

apparent that at this higher conversion level, the oxygenates are present at only about one-hundredth the fraction that they are for lower conversion levels with a similar catalyst. It therefore appears that with the silica containing catalyst, alcohol reincorporation and/or alcohol conversion (such as dehydration) occurs at high conversions to reduce the total oxygenates to a very low level. This observation with silica for the high conversion data does not appear to apply for a similar catalyst where alumina has been incorporated in place of silica. Even though the oxygenates in figure 10 are present in low concentrations, the distribution of the oxygenate compounds are essentially the same as shown in figures 8 and 9 for the lower CO conversion and higher oxygenates concentration.

The impact of the potassium content upon the carbon number distribution of the oxygenates present in the aqueous phase is illustrated in figure 11. While the carbon number (N) is plotted versus the $\ln(\text{wt.}\%/N)$, this is not intended to be a typical Anderson-Schulz-Flory plot since only the oxygenates present in the aqueous phase are included in the figure. The data make it clear that, as the potassium content of the catalyst is increased, the amount of methanol declines while there is a corresponding increase in the C_2 and C_3 fractions; furthermore, the increase in the C_3 fraction is greater than for the C_2 fraction.

The carbon number distribution of the oxygenate products do not depend to a measurable extent upon the content of either silica or alumina over the ranges (4 to 8 atomic % of the iron) examined in this study; this is illustrated figure 12 for the data for the alumina containing catalyst.

The water soluble C_1 - C_4 -oxygenates are formed in significant quantities during the Fischer-Tropsch synthesis. Thus, this water soluble oxygenate fraction represents

about 1.5-2 wt.% of the hydrocarbon/oxygenate products; the alumina containing catalyst produces about 0.5 wt.% more oxygenates than the silica containing catalyst with a similar potassium content. In general, as the catalyst ages, the amount of oxygenates produced per unit of syngas converted gradually increases. The oxygenates production in general mirrors that of the CO conversion; that is, the higher the conversion the lower the oxygenates production.

The distribution of the compounds within the oxygenates is primarily determined by the amount of potassium in the catalyst but is essentially independent of the alumina or silica content. Thus, for a given alkali loading, the carbon number distribution of the catalyst is independent of the amount of either alumina or silica in the catalyst in the 4 to 8 wt.% loading.

As the alkali loading of the catalyst is increased the normal alcohol fractions decrease. The oxygenate that increases most dramatically with an increase in potassium loading is the aldehyde class of compounds. The increase in ethanal is much less, relative to ethanol, than the increase in propanal relative to 1-propanol. At least some fraction of the ethanal is converted to products consistent with aldol condensation reactions to produce higher carbon number compounds that are not soluble in the aqueous phase. The ethanol-ethanal is essentially in equilibrium during synthesis using a C-73 catalyst manufactured by United Catalyst, Inc. (L.-M. Tau, H. A. Dabbagh and B. H. Dabbagh, *Energy & Fuels*, 5 (1991) 174); thus, the same ethanol/ethanal ratio was obtained whether ethanol or ethanal was added to the syngas feed. This was not the case in the present study. For the catalyst containing 3 to 5 wt.% potassium, the propanal/1-propanol ratio was about 4 whereas for the catalyst with 0.5 wt.% potassium this ratio was 0.1 or less. This observation implies

that for the high loadings of potassium, the inability of the catalyst to establish this equilibrium is due to the enhancement of the desorption of the aldehyde and/or CO inhibition retards readsorption of the aldehyde. Furthermore, at least for the high potassium loadings, the formation of the high concentration of aldehyde implies that the aldehyde, and not the primary normal alcohol, is a primary product of the Fischer-Tropsch synthesis. It seems likely that the direct formation of the aldehyde occurs by a reaction pathway that competes with the Fischer-Tropsch synthesis and which is similar to or is a hydrocarbonylation reaction.

In summary, it appears that a Fischer-Tropsch plant that has the objective of developing a chemicals component based upon oxygenates would want to use alumina as the structural promoter. Furthermore, the operator could have some control over the amount and distribution of the oxygenate products by controlling the level of potassium that is present in the catalyst.

A.3. Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity for both High- and Low-Alpha Catalysts

Low-alpha catalyst work has been successfully completed. Work is in progress on supported catalysts to increase the hydrocarbon production by increasing the amount of alkali.

A.4. Complete the Optimization of Two Best Low-Alpha, Iron-Based Catalysts Developed During the Previous Contract

Completed.

A.5. Schedule of Activities for Next Quarter

- Begin optimization of the robust alumina supported catalyst to increase conversion, selectivity and production.

B.0. - Task 2.0. Definition of Preferred Pretreatment for Both Low- and High-Alpha Catalysts

The goals of this task are to define the preferred treatment, to define the role of Cu and K during the pretreatment on activity and selectivity and to define the chemical and physical changes which occur during the preferred pretreatment. The subtasks address each of these goals.

B.1. Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron Based Fischer-Tropsch Catalysts

This task has been successfully completed for both high and low alpha catalysts.

B.2. Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.

The work on the method of addition has been completed.

B.3. Physical and Chemical Changes that Occur During Pretreatment and Use

No scheduled or further activity to report.

B.4. Effect of Carbon Deposition

No scheduled or further activity to report.

B.5. Schedule of Activities for Next Quarter

Continue to determine effectiveness of Ba and Zn as promoters.

C.0. - Task 3.0. Catalyst Structure and Characterization

The goal of this task is to provide basic analyses (surface area, XRD) of all catalyst prepared and to provide additional techniques as required (Mössbauer, SEM,

XPS, etc.) to answer specific questions or to provide basic required characterization data for the catalysts.

C.1. Schedule of Activities for Next Quarter

Continue to provide the characterization data as required.

D.0. - Task 4.0. Catalyst Testing

The goals of this task are to operate the eight CSTR reactors, measure catalyst performance, determine the stable phases that exist during synthesis at low and high conversions and to determine the rates of interconversion of iron oxide and carbide.

D.1. Verify the Quality of Data Obtained from the CSTRs.

This task is now successfully completed.

D.2. Measure Catalyst Performance

The run using a high alpha catalyst to evaluate the modification of the catalyst/wax separation has been successfully running for 700 hours. It appears the new modification for catalyst settling and return to reactor is working well; however, it will take approximately an additional month of continuous operation to verify this result.

D.3. Determine Stable Phases that Exist During Synthesis at High and Low CO

Conversion Levels

We have completed runs using an unpromoted Fe and a K promoted Fe catalyst which will provide samples for the analysis of the stable phases.

D.4. Obtain Data on Rates Involved in the Interconversion of Iron Oxide and Carbide

No scheduled or additional activity to report.

