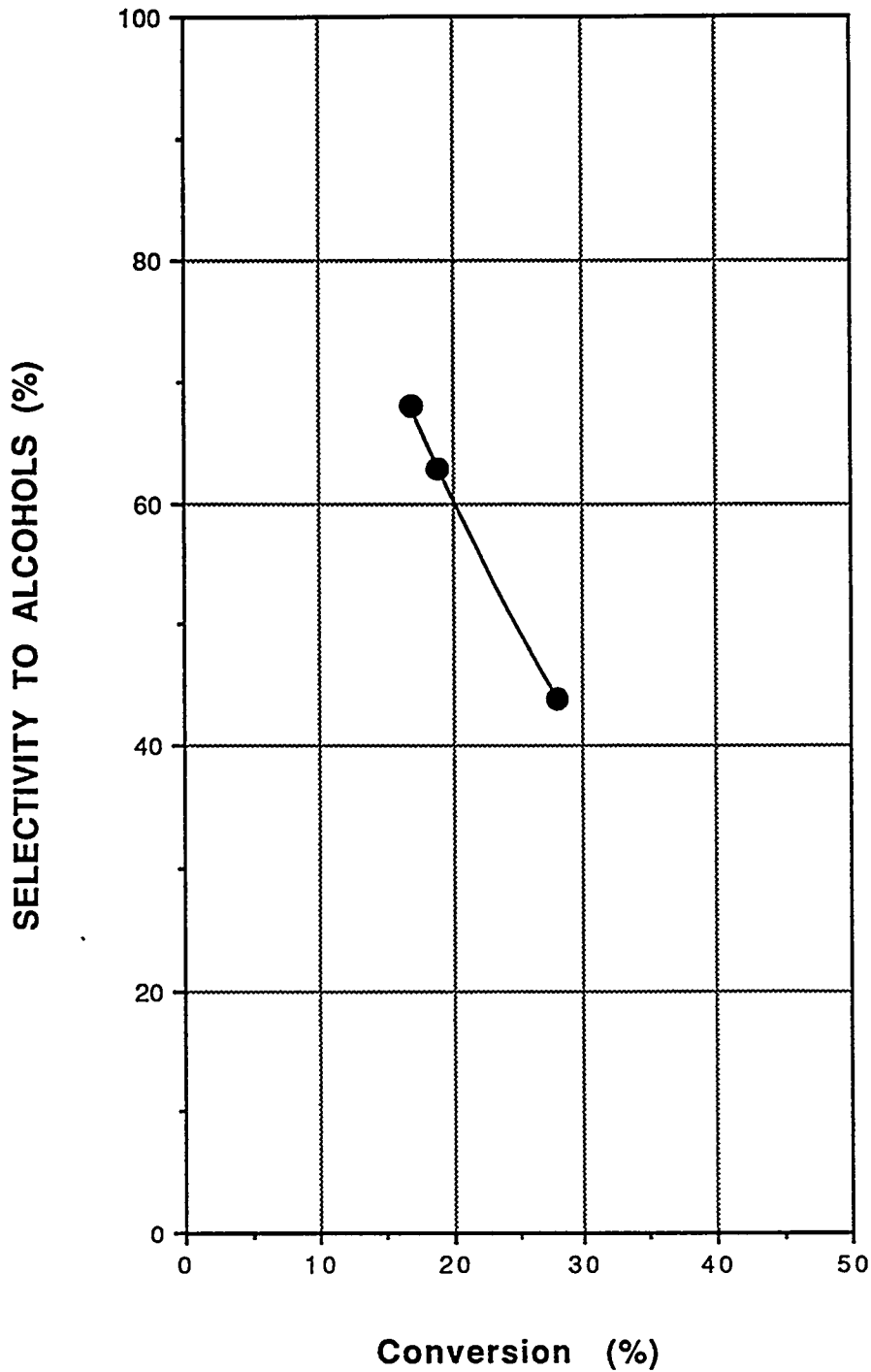for Catalyst 10-DAN-54. See Table 4.8-5 for Conditions.

