HETEROGENEOUS CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS

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OBJECTIVE This project is focused on the discovery and evaluation of novel heterogeneous catalyst for the production of oxygenated fuel enhancers from synthesis gas. Catalysts have been studied and optimized for the production of methanol and isobutanol mixtures which may be used for the downstream synthesis of MTBE or related oxygenates.

ACCOMPLISHMENTS We have studied higher alcohols synthesis (HAS) from syngas; the alcohols that are produced in this process may be used for the downstream synthesis of MTBE or related oxygenates. This work has resulted in the discovery of a catalyst system that is highly selective for isobutanol compared with the prior art **[1]**. The catalysts operate at high temperature (400°C), and consist of a spinel oxide support (general formula AB_2O_4, where $A = M^{2+}$ and $B = M^{3+}$), promoted with various other elements. These catalysts operate by what is believed to be an aldol condensation mechanism, giving a product mix of mainly methanol and isobutanol. In this study we report the effect of product feed/recycle (methanol, ethanol. n-propanol, isopropanol, carbon dioxide and water) on the performance of 10-DAN-55 (spinel oxide based catalyst) at 400°C, 1000 psi, GHSV = 12,000 and syngas (H_2/CO) ratio = 1:2 (alcohol addition) and 1:1 (carbon dioxide and water addition). We have also examined the effect of operation at high temperatures and pressures on the performance of an improved catalyst formulation.

Effect of Methanol Feed

There is little or no effect of methanol addition on higher alcohol synthesis with 10-DAN-55, a representative spinel oxide catalyst: this is illustrated in figure 1.

The methanol synthesis reaction is essentially at equilibrium over the catalysts used here. The equilibrium:

$$CO + 2H_2 = CH_3OH$$

lies heavily to the left-hand side at 400°C and above, thus the vast majority of the methanol feed reverts back to syngas. Methanol feed/recycle is thus not a viable option for boosting higher alcohol production.

Effect of Ethanol Feed

The effect of ethanol addition on the performance of 10-DAN-55 has been examined. Test conditions were 1000 psi 400°C, GHSV=12000 and syngas (H_2/CO) ratio = 1:2. The results are summarized below and in figure 2:

		Ethanol Feed		
	no EtOH	EtOH 29 g/kg-hr	EtOH 70 g/kg-hr	EtOH 127 g/kg-hr
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 rate (g/kg-hr)	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 increases by a modest 19% over the range studied. Significant quantities of n-propanol and isopropanol are observed as more ethanol is added. The methanol/i-butanol ratio falls from 3.3 to 2.2. Feeding a large excess of ethanol (~500 g/kg-hr) results in a doubling in the isobutanol rate, but with concurrent formation of large amounts of ethane.

Effect of n-Propanol Feed

The effect of n-propanol addition on the performance of 10-DAN-55 has been examined. Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas (H_2/CO) ratio = 1:2. The results are summarized in the following table and in figure 3.

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

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

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

	n-Propanol Feed			
	no n-PrOH	n-PrOH 25 g/kg-hr	n-PrOH 110 g/kg-hr	n-PrOH 236 g/kg-hr
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

Effect of Isopropanol Feed

The effect of n-propanol addition on the performance of 10-DAN-55 has been examined. Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas (H_2/CO) ratio = 1:2. The results are summarized below and in figure 4:

	Isopropanol Feed			
	no i-PrOH	i-PrOH 29 g/kg-hr	i-PrOH 106 g/kg-hr	i-PrOH 225 g/kg-hr
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 appears to qualitatively improves the performance; the isobutanol rate increases by 27% on the first incremental addition (isobutanol rate rises from 48 g/kg-hr to 61 g/kg-hr) and the methanol/i-butanol ratio falls from 4.5 to 3.3.

Further addition of up to 225 g/kg-hr of isopropanol results 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 increases and propane is the major hydrocarbon product.

Interestingly, the n-propanol rate also increases modestly, perhaps suggesting some pathway exists for conversion of isopropanol to n-propanol. The methanol rate falls with isopropanol addition and no ethanol is seen, suggesting that there is no back reaction to lighter alcohols from isopropanol.