D.5. Schedule of Activities for Next Quarter

- Continue the evaluation of the wax/catalyst separation.
- Continue to make additional supported Fe catalysts and test their activity, selectivity and productivity rate.
- Evaluate the data from the high temperature gas chromatograph (up to $\sim C_{100}$) for internal consistency to determine if a catalyst produces a 1 or 2 alpha product distribution.

Figure 1. Conversion of CO₂ and CO during FTS at 270°C, 8 atm, and the flows indicated in the text.

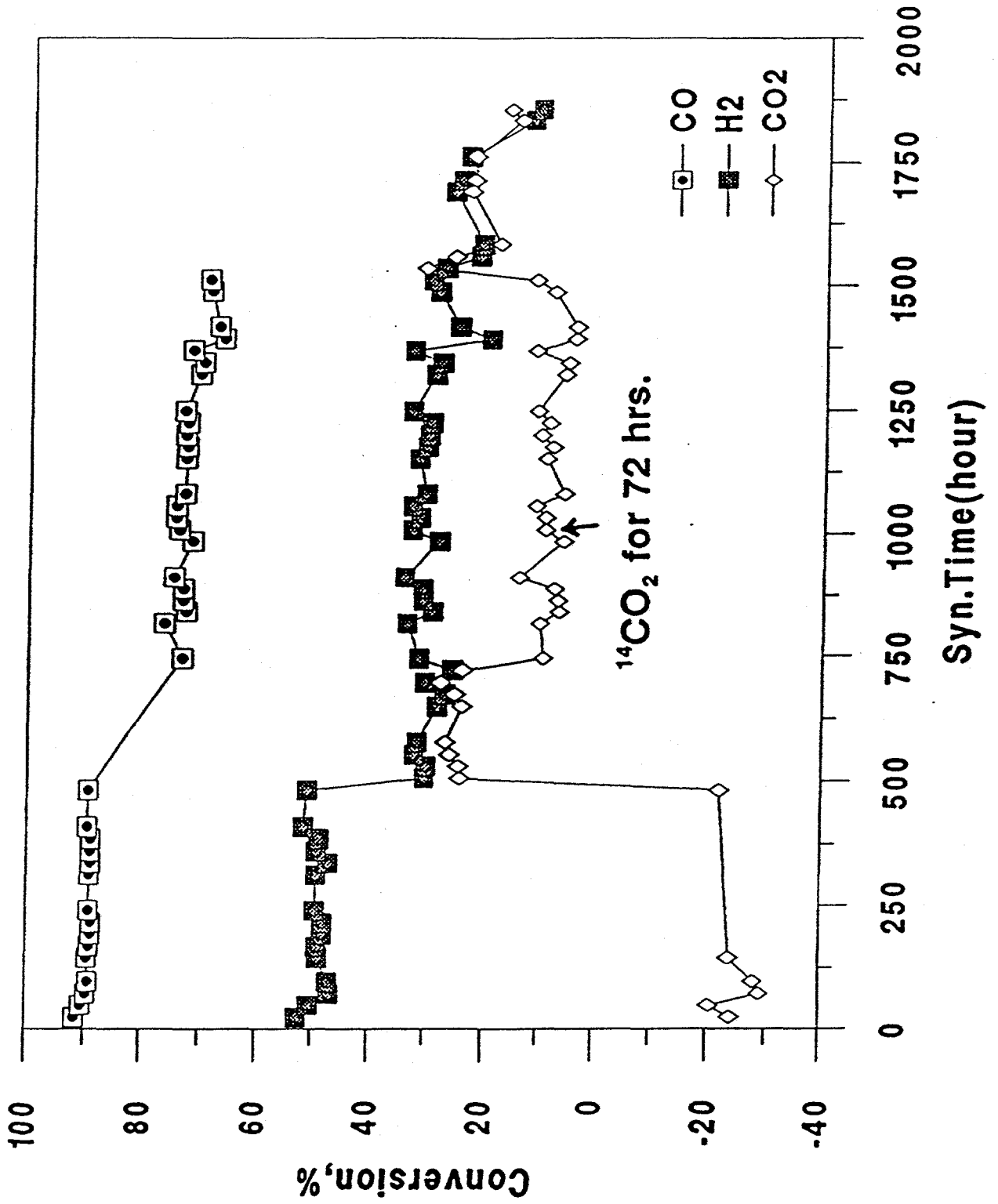


Figure 2. Radioactivity/mole for products generated while adding $^{14}\text{CO}_2$ (see text for conditions).