Figure 4.8-7. Plot of Product Composition vs. Conversion with Changing Space Velocity,
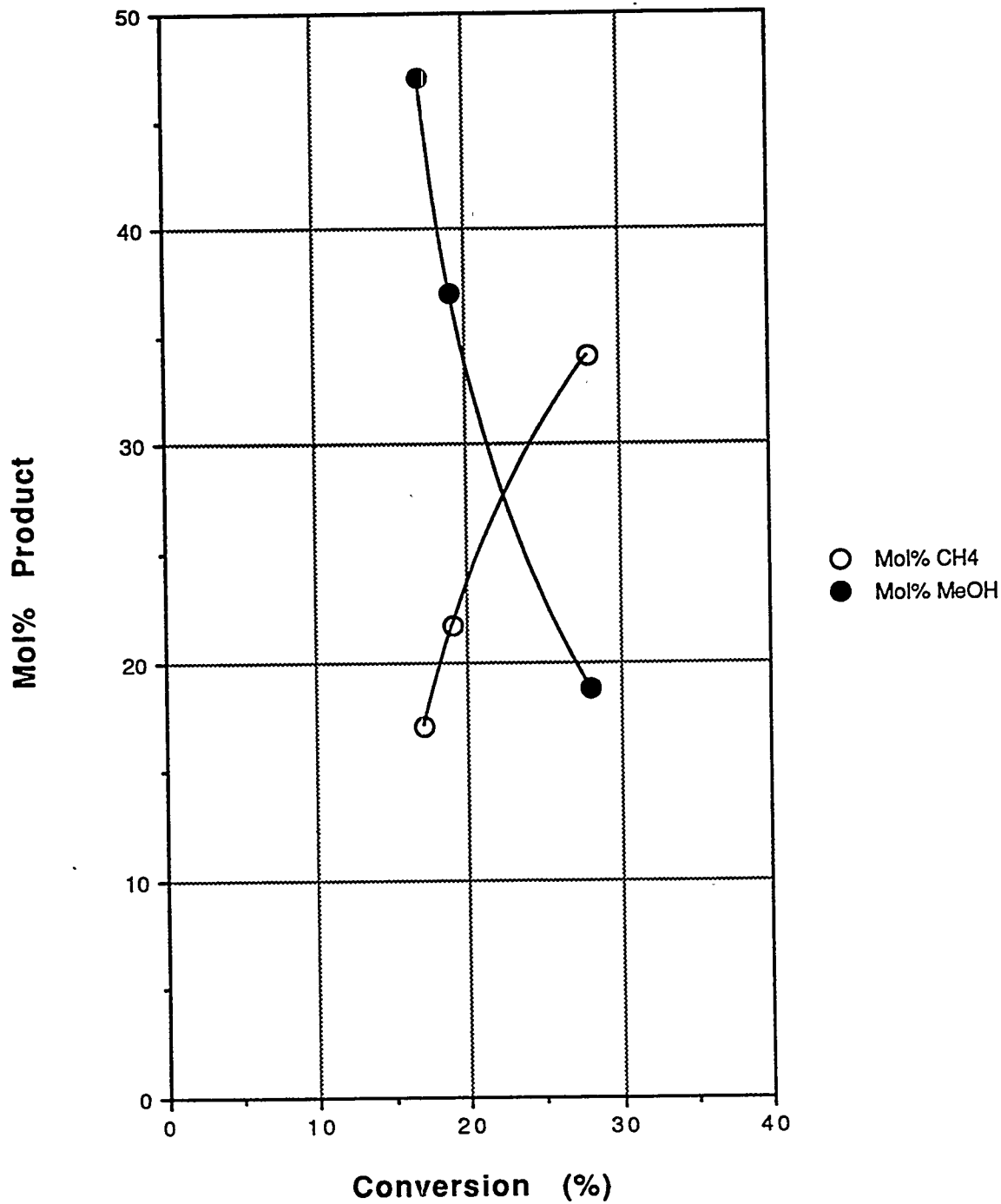for Catalyst 10-DAN-54. See Table 4.8-5 for Conditions.