Effect of Carbon Dioxide Feed

The effect of carbon dioxide addition on the performance of 10-DAN-55 has been examined. Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas (H_2/CO) ratio = 1:1. The results are summarized below and in figure 5:

	Carbon Dioxide Feed (%)			
	No CO2	3% CO2	6% CO2	No CO2
Sel. Total Alcohols (%)	83	89	89	84
Total Alcohol Rate (g/kg-hr)	192	137	107	165
Methanol Rate (g/kg-hr)	108	102	90	103
Ethanol Rate (g/kg-hr)	1	2	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	18	12	6	12
Isobutanol Rate (g/kg-hr)	64	21	11	51
MeOH/i-BuOH mole ratio	7	19	33	8
Hydrocarbon rate (g/kg-hr)	23	9	6	18

Addition of carbon dioxide to the syngas feed adversely affects the performance of a spinel oxide catalyst; the total alcohol rate falls by 44% and the isobutanol rate by 83% on addition of 6% carbon dioxide. In concert, the methanol rate decreases by a modest 17%, such that the methanol/i-butanol ratio rises from 7 to 33.

It should be remembered that the water gas shift (WGS) equilibrium must be taken into account when viewing these results, as these materials are excellent WGS catalysts. The equilibrium

$$CO + H_2O = CO_2 + H_2$$

lies to the right under the reaction condition employed here (Keq = 8), so the effect of carbon dioxide on catalyst performance cannot be disentangled from that of water: the introduction of carbon dioxide to the system will automatically result in an increase in the water content of the gas mixture.

Effect of Operation at Higher Temperatures and Pressures

We have tested 16-DMM-68, an improved formulation over 10-DAN-55, at elevated temperatures (>400°C) and pressures (>1000 psi). GHSV was held constant at 12000 and the syngas (H_2/CO) ratio was also held constant at 1:1. The results are summarized below:

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1180 psi	T = 440°C P = 1500 psi
Sel. Total Alcohols (%)	84	86	54	64
Total Alcohol Rate (g/kg-hr)	233	407	159	304
Methanol Rate (g/kg-hr)	119	248	35	99
Ethanol Rate (g/kg-hr)	0	7	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	12	21	15	27
Isobutanol Rate (g/kg-hr)	102	130	109	179
MeOH/i-BuOH mole ratio	4.7	7.6	1.3	2.2
Hydrocarbon rate (g/kg-hr)	26	37	94	112
Conversion (%)	14	24	23	28

The data show that the catalyst is most effective for higher alcohol synthesis (HAS) at elevated temperatures and pressures. Note that the *combination* of high temperature and high pressure is required for optimal higher alcohol formation:

	Methanol Synthesis	Hydrocarbon Formation	Higher Alcohol Synthesis
High temperature	- -	+ +	+
High Pressure	+ +	- -	+

CONCLUSIONS:

- Methanol feed/recycle is not a viable option for higher alcohol production.
- Ethanol feed is moderately effective for boosting isobutanol activity: the isobutanol rate increases by a modest 19% over the range studied. A large amount of ethanol is converted to ethane. There is no back reaction to methanol.

The inhibition of higher alcohol synthesis by carbon dioxide has been observed in other HAS catalyst systems [1]. This observation is explained by assuming that water rather than carbon dioxide inhibits HAS by competing for adsorption with the intermediate C_1 species on the catalyst surface, preventing the homologation reactions from proceeding. Methanol formation is thus not as sensitive to the water/carbon dioxide equilibrium and, in addition, the mechanism proposed for methanol synthesis involves carbon dioxide as an intermediate. The extra water produced via the WGS equilibrium may help to drive the alcohol equilibrium back to the left, viz.:

$$n\,CO + 2n\,H_2 = C_nH_{2n+1}OH + (n-1)\,H_2O$$

An advantage of carbon dioxide addition is that the rate of hydrocarbon formation is suppressed in an even greater extent such that the selectivity to total alcohols shows a modest increase from 83% to 89%. The extra water produced via the WGS equilibrium may also help to drive the hydrocarbon equilibrium back to the left, viz.:

$$n\,CO + (2n+1)\,H_2 = C_nH_{2n+2} + n\,H_2O$$

or perhaps water helps to titrate acid sites on the catalysts responsible for hydrocarbon formation. The catalyst recovers slowly after stopping the addition of carbon dioxide - see figure 6. Normally, a change in process parameters and alcohol feeds results in a new steady state within 4-8 hours, but on turning off the carbon dioxide feed, the catalyst is still returning to pre-carbon dioxide feed performance after 48 hrs. This suggests some surface intermediate is being slowly lost, perhaps carbonate.

An initial boost in methanol formation is also seen on removing the carbon dioxide feed and is reflected in a transient increase in the methanol/isobutanol mole ratio - see figure 7. It appears that the carbon dioxide released on decomposition of the surface carbonate layer formed by carbon monoxide addition enhances methanol formation, suggesting that carbon dioxide is an intermediate in methanol synthesis over these catalysts.

Effect of Water Feed

The effect of carbon dioxide addition on the performance of 10-DAN-55 has been examined. Test conditions were 1000 psi, 400°C, GHSV=12000 and syngas (H_2/CO) ratio = 1:1.

