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Fischer-Tropsch Quarterly Report for Period Ending January 31, 1986

ABSTRACT

A silica supported iron (9.2% Fe) catalyst was found to retain activity over 20 days of use at 90 psig conditions. During the 20 days, unlabeled ethanol or pentanol was added with the CO/H_2 reaction mixture. Product distributions from the run when alcohol was present differed from those when the reactant was only CO and H_2. A run was accomplished at the end of the month in which 14-C labeled ethanol was added and the 14-C distribution confirmed that added ethanol was incorporated into the Fischer-Tropsch products.

REPORT

Separations to date have been effected to show that separation of pure PETC Fischer-Tropsch sample into pure alkane and alkene fractions could be effected using dry silica gel chromatography. A sample of Fischer-Tropsch product was obtained from Professor Satterfield to confirm that the separation scheme would be effective with a variety of samples. Thus, separations were carried out as described in our first yearly report (October 1985). The separation was as efficient with this sample as for the PETC sample (Figures 1 and 2). Total recovery, based on the combined weight of some 20 fractions, was 91%. A further separation of the alkane fraction into normal and iso-alkane subfractions was effected using 5A zeolites. To effect this separation the alkane fraction was dissolved in isooctane and refluxed for about 2 days. The zeolite was separated from the solvent and the n-alkanes were then dispersed into n-pentane by adding water to the zeolite. Chromatograms of the normal and isoalkane fractions are shown in Figure 3. The distributions of normal alkanes in the whole sample and the separated

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fraction are in excellent agreement (Figure 4). There are slight deviations between the amounts of isoalkanes in the whole and separated fractions; however, these are not appreciable and are likely due to including an alkene or alcohol in the peaks considered to be isoalkanes in the whole sample.

An iron catalyst was prepared by adding sufficient iron nitrate to Davison Grade 923 silica to produce a catalyst containing 9.2% Fe. 120g of catalyst was reduced in hydrogen and this reduced catalyst was charged to the stirred autoclave reactor which contained about 500cc of n-octacosane.

After about six days use at a reaction temperature of 265°C, 90 psig, reactant flow of 0.6 ft^3/hr and a CO/H_2 ratio of 0.77, a steady-state activity was attained that corresponded to slightly less than 20% CO conversion.

Runs were made with unlabeled ethanol and pentanol. The change in products between sample collection periods when alcohol was added to the CO/H_2 and when only CO/H_2 were present clearly indicated that alcohols were incorporated into higher carbon products. There have been earlier claims to the effect that alcohols will or will not build into Fischer-Tropsch products at higher pressures.

A run was made at the end of the 20 day period in which C-14 labeled ethanol was added to the CO/H_2 feed. A chromatogram of the gaseous products when only CO/H_2 was converted is shown in figure 5a. A similar gc chromatogram for products from a run when both ethanol and CO/H_2 were reactants is shown in figure 5b. Note that the chromatogram in figure 5b contains two large peaks that have not been identified to date but are believed to be acetaldehyde and ethylacetate. A trace from the proportional counter, shown in figure 5c, corresponds to the gc shown in figure 5b. It is apparent that C-14 has been incorporated into the products from this run.

PLANNED FOR NEXT MONTH

1. Detailed analysis of the product from the conversion of CO/H_2 with added C-14 labeled ethanol will be carried out.

2. Runs with pentanol and decanol labeled with C-14 are planned.

3. A catalyst identical to the $Fe-SiO_2$ catalyst but containing an alkali promoter will be prepared.

4. Operational difficulties have been encountered in carrying out the 7 atm pressure runs. For example, it is necessary to make a 24 hour runs with added C-14 alcohol in order to collect sufficient sample products for an adequate mass balance. This means that it will require a longer time period to investigate each catalyst than was anticipated in the original statement of work. We will be able to make a better judgment about the impact of this unanticipated complication within the next two months.