Figure 4.8-8.   Plot of Methanol vs. Methane Yields with Changing Space Velocity, for
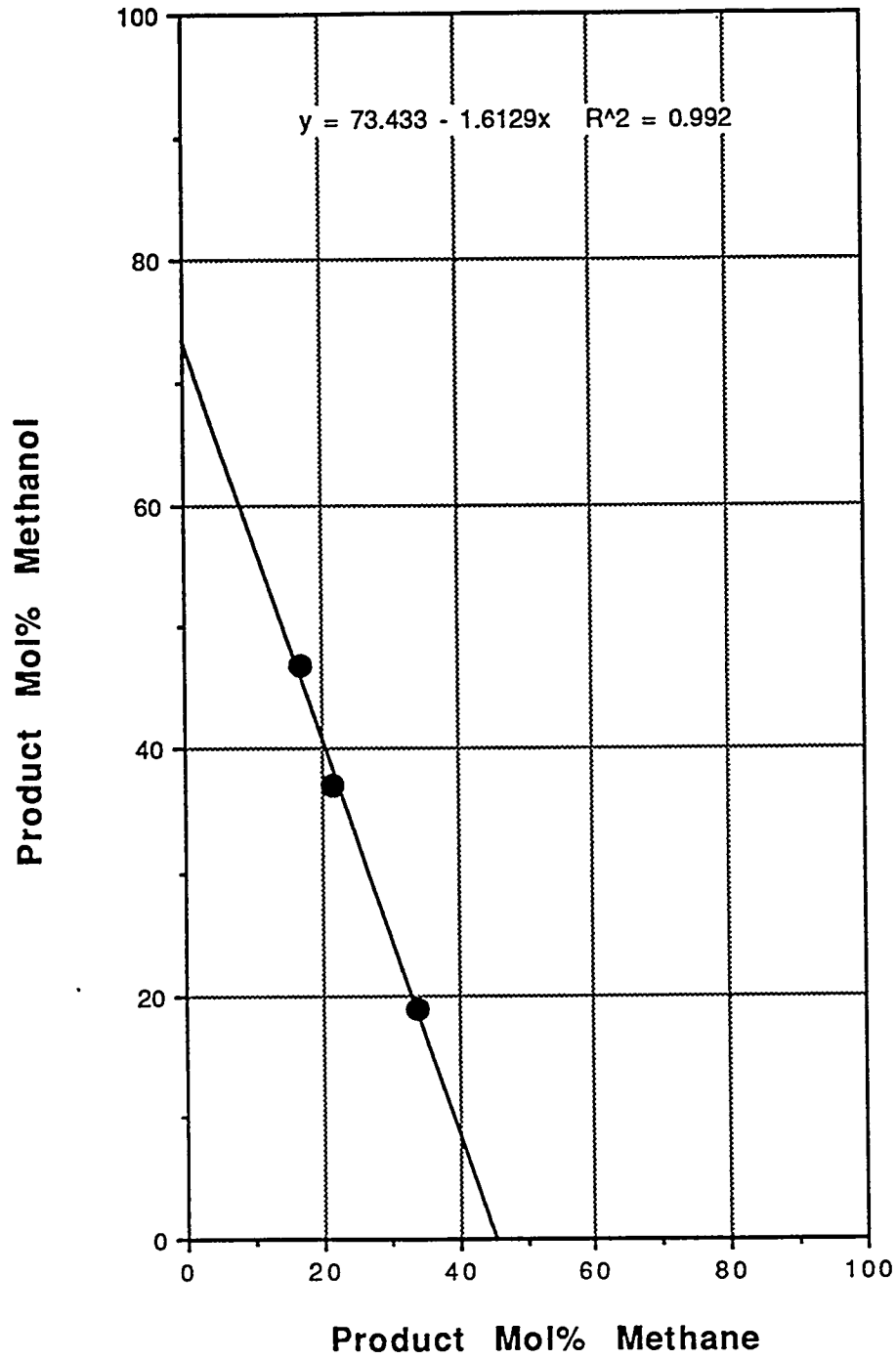   Catalyst 10-DAN-54. See Table 4.8-5 for Conditions.

