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Project Status Report

Mechanism of Promotion of Iron Fischer-Tropsch Catalysts (Quarterly Report for the Period Ending June 30, 1986)

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Anderson-Schulz-Flory Behavior of ^{14}C-ethanol with Unpromoted Fe Catalyst at 7 Atmosphere

Significant difficulties were encountered in our efforts to measure the amount of ^{14}C in the higher carbon liquid products (C_6 and higher) but they have now been overcome. Only 15%, or less, of the ^{14}C added to the reactor during a 24 hour period was incorporated into the non-oxygenated components. The activity in the small amount of each individual compound is therefore so low that it is not detectable above background using g.c..-radiochromatography. An alternate method to determine ^{14}C in these higher carbon number compounds had to be developed.

Liquid chromatographic separation, following separation into alkene and alkane fractions by dry column silica gel chromatography, permitted collection of samples corresponding to each of the normal alkanes between C_9 and C_{15}. The refractive index detector permitted quantitative determination of the amount of each n-alkane collected. The ^{14}C content of each n-alkane fraction was determined by liquid scintillation counting. The activity/carbon number (figure 1) and an Anderson-Schulz-Flory (A.S.F.) plot is shown in figure 2. If the ^{14}C in ethanol became equivalent to the carbon in CO from the synthetic gas, the slope in figure 2 should have been zero, or at least nearly zero. Rather, the slope of ca. 0.77 is reasonably close to that of ca. 0.7 obtained for synthesis using either a CO/H_2 mixture or CO/H_2/ethanol reactant feed. This plot is, as far as we are aware, the first one to show that the ^{14}C in these higher carbon number alkanes obey the A.S.F. plot. These results indicate that we should be able to discern whether promoters alter the ^{14}C build-in by added "chain initiators".

The ability to change conditions rapidly in the autoclave reactor prompted us to construct a reactor system that operates at one atmosphere for this purpose. The data in figure 3 compares the alkane percentage as a function of carbon number for operation at 1 or 7 atmospheres. It is apparent that (1) the same trend is obtained for both pressures and (2) that up to C-6 the qualitative agreement is excellent. At the lower flow rate at 1 atm., the higher alkenes are hydrogenated more than at the higher space velocity. However, the selectivity data is similar enough that we should be able to use

the 1 atm. reactor system to screen the promoted catalysts. This will permit us to accelerate the screening of promoted catalysts and to utilize the 7 atm reactor for verifying results.

The data in figure 4 again demonstrates the utility of the 1 atm. reactor system. The addition of ethanol to the CO/H_2 feed decreases the percent of alkane for each carbon number fraction (figure 3). The addition of ethanol or pentanol to the CO/H_2 change reduces the fraction of alkane for each of the lower carbon number fractions; this is true for both the one and seven atmosphere conditions.

Future Work

Runs with potassium promoted $Fe-SiO_2$ and the United Catalyst C-73 sample will be initiated next month.