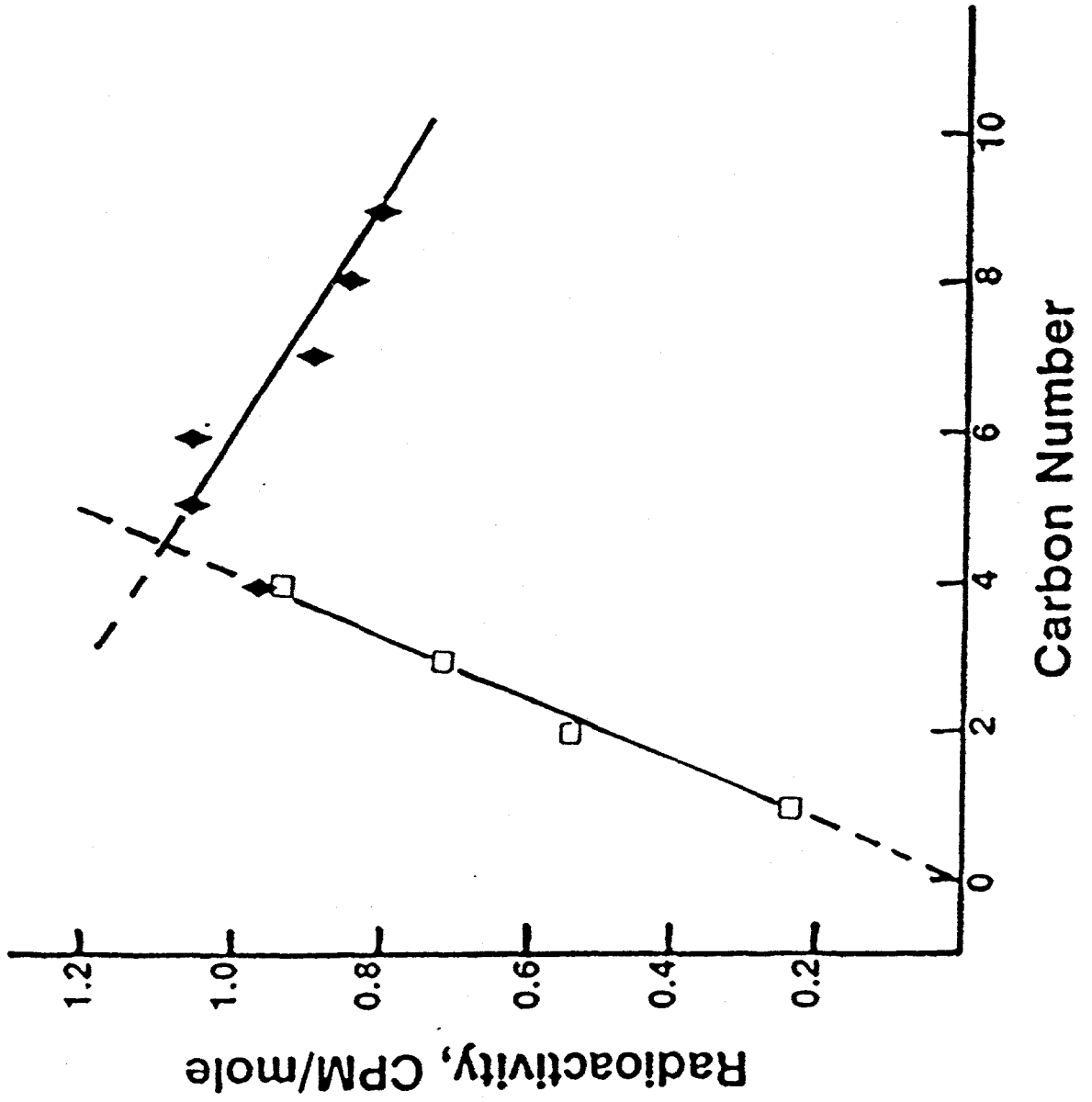


Figure 3. Composite figure showing relative radioactivity for the lower carbon number compounds (●); the measured values for the higher carbon number compounds (●), and the values for the higher carbon number compounds (◆) after correcting for reactor accumulation effects.

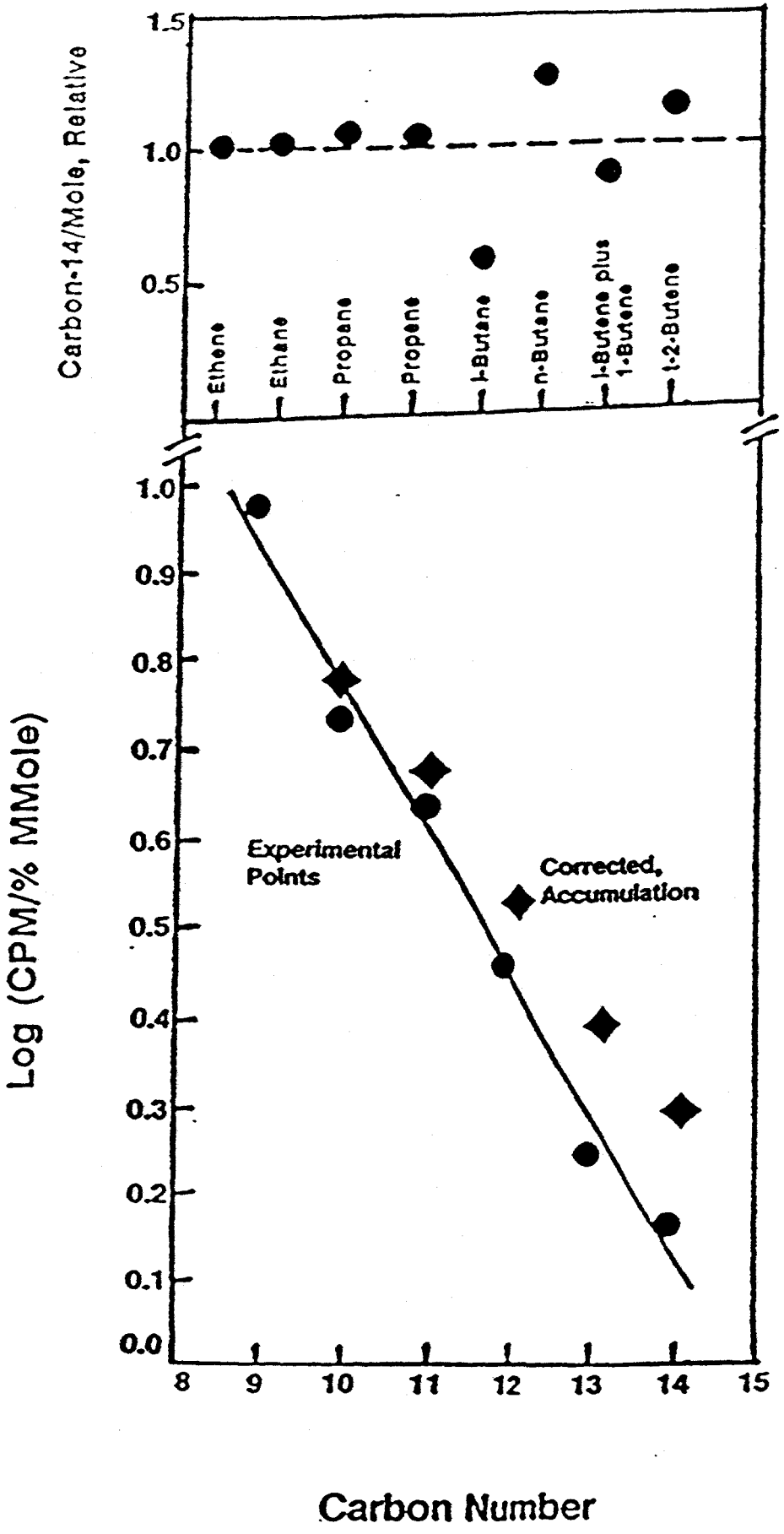


Figure 4. The percentage of oxygenates in the hydrocarbonate plus oxygenate fraction from the conversion of synthesis gas ($H_2/CO = 0.7$; $T = 230$ or $270^\circ C$; $P = 170$ psig; 3.1 NL/hr.-g.Fe) with iron catalysts containing silica or alumina (Si or Al/Fe = 0.044) with varying amounts of potassium (o, alumina at $230^\circ C$; ●, alumina at $270^\circ C$; □, silica at $270^\circ C$; and ■, silica at 270°).