Figure 4.8-9. Plot of Selectivity to Alcohols vs. Conversion with Changing Temperature, for Catalyst 10-DAN-54. See Table 4.8-7 for Conditions.
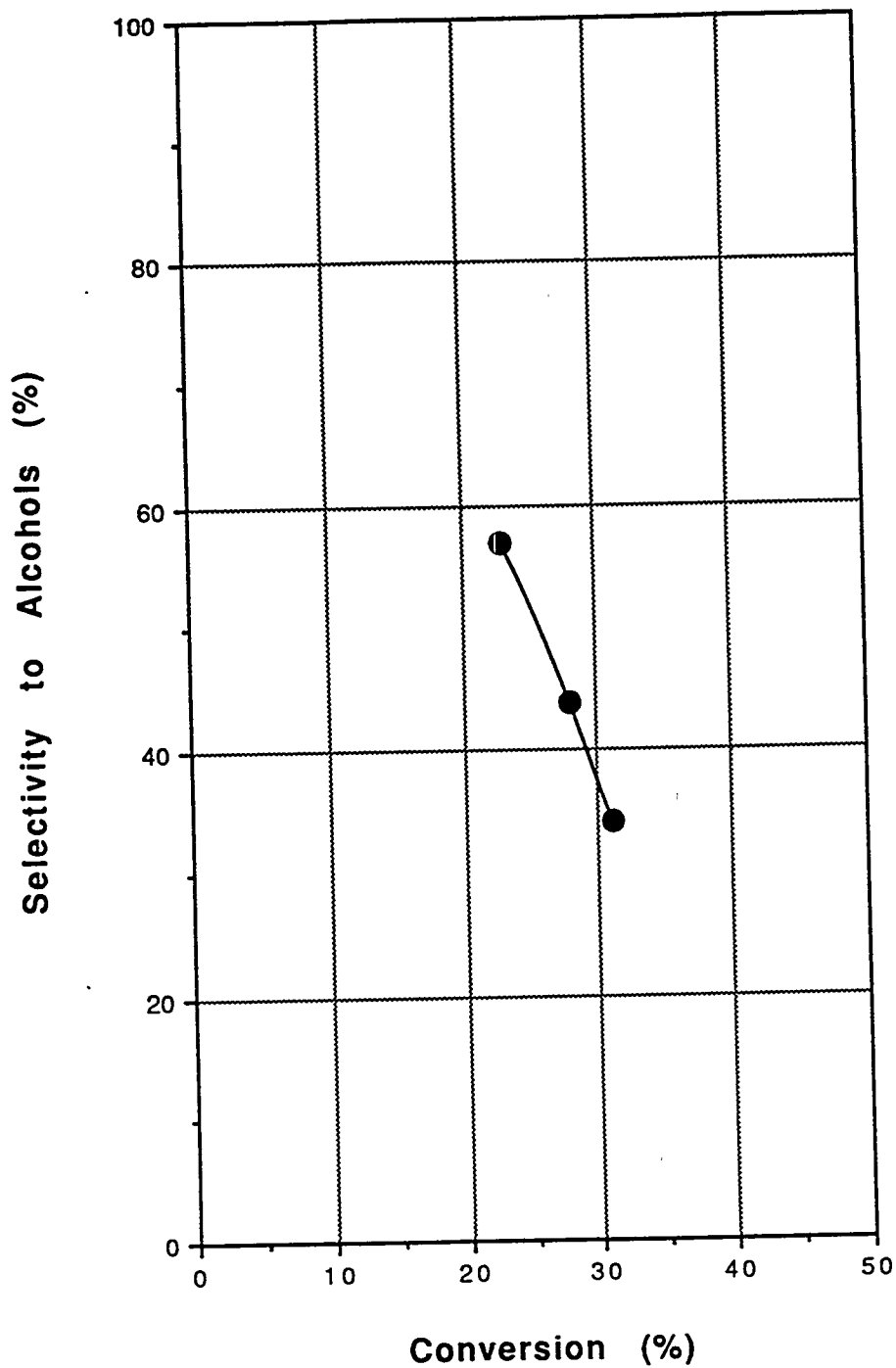