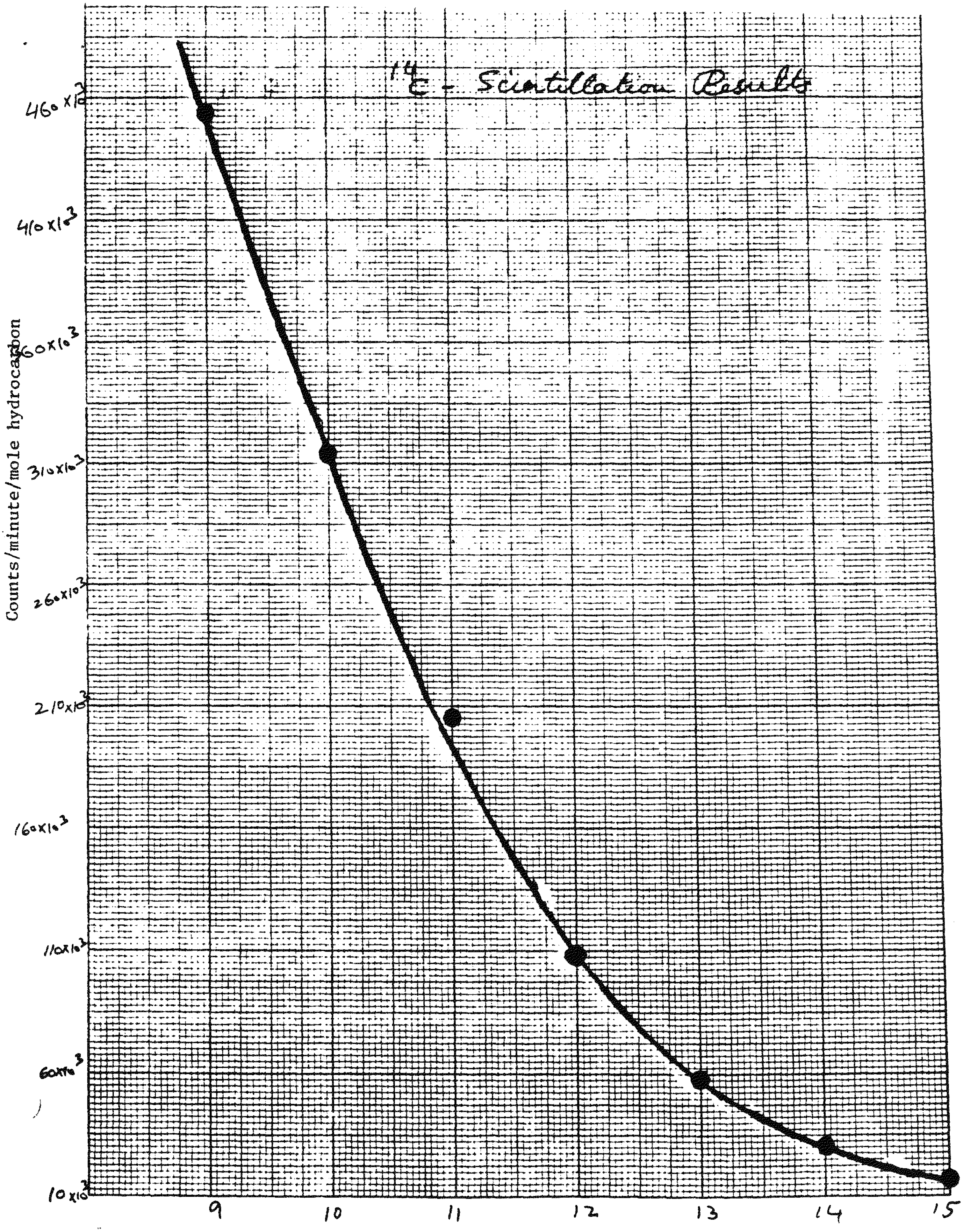

Figure 1. Radioactivity (cpm by liquid scintilation counting) of the n-alkane fraction obtained by adding C-14 labeled ethanol to the CO/H_2 conversion at 7 atms. n-Alkane fractions obtained by liquid chromatography.