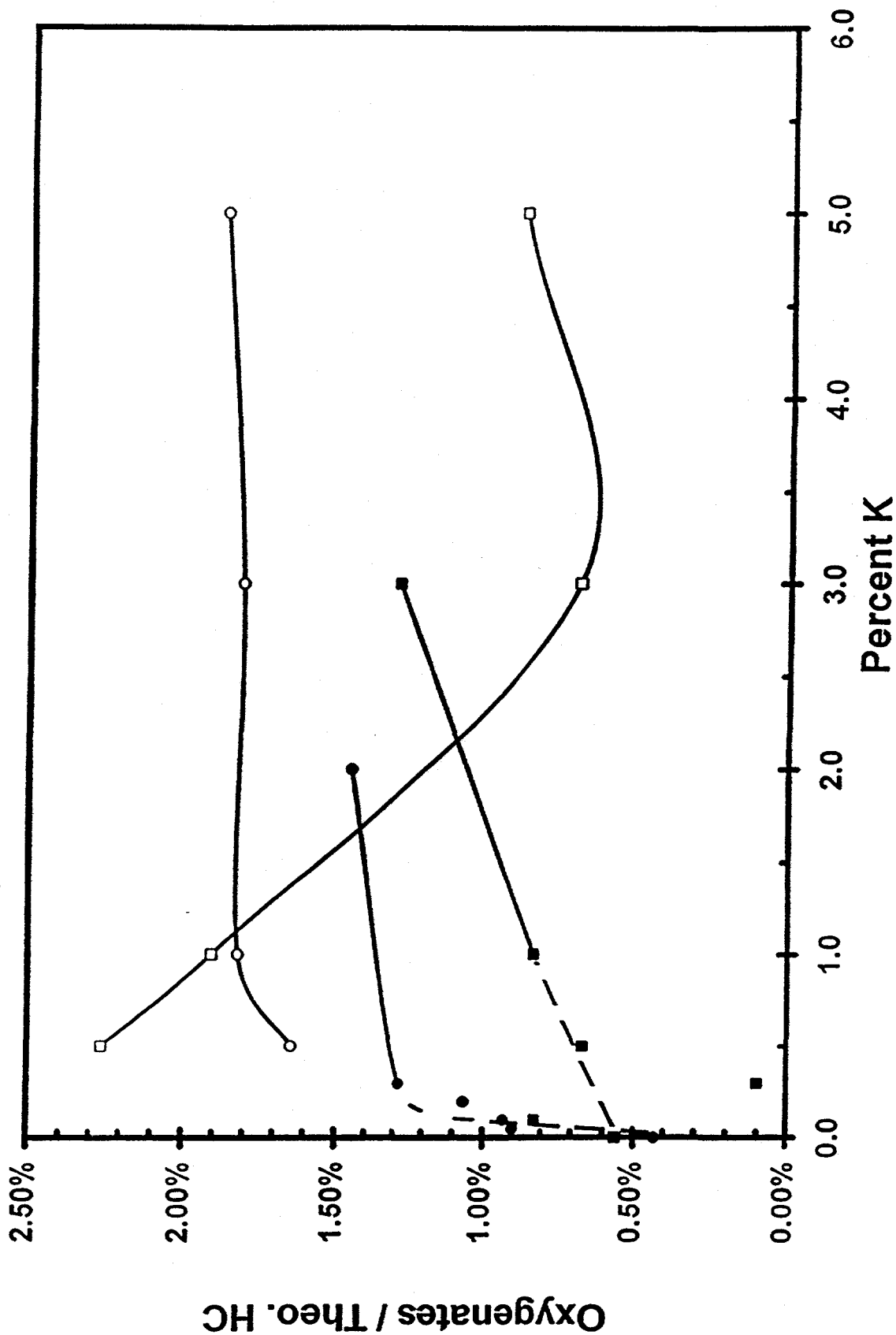


Figure 5. The conversion of CO during the conversion of synthesis gas ($H_2/CO = 0.7$; $T = 230$ or $270^\circ C$; $P = 170$ psig; 3.1 NL/hr.-g.Fe) with iron catalysts containing silica or alumina (Si or Al/Fe = 0.044) with varying amounts of potassium (O, alumina at 230° ; ■, alumina at $270^\circ C$; □, silica at 230° ; and ●, silica at 270°).