78

Figure 4.8-10.   Plot of Product Composition vs. Conversion with Changing Temperature, for Catalyst 10-DAN-54. See Table 4.8-7 for Conditions.
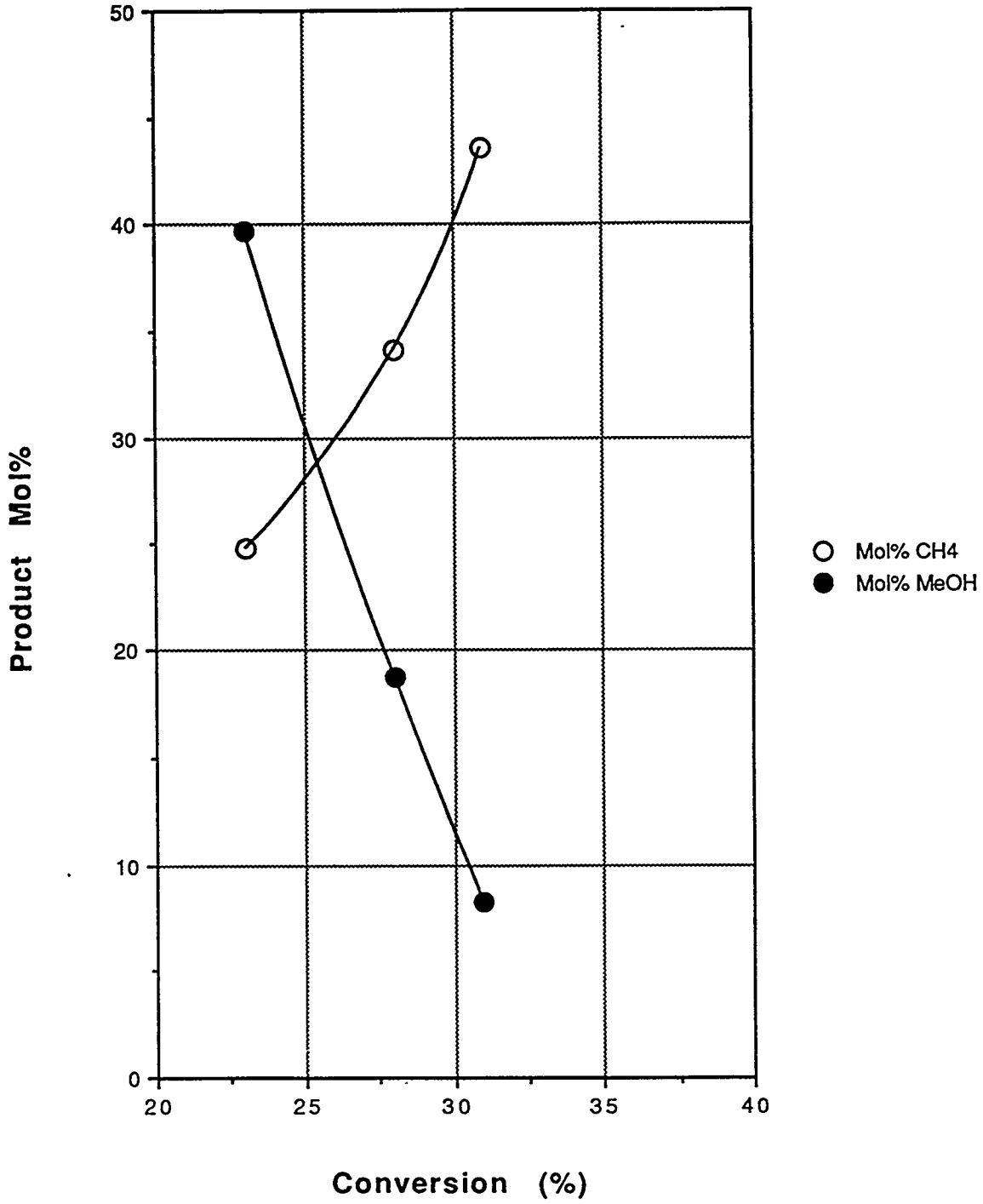
Figure 4.8-11.   Plot of Methanol vs. Methane Yields with Changing Temperature, for
                  Catalyst 10-DAN-54. See Table 4.8-7 for Conditions.