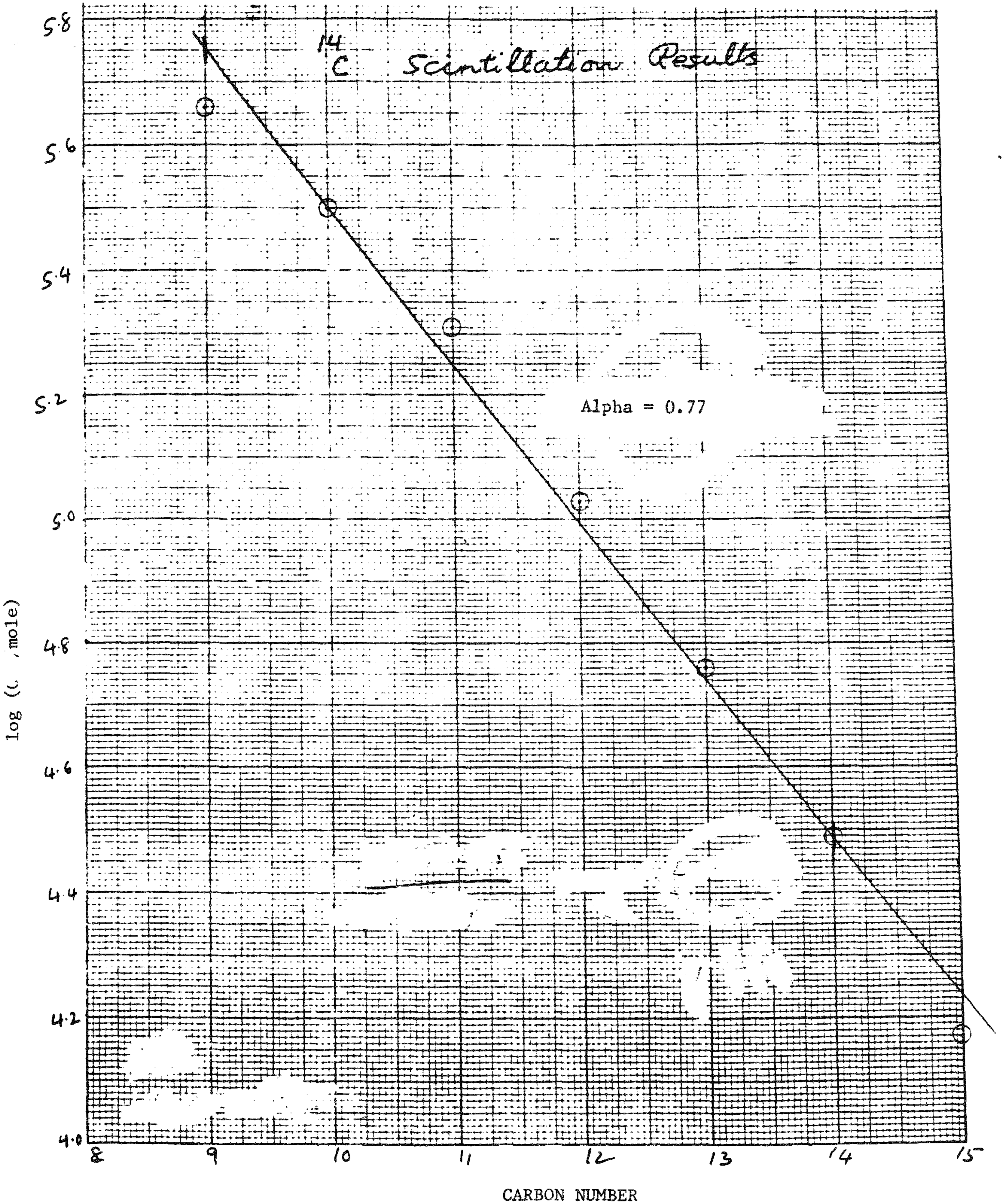

Figure 2. Anderson-Schulz-Flory plot of activity data from figure 1.