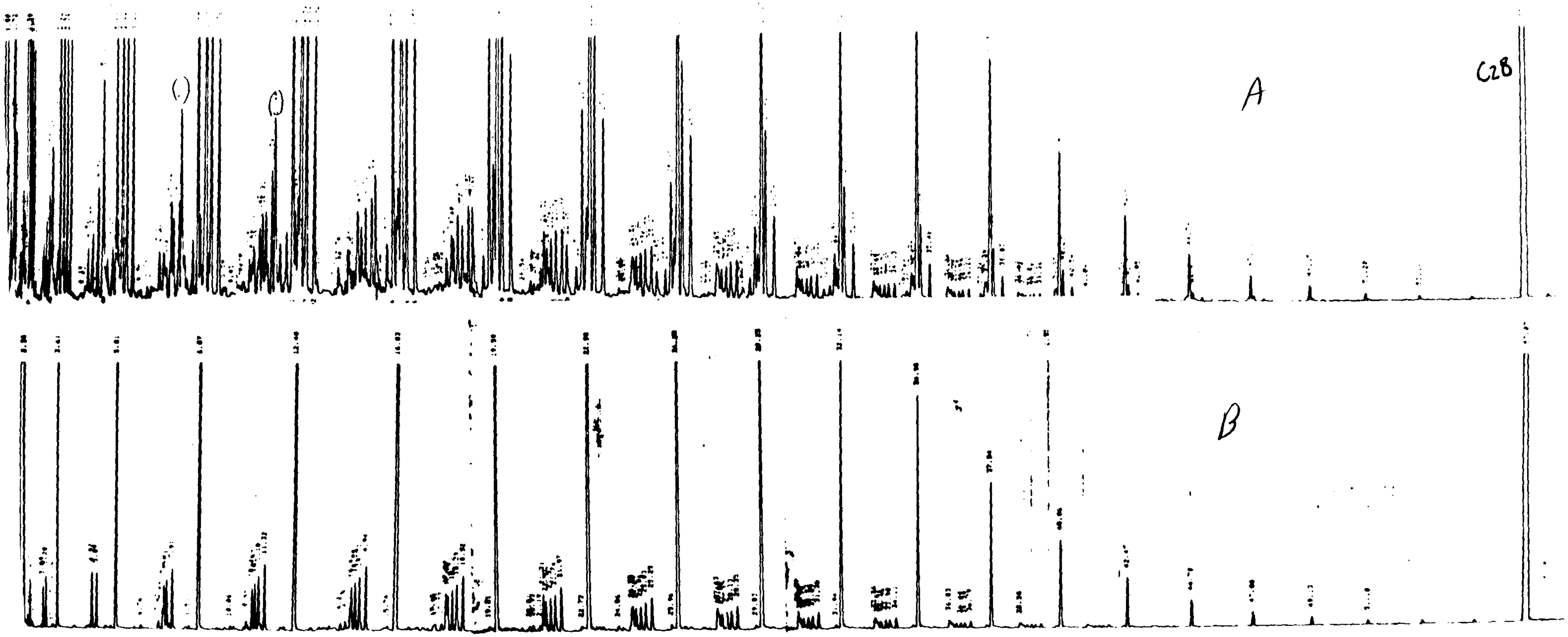

Figure 1. Capillary gas chromatograms of a whole sample from Saterfield (Top, Fig 1A), and alkane fraction (Bottom, Fig. 1B).