y = 79.466 - 1.6735x   R^2 = 0.963

(Axes: X-axis — Product Mol% Methane; Y-axis — Product Mol% Methanol)
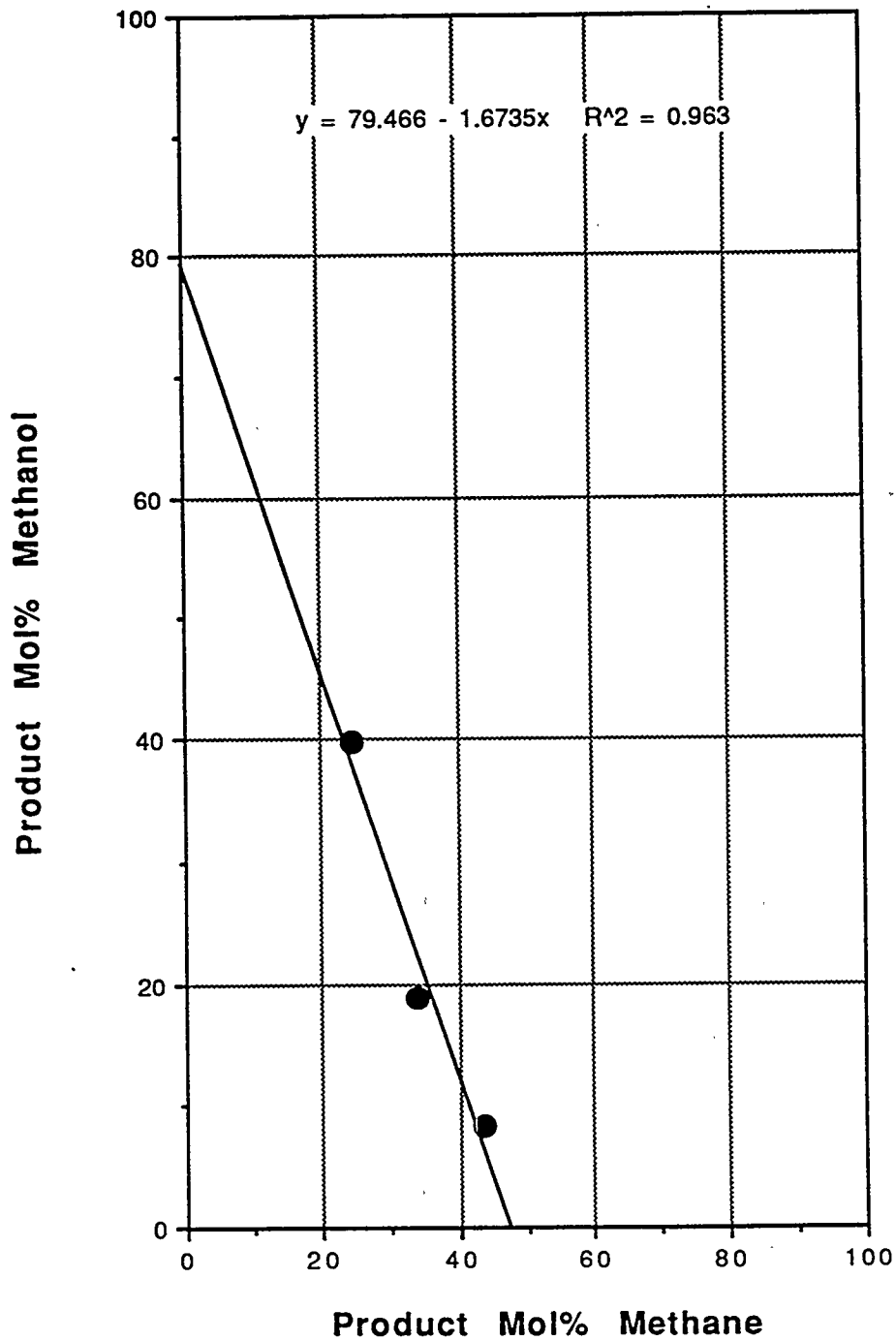
Table 4.8-5. Effect of Changing Space Velocity on Performance of Catalyst 10-DAN-54.

	GHSV = 12000	GHSV = 6000	GHSV = 3000
Total alcohol rate (g/kg-hr)	200	144	78
Total alcohol selectivity (%)	68	63	44
Isobutanol rate (g/kg-hr)	94.3	89	48
MeOH/i-BuOH mole ratio	3.2	2.3	1.7
Total hydrocarbon rate (g/kg-hr)	60	57	69
% Conversion	17	19	28

Conditions: 1000 psi, 400°C, $H_2/CO = 1.0$

Table 4.8-6. Effect of Conversion on Product Composition for Catalyst 10-DAN-54, with Changing Space Velocity. See Table 4.8-5 for Conditions.

	17% Conversion	19% Conversion	28% Conversion
Mol% CH_4	17.03	21.71	34.12
Mol% C_2H_6	9.36	11.24	14.8
Mol% C_3H_8	3.67	4.86	9.21
Mol% C_4H_{10}	3.04	3.45	4.73
Mol% MeOH	47	36.99	18.79
Mol% EtOH	0	0.32	0.72
Mol% i-PrOH	0	0	1.67
Mol% n-PrOH	2.29	2.24	2.34
Mol% Total PrOH	2.29	2.24	4.01
Mol% secBuOH	2.36	2.26	2.26
Mol% i-BuOH	14.72	15.89	11.08
Mol% n-BuOH	0	0	0
Mol% Total BuOH	17.08	18.15	13.33

Table 4.8-7. Effect of Changing Temperature on Performance of Catalyst 10-DAN-54.

	T = 380°C	T = 400°C	T = 420°C
Total alcohol rate (g/kg-hr)	92	78	81
Total alcohol selectivity (%)	57	44	34
Isobutanol rate (g/kg-hr)	45	48	54
MeOH/i-BuOH mole ratio	3.6	1.7	1
Total hydrocarbon rate (g/kg-hr)	43	69	114
% Conversion	23	28	31

Conditions: 1000 psi, GHSV = 3000, $H_2/CO = 1.0$

Table 4.8-8.   Effect of Conversion on Product Composition for Catalyst 10-DAN-54, with Changing Temperature. See Table 4.8-7 for Conditions.