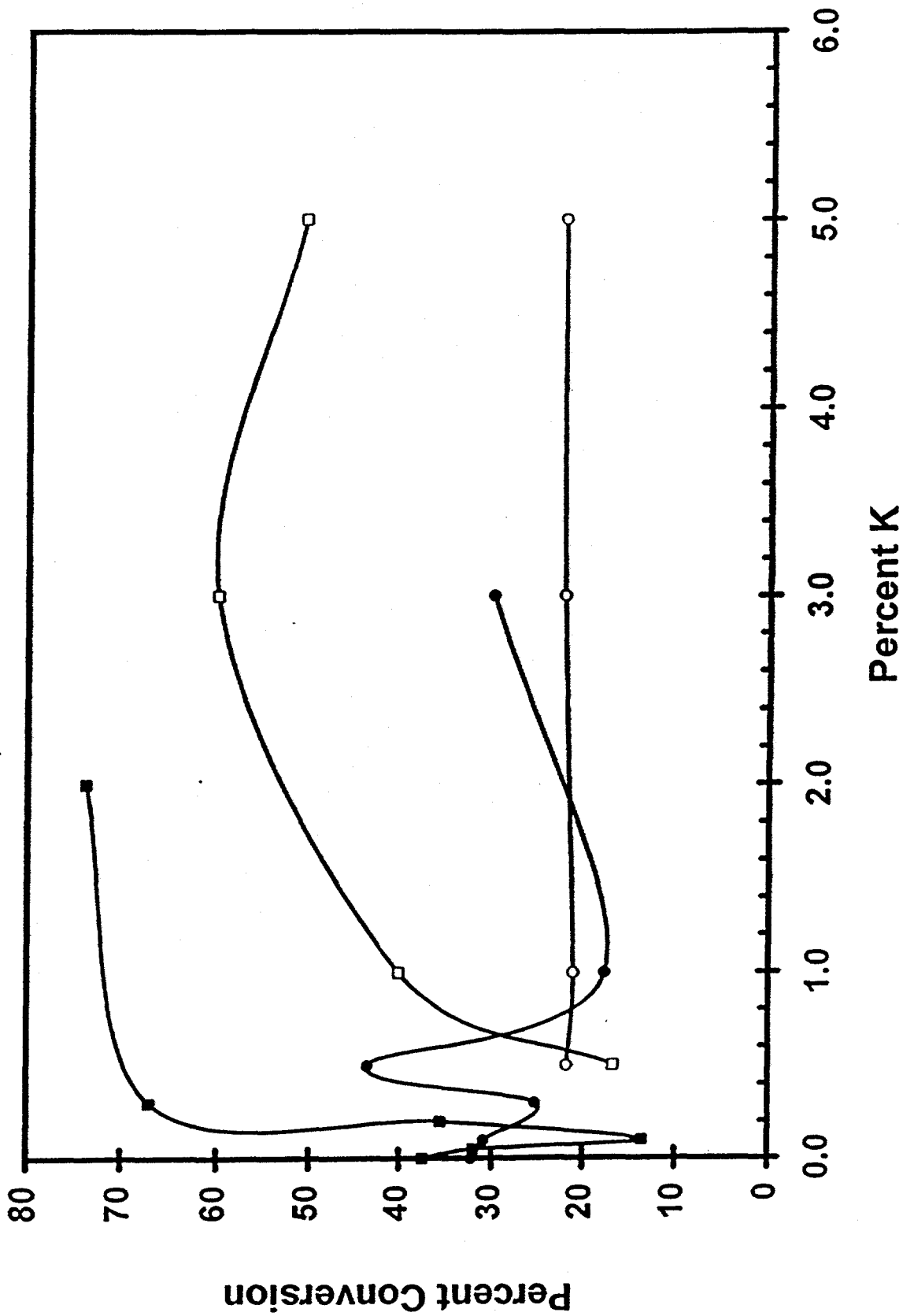


Figure 6. The weight percent of oxygenate compounds in the aqueous phase formed during the conversion of synthesis gas with an alumina (Al/Fe = 0.044) containing iron catalyst and 0.5 wt.% potassium ($H_2/CO = 0.7$; T = 230 or 270°C; P = 170 psig; 3.1 NL/hr.-g.Fe; ◆, methanol; ■, ethanol; ▲, ethanal; x, acetone; *, 2-propanol; ●, 1-propanol; and +, 1-butanol).

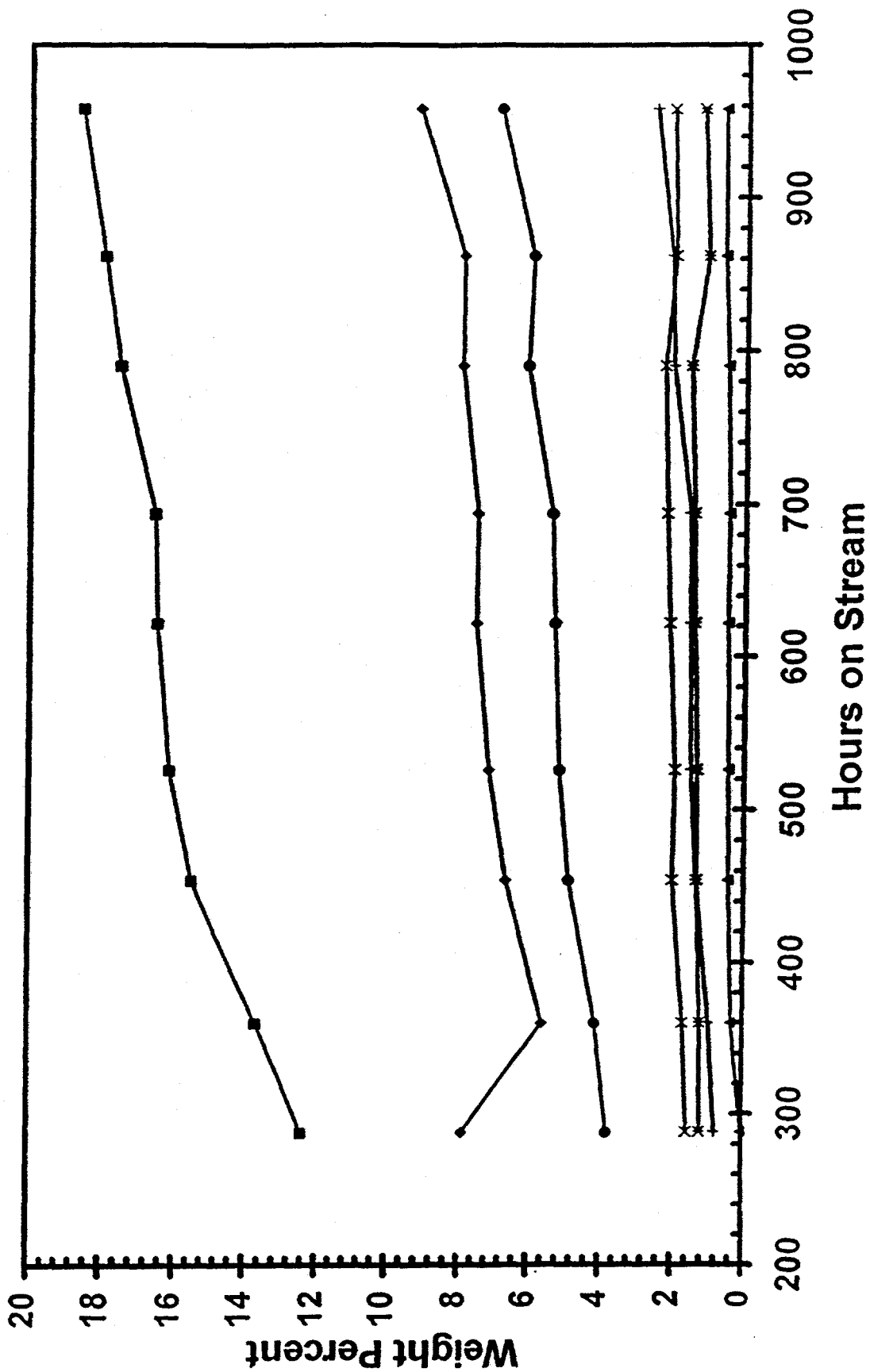


Figure 7. The weight percent of oxygenate compounds in the aqueous phase formed during the conversion of synthesis gas with an silica (Si/Fe = 0.044) containing iron catalyst and 0.5 wt.% potassium ($H_2/CO = 0.7$; $T = 230$ or $270^\circ C$; $P = 170$ psig; 3.1 NL/hr.-g.Fe; \blacklozenge , methanol; \blacksquare , ethanol; \blacktriangle , ethanal; x, acetone; *, 2-propanol; \bullet , 1-propanol; and +, 1-butanol).