Addition of water to the syngas feed adversely affects the performance of a spinel oxide catalyst 10-DAN-55; the total alcohol rate falls by 44% and the isobutanol rate by 86% on addition of up to 490 g/kg-hr of water. In concert, the methanol rate decreases by only 17%, resulting in an increase in the methanol/i-butanol ratio from 8 to 48.

These results are essentially identical to those obtained through carbon dioxide addition. The introduction of water to the system will automatically result in an increase in the carbon dioxide content of the gas mixture through the WGS equilibrium, which, under the reaction conditions employed here, lies heavily on the side of carbon dioxide.

ESCA analysis of the spent catalyst, after water addition, indicates the formation of a carbonate layer on the catalyst surface, supporting this hypothesis. The WGS activity is a plus, as it is less expensive to remove carbon dioxide from the recycle stream by extraction than water via distillation.

- n-Propanol feed is more effective than ethanol feed, with the rate increasing by a factor of 4, and only a small increase in propane formation up to surface saturation. There is no back reaction to lighter alcohols from n-propanol.

- Isopropanol is as effective as ethanol in boosting the isobutanol rate, but a large amount is hydrogenated to propane. Interestingly, the n-propanol rate also increases modestly: perhaps suggesting some pathway exists for conversion of isopropanol to n-propanol. There is no back reaction to lighter alcohols from isopropanol.

- Addition of carbon dioxide to the syngas feed adversely affects catalyst performance; the total alcohol rate falls by 44% and the isobutanol rate by 83% on addition of 6% carbon dioxide. An advantage of carbon dioxide addition is that the rate of hydrocarbon formation is suppressed so that the selectivity to total alcohols shows a modest increase from 83% to 89%.

- The catalyst recovers slowly from the carbon dioxide addition, suggesting some surface species is formed in the presence of carbon dioxide, probably carbonate. Carbon dioxide released on decomposition of the surface carbonate layer enhances methanol formation, suggesting that carbon dioxide is an intermediate in methanol synthesis over these catalysts.

- Addition of water to the syngas feed adversely affects catalyst performance in a manner that mirrors the effect of carbon dioxide addition. These results are essentially identical to those obtained through carbon dioxide addition. This can be explained by the production of carbon dioxide via the water-gas-shift equilibrium.

- ESCA analysis of the spent catalyst, after water addition, indicates the formation of a carbonate layer on the catalyst surface, supporting this hypothesis. The WGS activity is a plus, as it is less expensive to remove carbon dioxide from the recycle stream by extraction than water via distillation.

- Operation at higher temperatures *and* higher pressures is optimal for higher alcohol synthesis, with isobutanol rates as high as 179 g/kg-hr at 440°C and 1500 psi.

FUTURE PLANS

- Catalyst formulation optimization through changes in both support and promoters.