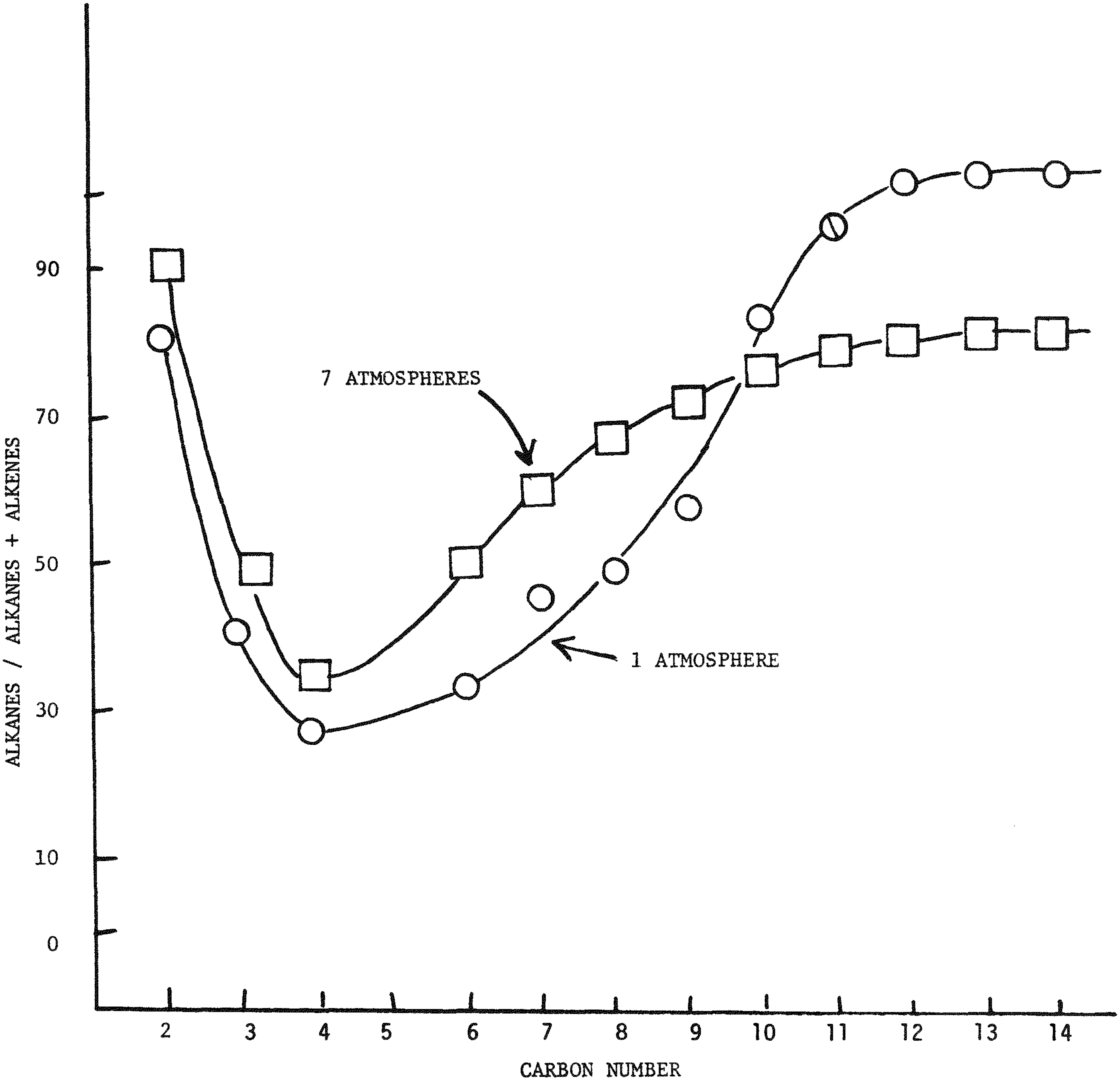

Figure 3. Alkane percentage for the conversion of CO/H_2 = 1 at 1 atmosphere and GHSV = 760 (○) and 7 atmospheres with GHSV = 130 (□).