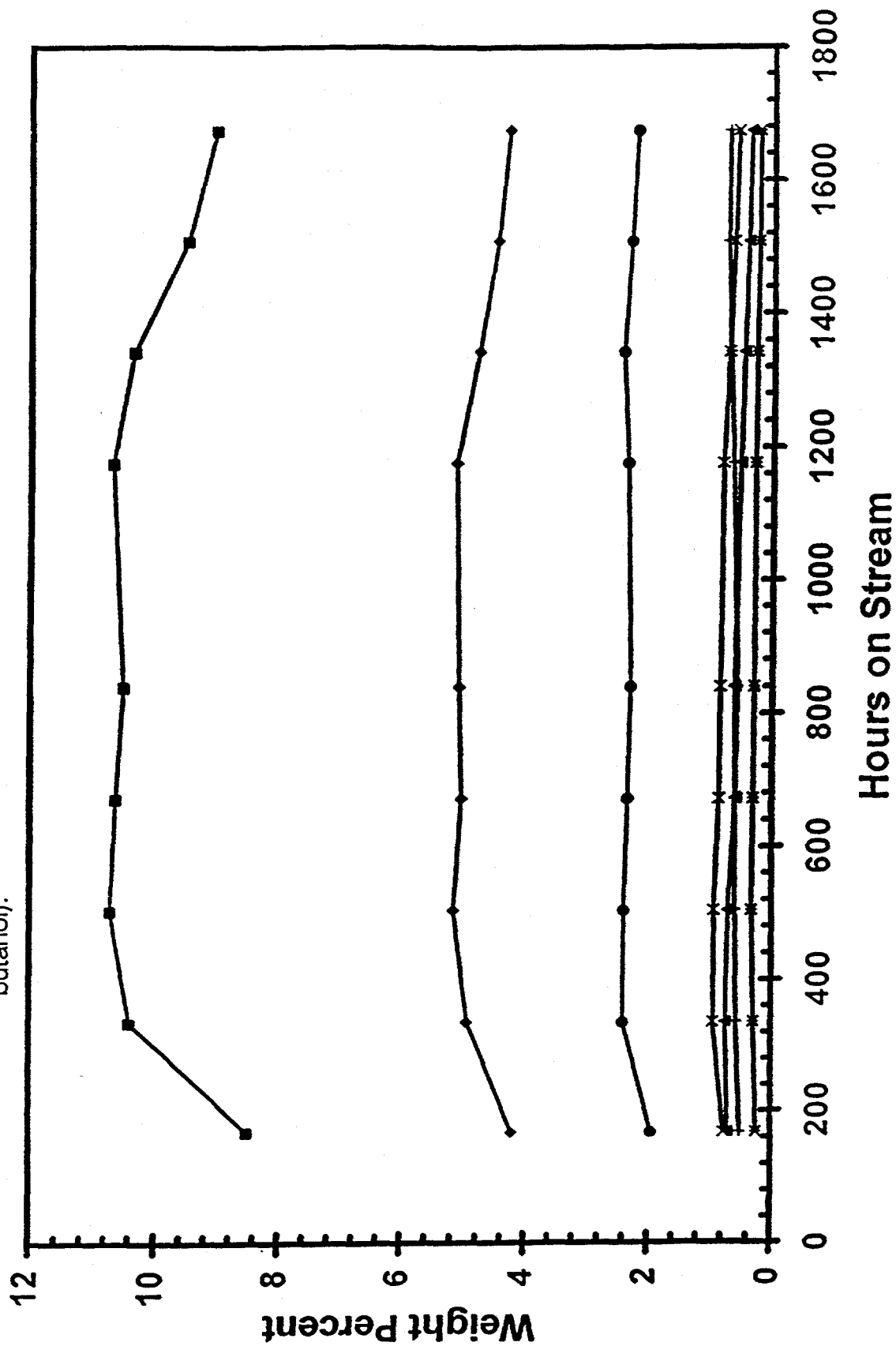


Figure 8. The percentage of the oxygenate fraction made up by individual compounds (●, methanol; ▲, ethanol; x, ethanal; ■, 1-propanol; and ◆, propanal) from the conversion of syngas with an silica (Si/Fe = 0.044) containing iron catalyst and 0.5 wt.% potassium ($H_2/CO = 0.7$; $T = 270^\circ C$; $P = 170$ psig; 3.1 NL/hr.-g.Fe).

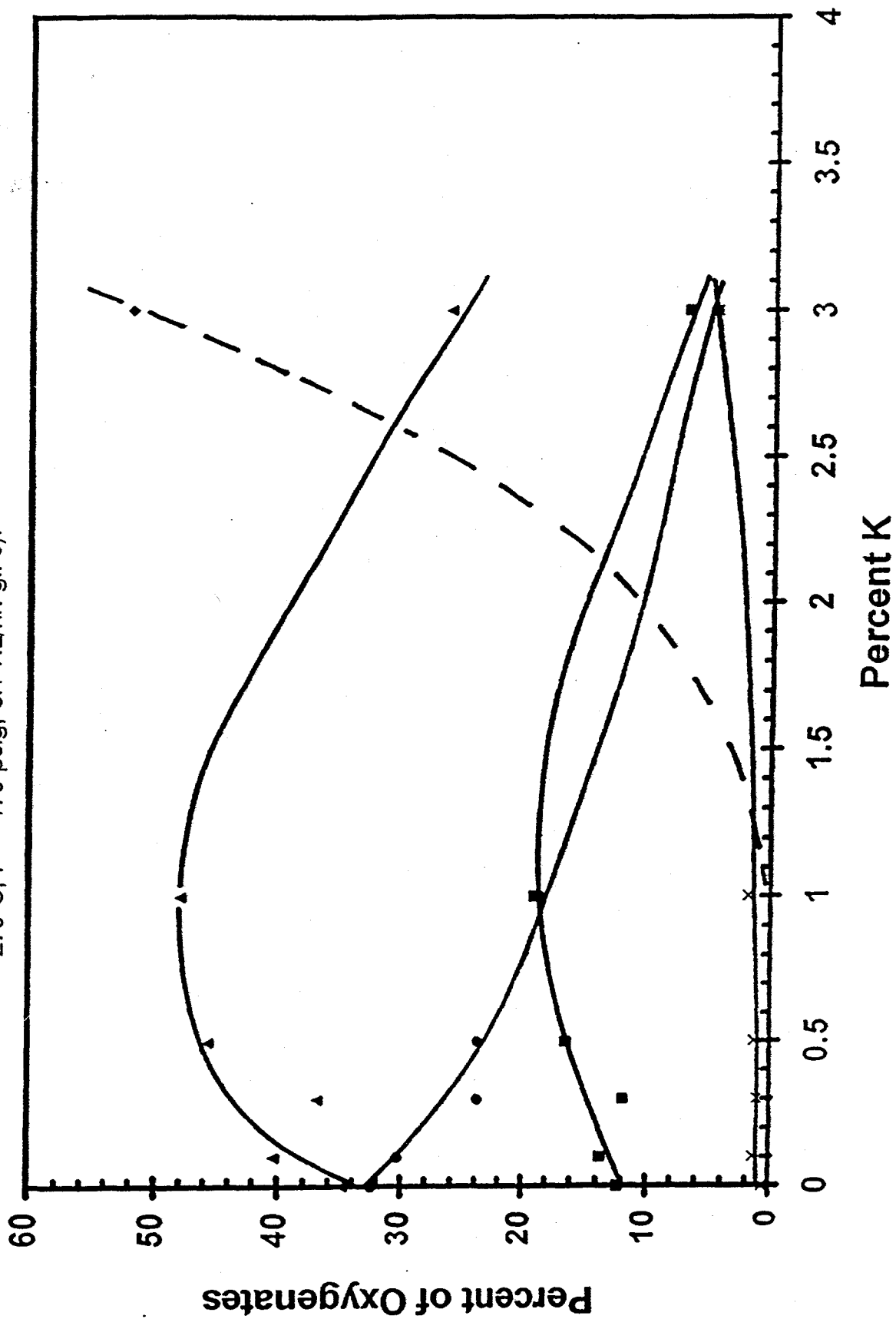


Figure 9. The percentage of the oxygenate fraction made up by individual compounds (●, methanol; ▲, ethanol; x, ethanal; ■, 1-propanol; and ◆, propanal) from the conversion of syngas with an silica (Si/Fe = 0.044) containing iron catalyst and 0.5 wt.% potassium ($H_2/CO = 0.7$; $T = 230^\circ C$; $P = 170$ psig; 3.1 NL/hr.-g.Fe).