- Surface analysis of catalysts to uncover structure/property relationships

REFERENCES

1. P. Forzatti, E. Tronconi and I. Pasquon, Catal.Rev.-Sci.Eng, 33(1&2), 109-168 (1991)

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FIGURE 1

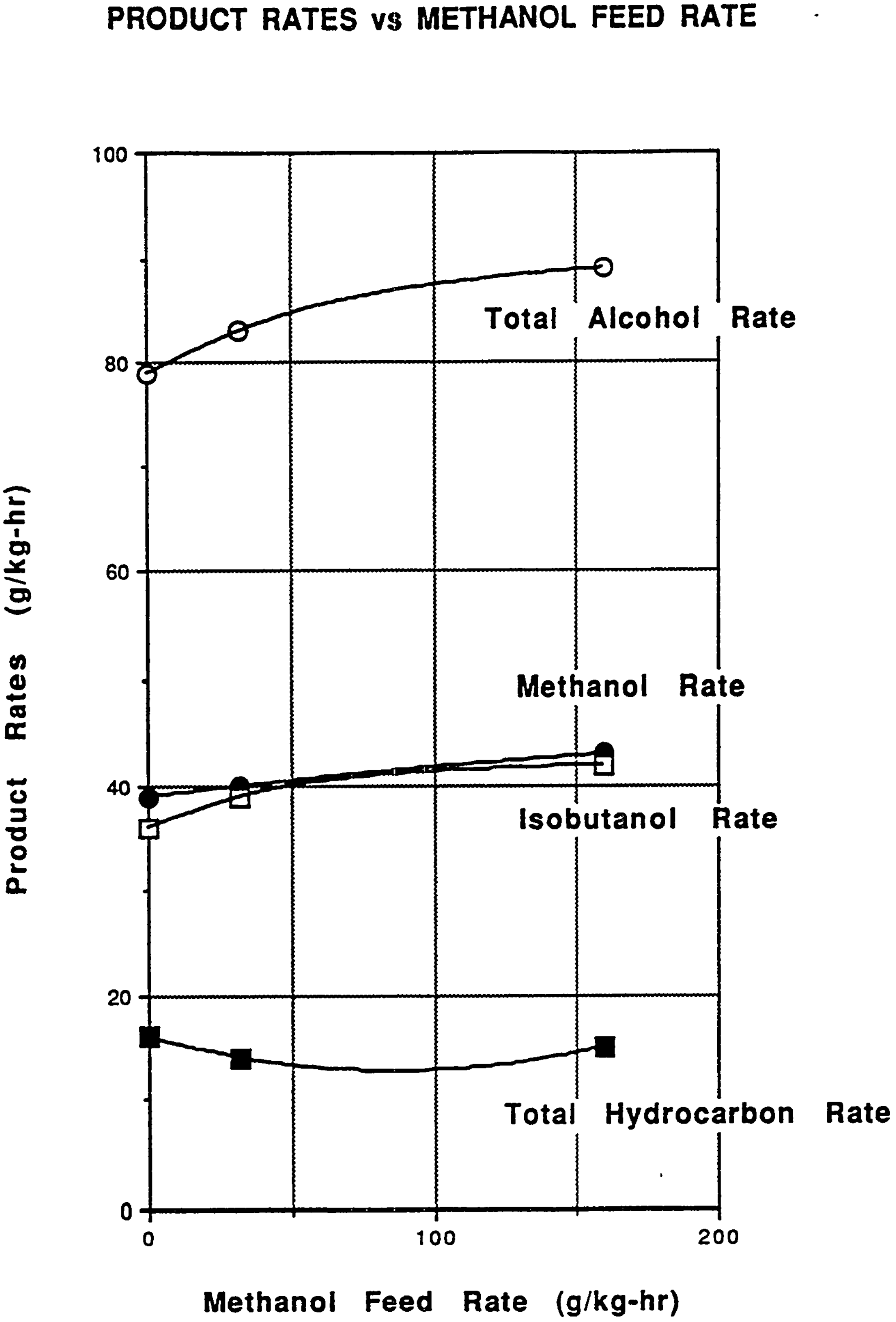
PRODUCT RATES vs METHANOL FEED RATE
Total Alcohol Rate
Methanol Rate
Isobutanol Rate
Total Hydrocarbon Rate
Product Rates (g/kg-hr)
Methanol Feed Rate (g/kg-hr)
0
20
40
60
80
100
0
100
200