	23% Conversion	28% Conversion	31% Conversion
Mol% CH_4	24.8	34.12	43.61
Mol% C_2H_6	10.52	14.8	16.35
Mol% C_3H_8	5.67	9.21	10.99
Mol% C_4H_{10}	3.04	3.45	4.73
Mol% MeOH	39.77	18.79	8.26
Mol% EtOH	0.43	0.72	0.79
Mol% i-PrOH	1.11	1.67	1.32
Mol% n-PrOH	2.06	2.34	2.26
Mol% Total PrOH	3.17	4.01	3.58
Mol% secBuOH	1.44	2.26	2.39
Mol% i-BuOH	11.04	11.08	8.23
Mol% n-BuOH	0	0	0
Mol% Total BuOH	12.47	13.34	10.62

4.8.3 Tests with 10-DAN-55

Using copper-lined reactor tubes, we were able to test catalysts at a 1:2 syngas ratio at 400°C without catalysis being dominated by the tube walls. We conducted some scoping studies with 10-DAN-55, a K/Pd promoted Zn/Cr spinel oxide catalyst with promise for higher alcohol synthesis. The intent of these tests was to see what effect higher pressures and higher temperatures had on catalyst performance at a syngas ratio of 1:2 and a GHSV of 6000. Pressure was first increased to 1500 psi (from 1000), then temperature was raised to 420°C, then 450°C. The results are shown below.

	400°C 1000 psi	400°C 1500 psi	420°C 1500 psi	450°C 1500 psi
Sel. Total Alcohols (%)	83	85	79	44
Total Alcohol Rate (g/kg-hr)	47	86	85	90
Isobutanol Rate (g/kg-hr)	26	41	52	53
MeOH/i-BuOH mole ratio	2.2	3.1	1.4	1.4
Hydrocarbon rate (g/kg-hr)	6	10	16	80
Estimated conversion (%)	14	16	15	13

Increasing pressure from 1000 to 1500 psi nearly doubled the rate to total alcohols with no loss in selectivity, but the methanol to isobutanol mole ratio increased from 2.2 to 3.1. These trends were observed for 10-DAN-52 and 10-DAN-54 in our earlier pressure traverse at a 1:1 syngas ratio.

Increasing temperature to 420°C showed an increase in isobutanol rate and in a decrease in the methanol to isobutanol mole ratio with little loss in selectivity. At 420°C and 1500 psi, the catalyst had a selectivity to total alcohols of 79% and produced 52 g/kg-hr of isobutanol with a methanol to isobutanol mole ratio of 1.42.

However, increasing temperature above 420°C resulted in a marked increase in hydrocarbon formation and the production of isobutyraldehyde and olefins (confirmed by GC/MS). Here the copper tube may have been partially dehydrogenating the products.

4.9 Effects of Co-Feeding Products and Intermediates with Syngas

The addition of various products or intermediates to the feed can provide useful information concerning the path of a reaction and also can help in considering possible process alternatives. The following studies were conducted with catalyst 10-DAN-55 (Pd on $ZnCr_2O_4$), and should be representative of results with other members of this catalyst family.

4.9.1 Effect of Methanol Feed

The effect of methanol addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) has been examined. Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio of 1:2. The results are summarized below.

		Methanol Feed		
	no MeOH	MeOH (32 g/kg-hr)	MeOH (160 g/kg-hr)	MeOH (3200 g/kg-hr)
Sel. Total Alcohols (%)	75	78	78	96
Total Alcohol Rate (g/kg-hr)	79	83	89	1246
Methanol rate (g/kg-hr)	39	40	43	1183
Isobutanol Rate (g/kg-hr)	36	39	42	62
MeOH/i-BuOH mole ratio	4.3	4.1	4.1	32.3
Hydrocarbon rate (g/kg-hr)	16	14	15	23
Estimated conversion (%)	13	11	11	-

Methanol addition had no significant effect on catalyst performance. At the temperature of operation (400°C), the methanol synthesis equilibrium lies heavily in favor of the reactants (CO and H_2). The methanol feed simply reverts to CO and H_2 over the catalyst rather than continuing on to higher alcohols.

Thus, for this catalyst system, methanol feed/recycle will have no obvious advantages for boosting HAS for this catalyst system. The methanol to ethanol step is generally accepted as being rate determining in HAS, so the effect of ethanol addition was examined next.