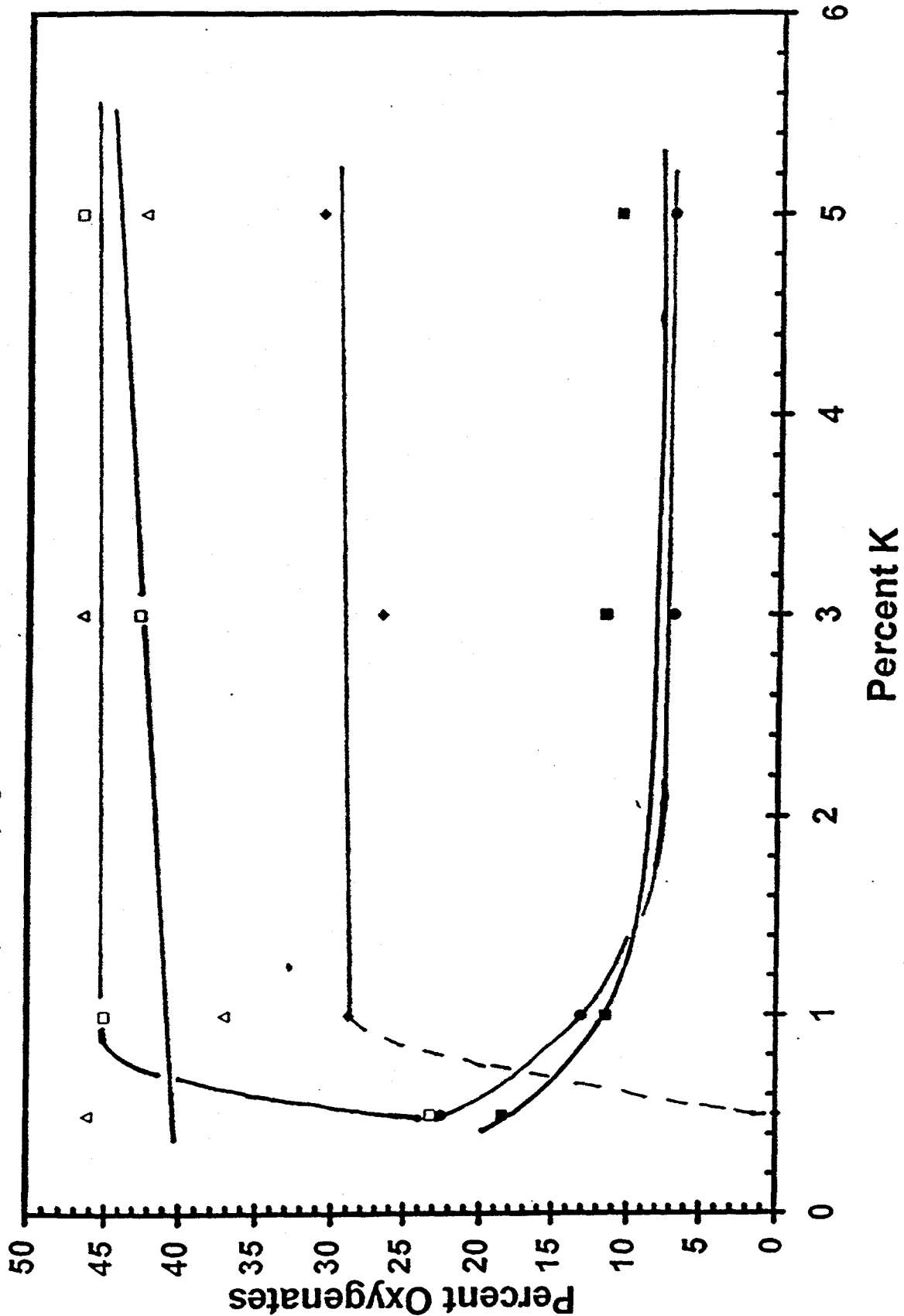


Figure 10. The conversion and oxygenates production during long term testing of a precipitated iron catalyst containing silica (Si/Fe = 0.044) and potassium (0.5 wt.%).