FIGURE 2

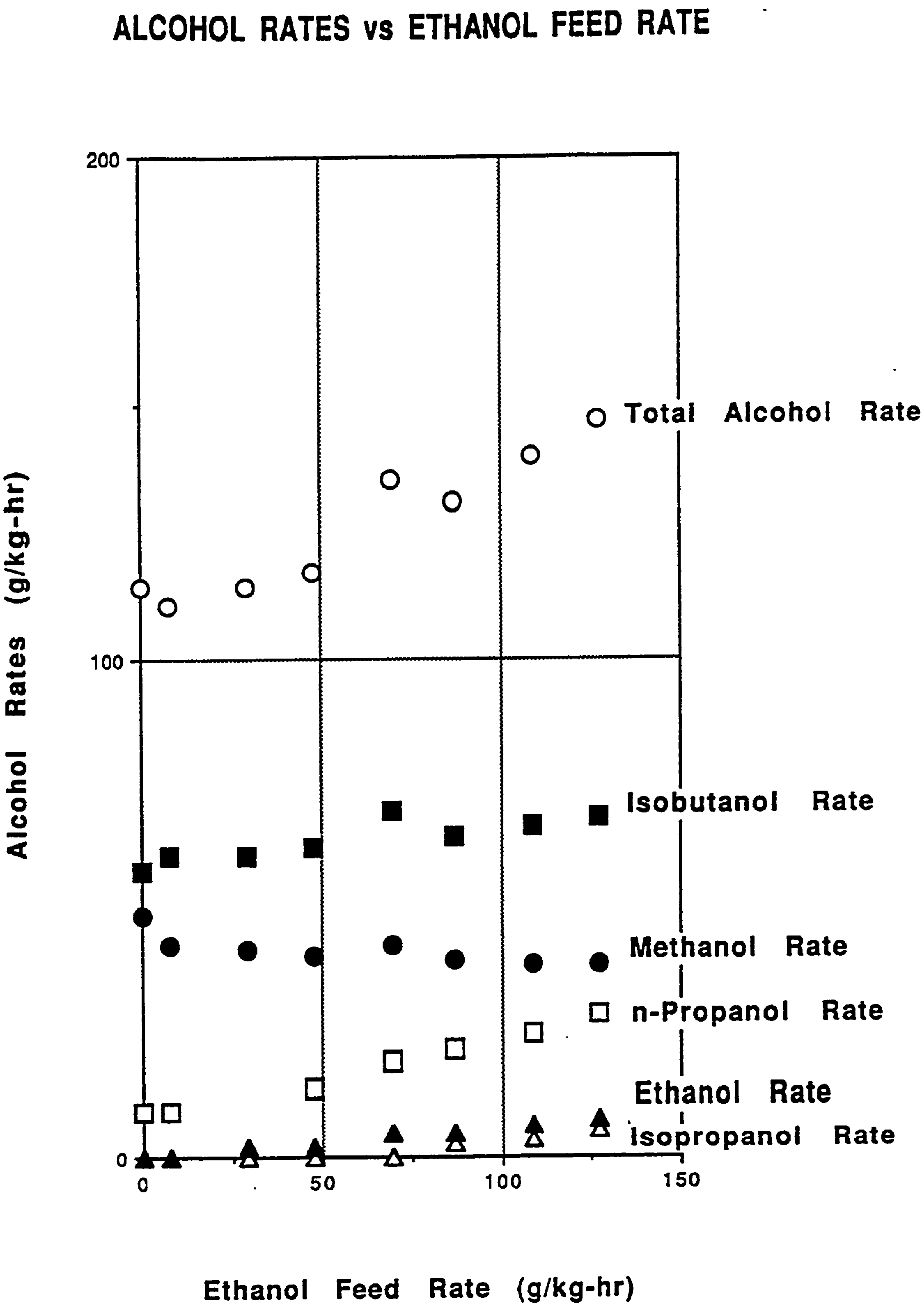
ALCOHOL RATES vs ETHANOL FEED RATE
200
100
0
0
50
100
150
Alcohol Rates (g/kg-hr)
Ethanol Feed Rate (g/kg-hr)
○ Total Alcohol Rate
■ Isobutanol Rate
● Methanol Rate
□ n-Propanol Rate
▲ Ethanol Rate
△ Isopropanol Rate