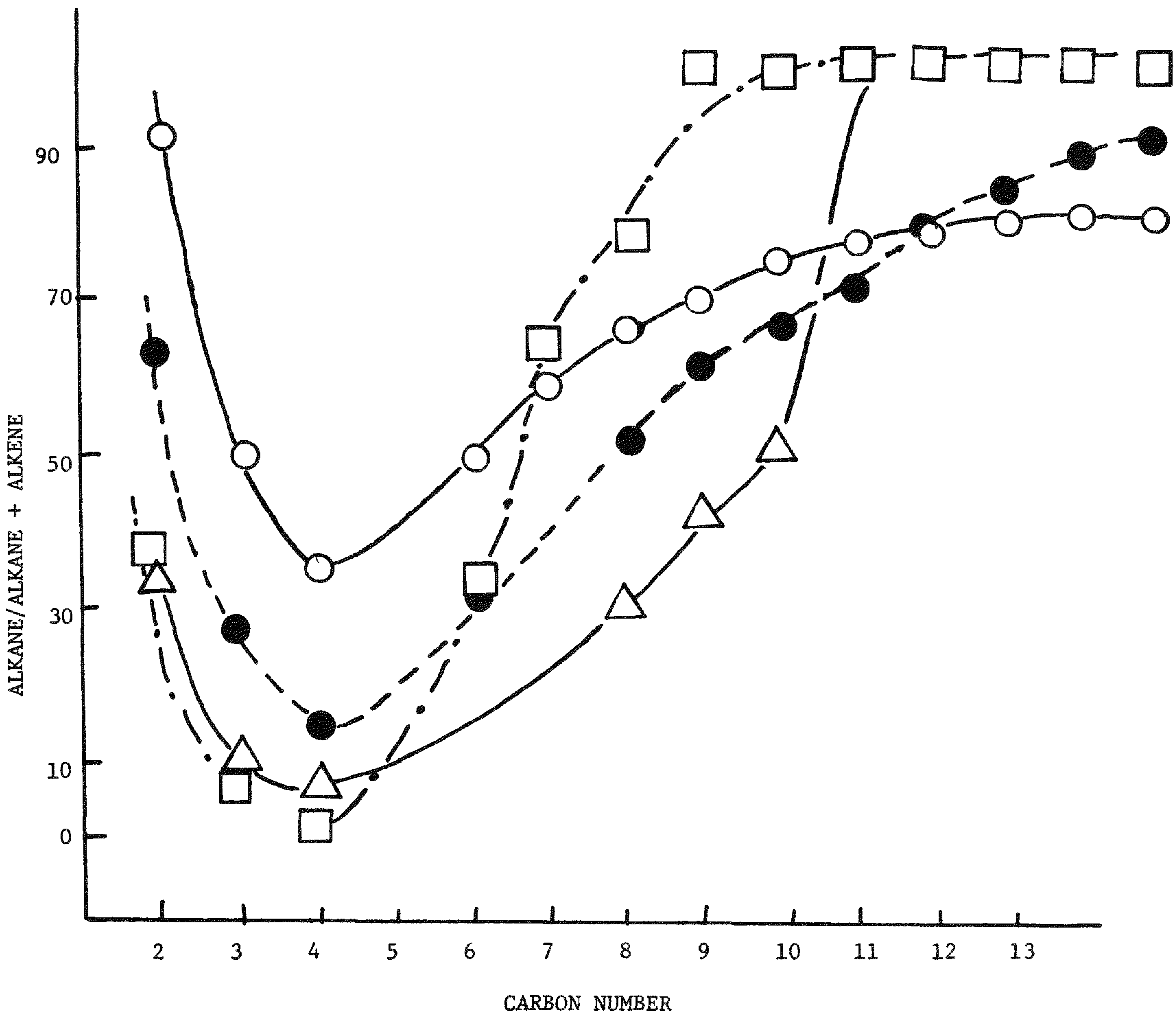

Figure 4. Alkane percentage for the conversion at 7 atmospheres, CO/H_2 = 1, GHSV = 130 (○); 7 atmospheres, CO/H_2 = 1 with 2 mole ethanol (based on CO), GHSV = 130 (●); 1 atmosphere, CO/H_2 = 1 with gas saturated with ethanol at 25°C, GHSV = 230 (△); and 1 atmosphere, CO/H_2 = 1 with gas saturated with pentanol, GHSV = 230 (□).