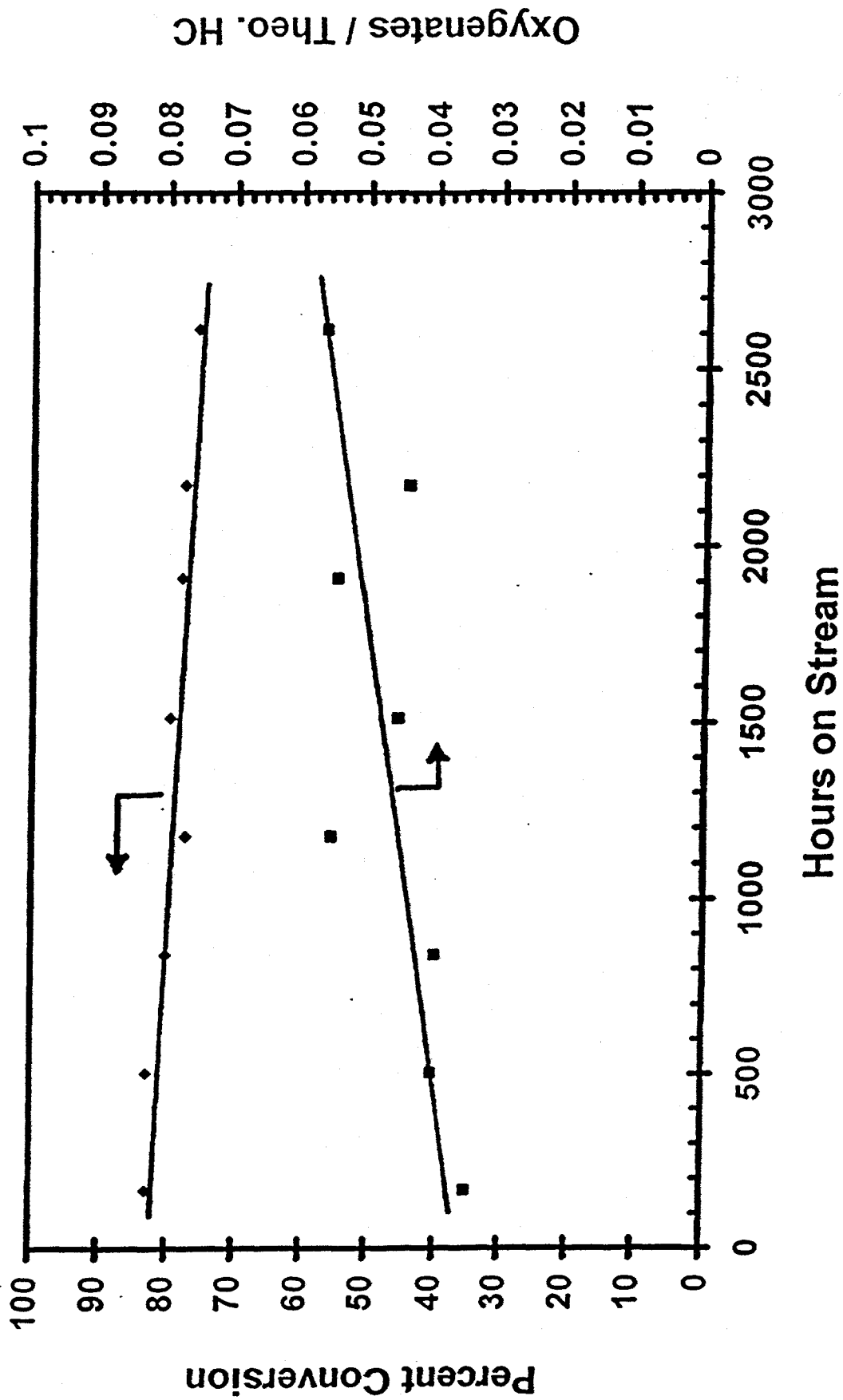


Figure 11. The $\ln [(Wt.\% N)/N]$ versus the carbon number, N , of the oxygenates formed from the conversion of syngas with an alumina ($Al/Fe = 0.044$) containing iron catalyst and various wt.% potassium indicated by numbers with each curve ($H_2/CO = 0.7$; $T = 270^\circ C$; $P = 170$ psig; 3.1 NL/hr.-g.Fe.

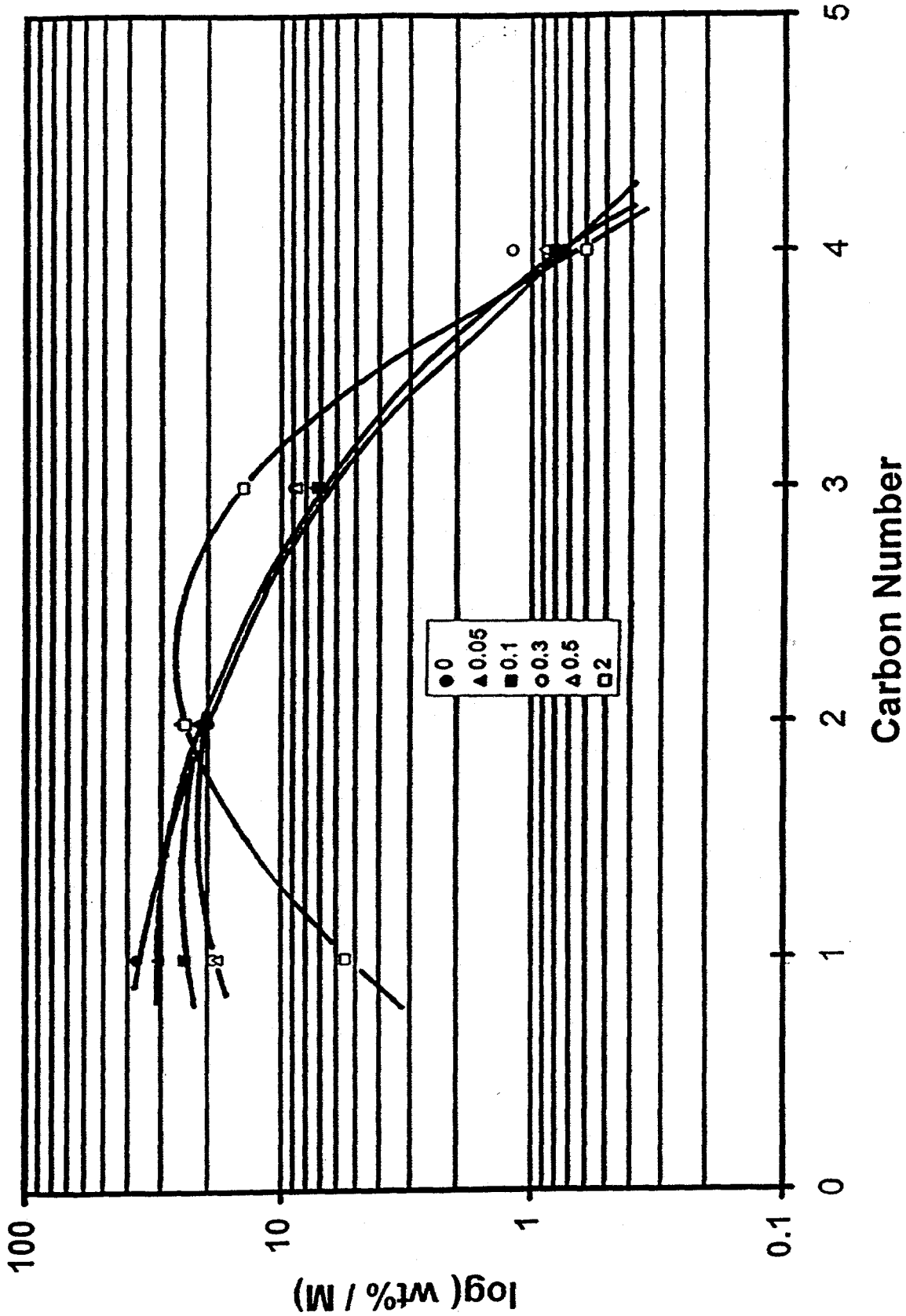


Figure 12. The $\ln [(Wt.\% N)/N]$ versus the carbon number, N , of the oxygenates formed from the conversion of syngas with an alumina (\blacktriangle , $Al/Fe = 0.044$; \bullet , $Al/Fe = 0.06$; and \blacksquare , $Al/Fe = 0.08$) containing iron catalyst with 0.5 wt.% potassium ($H_2/CO = 0.7$; $T = 270^\circ C$; $P = 170$ psig; 3.1 NL/hr.-g.Fe.