FIGURE 3

ALCOHOL RATES vs n-PROPANAL FEED RATE

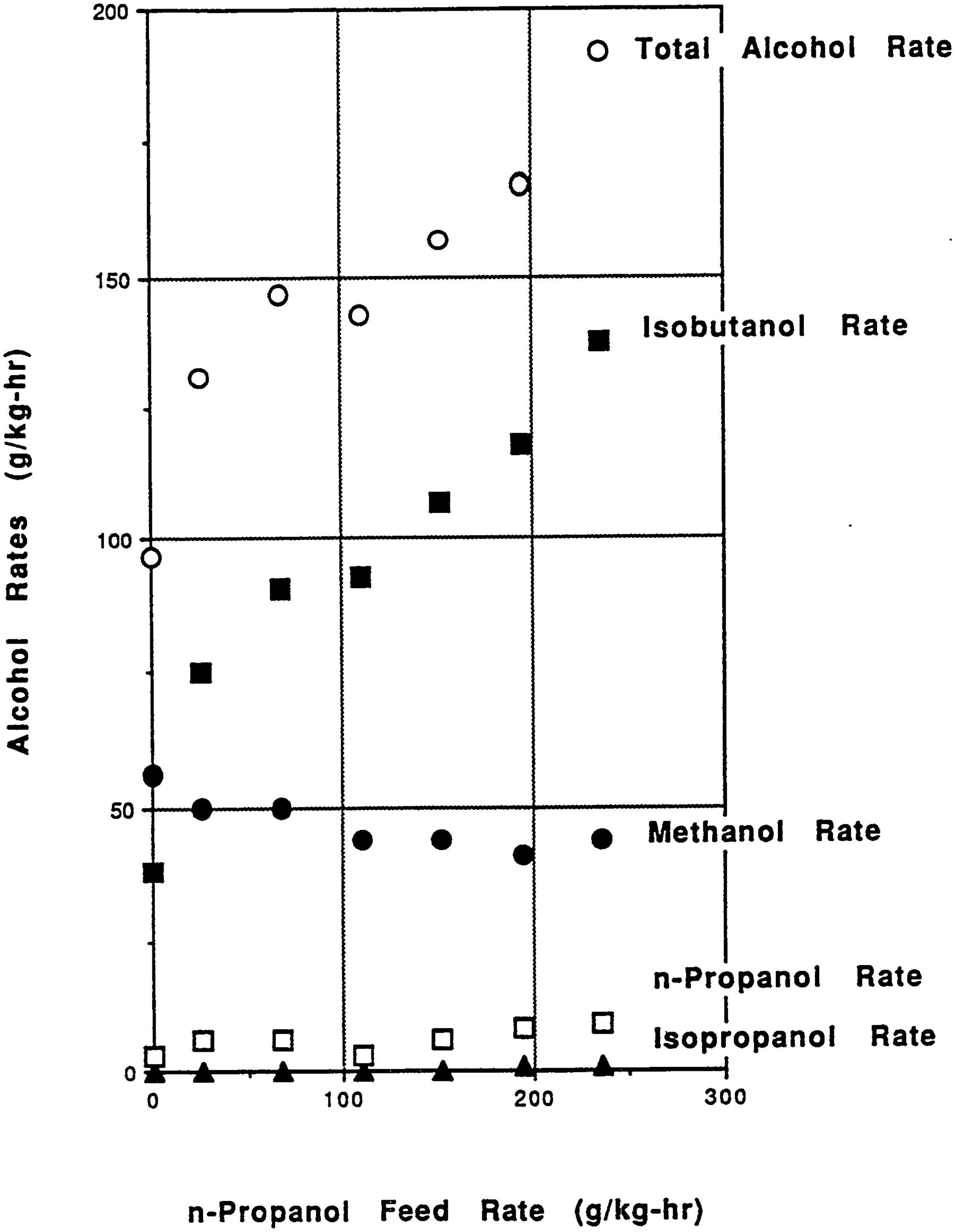

FIGURE 4

ALCOHOL RATES vs ISOPROPANOL FEED RATE

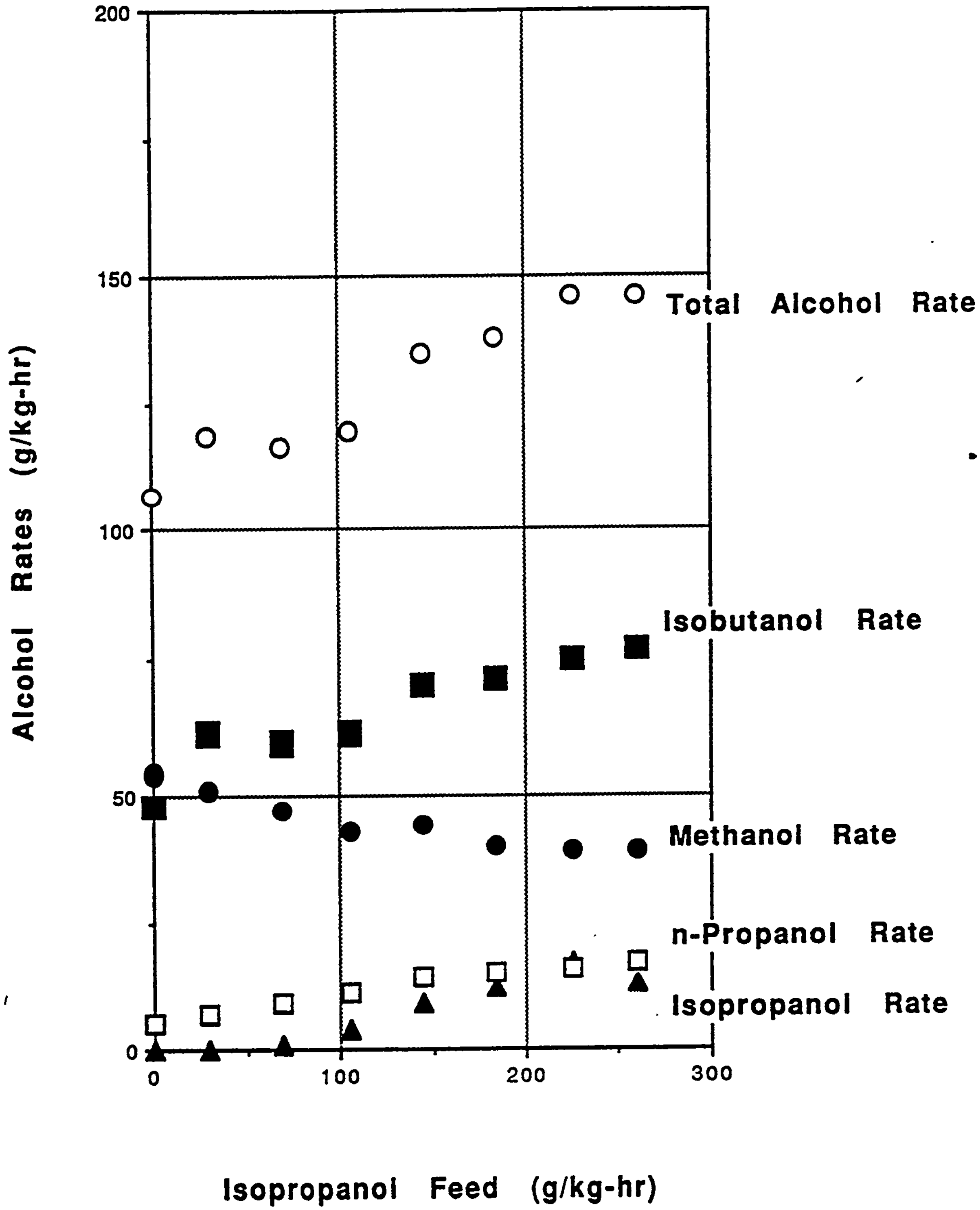