4.9.2 Effect of Ethanol Feed

The effect of ethanol addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-58). Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio = 1:2. (Synthesis gas ratio refers to the mole ratio of H_2 to CO.) The results are summarized below:

Ref	no EtOH PR 220	Ethanol Feed		
		29 g/kg-hr PR 265	70 g/kg-hr PR 290	127 g/kg-hr PR 321
Time on Stream, hrs	72	118	142	161
Sel. Total Alcohols (%)	84	77	72	68
Total Alcohol Rate (g/kg-hr)	115	115	135	147
Methanol Rate (g/kg-hr)	48	41	42	38
Ethanol Rate (g/kg-hr)	0	0	0	6
n-Propanol rate (g/kg-hr)	0	-	19	28
Isopropanol rat (g/kg-hr)e	0	2	5	8
Isobutanol Rate (g/kg-hr)	57	60	69	68
MeOH/i-BuOH mole ratio	3.3	2.7	2.4	2.2
Hydrocarbon rate (g/kg-hr)	14	22	34	45

The isobutanol rate increased by a modest 19% over the range studied. Significant quantities of n-propanol and isopropanol were observed as more ethanol is added. The methanol/i-butanol ratio fell from 3.3 to 2.2. Feeding a large excess of ethanol (~500 g/kg-hr) resulted in a doubling in the isobutanol rate, but with concurrent formation of large amounts of ethane.

4.9.3   Effect of n-Propanol Feed

The effect of n-propanol addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-62). Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas ratio = 1:2. The results are summarized below:

Ref	no n-PrOH PR 499	n-Propanol Feed		
		25 g/kg-hr PR 517	110 g/kg-hr PR 541	236 g/kg-hr PR 583
Time on Stream, hrs	570	588	612	654
Sel. Total Alcohols (%)	67	70	72	72
Total Alcohol Rate (g/kg-hr)	97	131	143	192
Methanol Rate (g/kg-hr)	54	50	44	44
Ethanol Rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	3	6	3	9
Isopropanol rate (g/kg-hr)	0	0	0	1
Isobutanol Rate (g/kg-hr)	38	75	93	138
MeOH/i-BuOH mole ratio	5.8	2.7	1.9	1.3
Hydrocarbon rate (g/kg-hr)	27	35	37	52

Addition of small amounts of n-propanol to the syngas feed appeared to qualitatively improve the performance; the isobutanol rate doubled on the first incremental addition (isobutanol rate rises from 38 g/kg-hr to 75 g/kg-hr) and the methanol/i-butanol ratio fell from 5.8 to 2.7.

Further addition of up to 236 g/kg-hr of isopropanol resulted in an additional increase in the isobutanol rate to 138 g/kg-hr (MeOH/i-BuOH ratio = 1.3). The hydrocarbon rate also increased and propane was the major hydrocarbon product. The overall rate was increased by a factor of 4 over the range studied. n-Propanol addition was more effective than ethanol addition in boosting the isobutanol rate.

The isopropanol rate was not significantly affected by the addition of n-propanol. The methanol rate fell with n-propanol addition and no ethanol was seen, suggesting that there is no back reaction to lighter alcohols from n-propanol.

4.9.4   Effect of Isopropanol Feed

The effect of i-propanol addition on the performance of 10-DAN-55 (Pd on $ZnCr_2O_4$) was examined (16-DMM-61). Test conditions were 1000 psi 400°C, GHSV=12000 and syngas ratio = 1:2. The results are summarized below:

		Isopropanol Feed		
	no i-PrOH	29 g/kg-hr	106 g/kg-hr	225 g/kg-hr
Ref	PR 398	PR 418	PR 439	PR 487
Time on Stream, hrs	403	423	444	492
Sel. Total Alcohols (%)	72	67	61	58
Total Alcohol Rate (g/kg-hr)	107	119	120	146
Methanol Rate (g/kg-hr)	54	51	43	39
Ethanol Rate (g/kg-hr)	0	0	0	0
n-Propanol Rate (g/kg-hr)	5	7	11	16
Isopropanol Rate (g/kg-hr)	0	0	4	17
Isobutanol Rate (g/kg-hr)	48	61	61	75
MeOH/i-BuOH mole ratio	4.5	3.3	2.8	2.1
Hydrocarbon rate (g/kg-hr)	25	36	49	69

Addition of small amounts of isopropanol to the syngas feed appeared to qualitatively improve the performance; the isobutanol rate increased by 27% on the first incremental addition (isobutanol rate rose from 48 g/kg-hr to 61 g/kg-hr) and the methanol/i-butanol ratio fell from 4.5 to 3.3.

Further addition of up to 225 g/kg-hr of isopropanol resulted in isopropanol breakthrough and an additional increase in the isobutanol rate to 75 g/kg-hr (MeOH/i-BuOH ratio = 2.1). The hydrocarbon rate also increased and propane was the major hydrocarbon product.