FIGURE 5

PLOT OF ALCOHOL RATES vs ADDITION OF CARBON DIOXIDE TO FEED

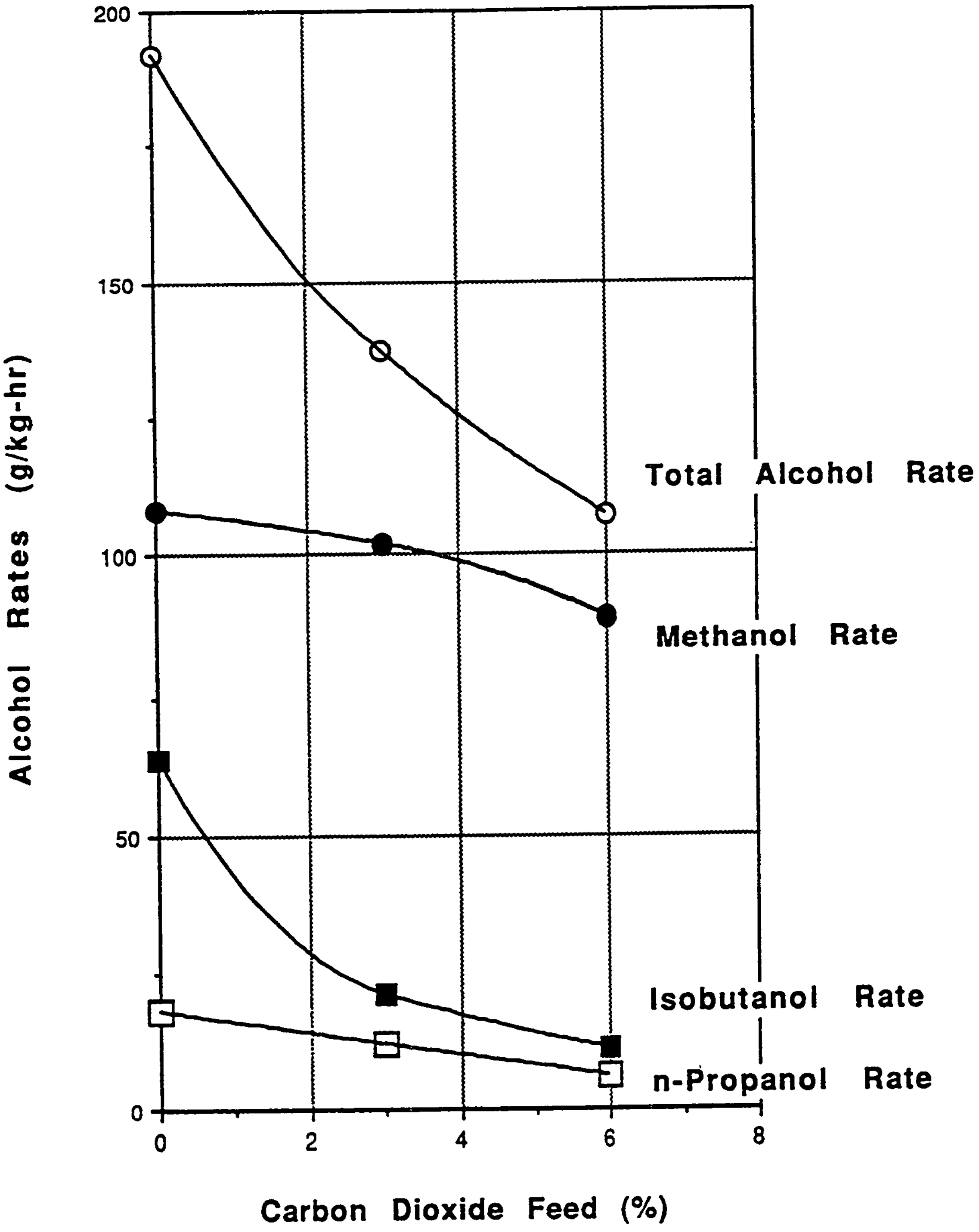

FIGURE 6

PLOT OF ALCOHOL RATES vs TIME AFTER REMOVAL OF 6% CARBON DIOXIDE FROM FEED

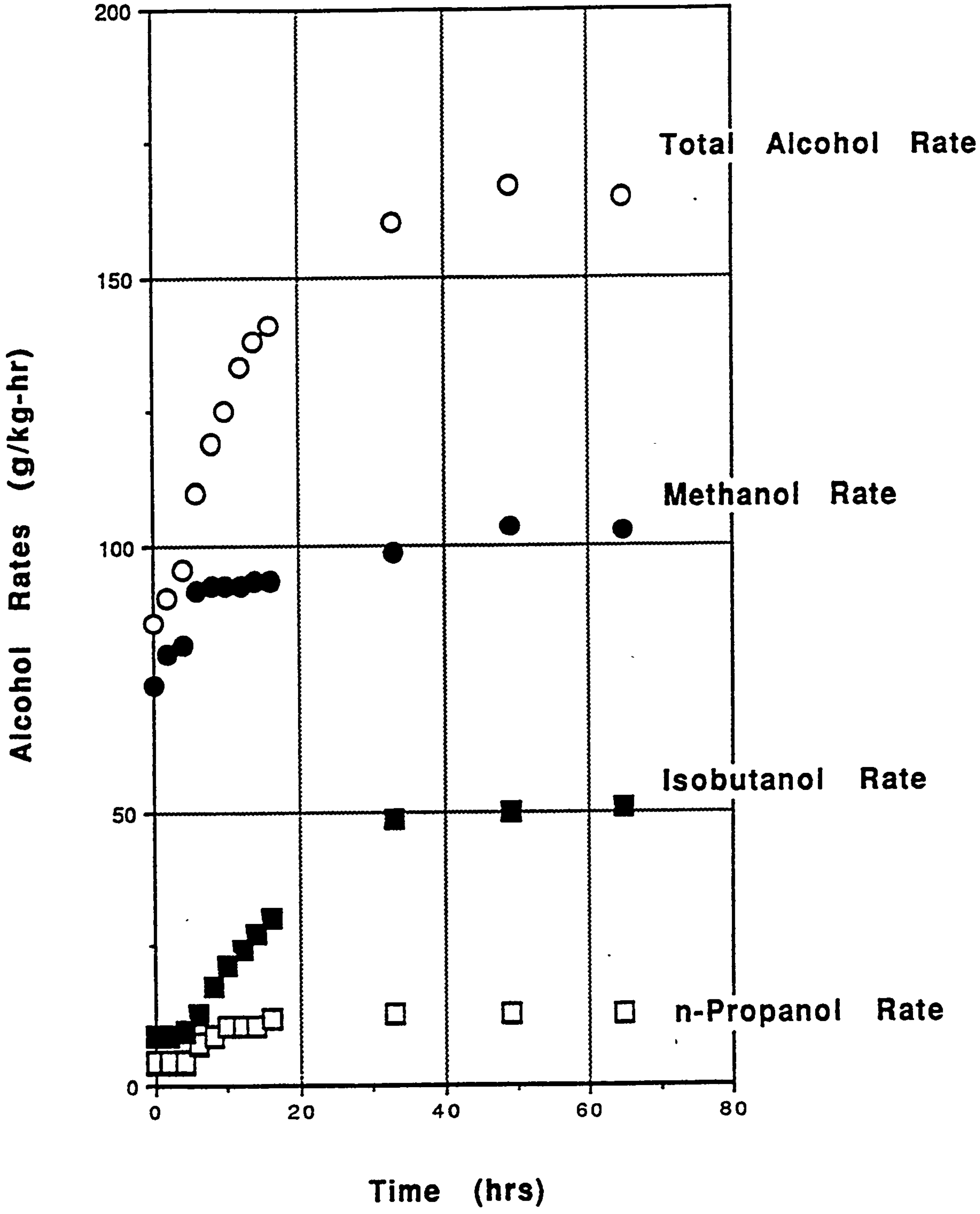

FIGURE 7

PLOT OF MeOH/i-BuOH MOLE RATIO vs TIME AFTER REMOVAL OF 6% CARBON DIOXIDE FROM THE FEED