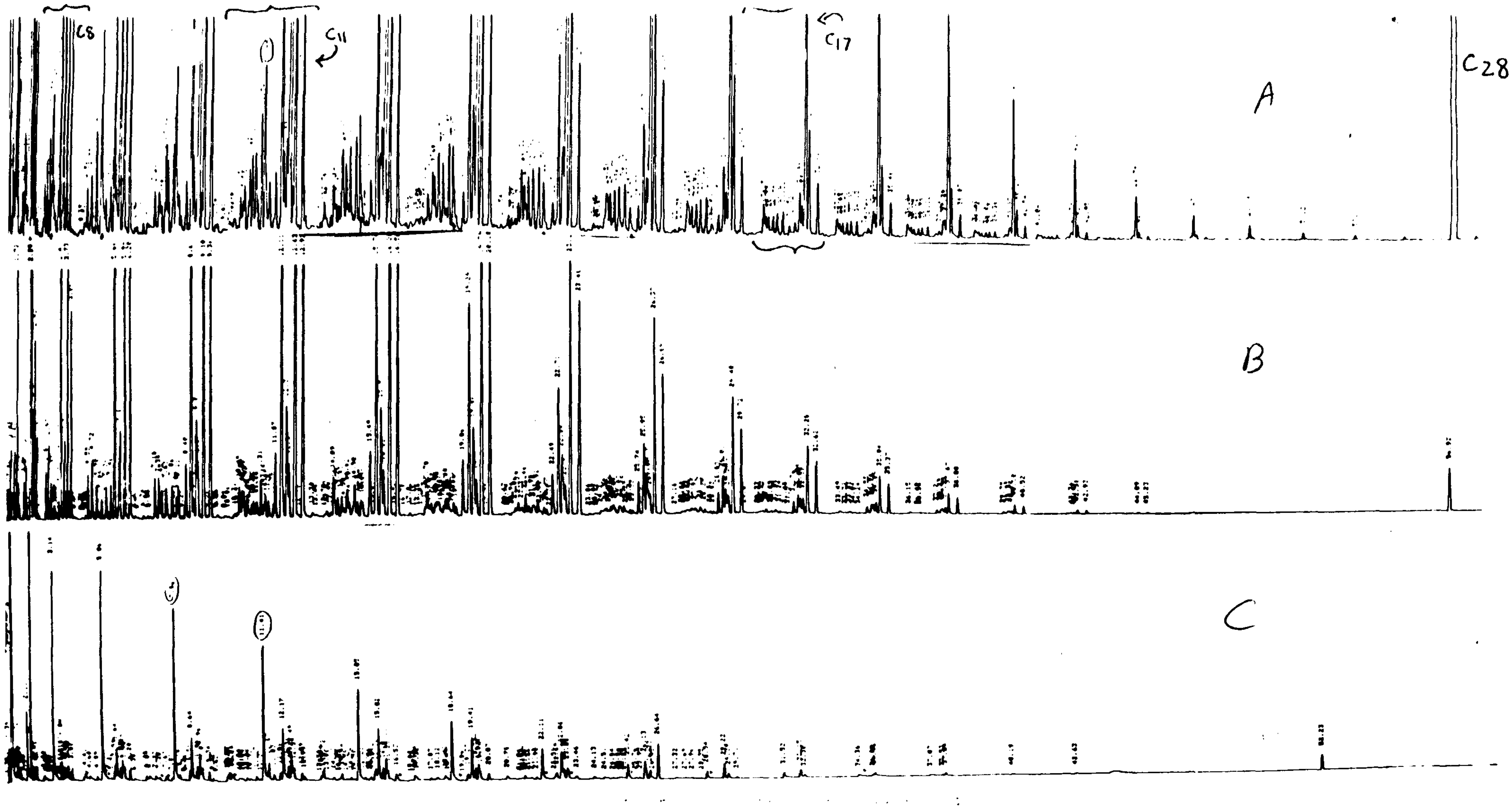

Figure 2. Capillary gas cheomatograms of a whole sample from Saterfield (Top, Fig. 2A), and alkene fraction (Middle, Fig. 2B), and oxygenated compound (Bottom, Fig. 2C).

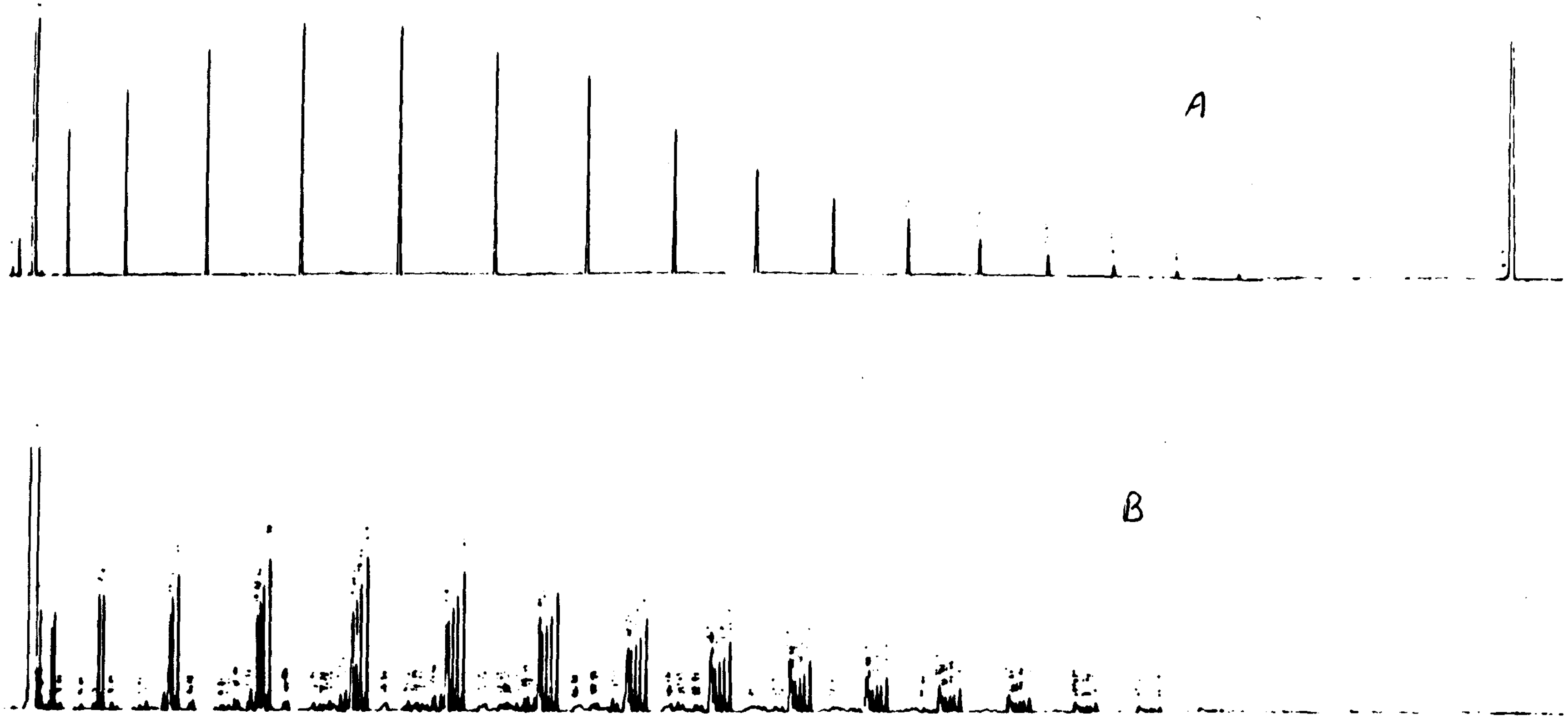

Figure 3. Capillary gas chromatograms of an alkane fraction desorbed from 5A zeolite (Top, Fig. 3A) and iso-alkane not adsorbed by zeolite (Bottom, Fig. 3B).

Fig 4. The Total % OF n-alkanes and iso-alkanes
befor and after zeolite separation

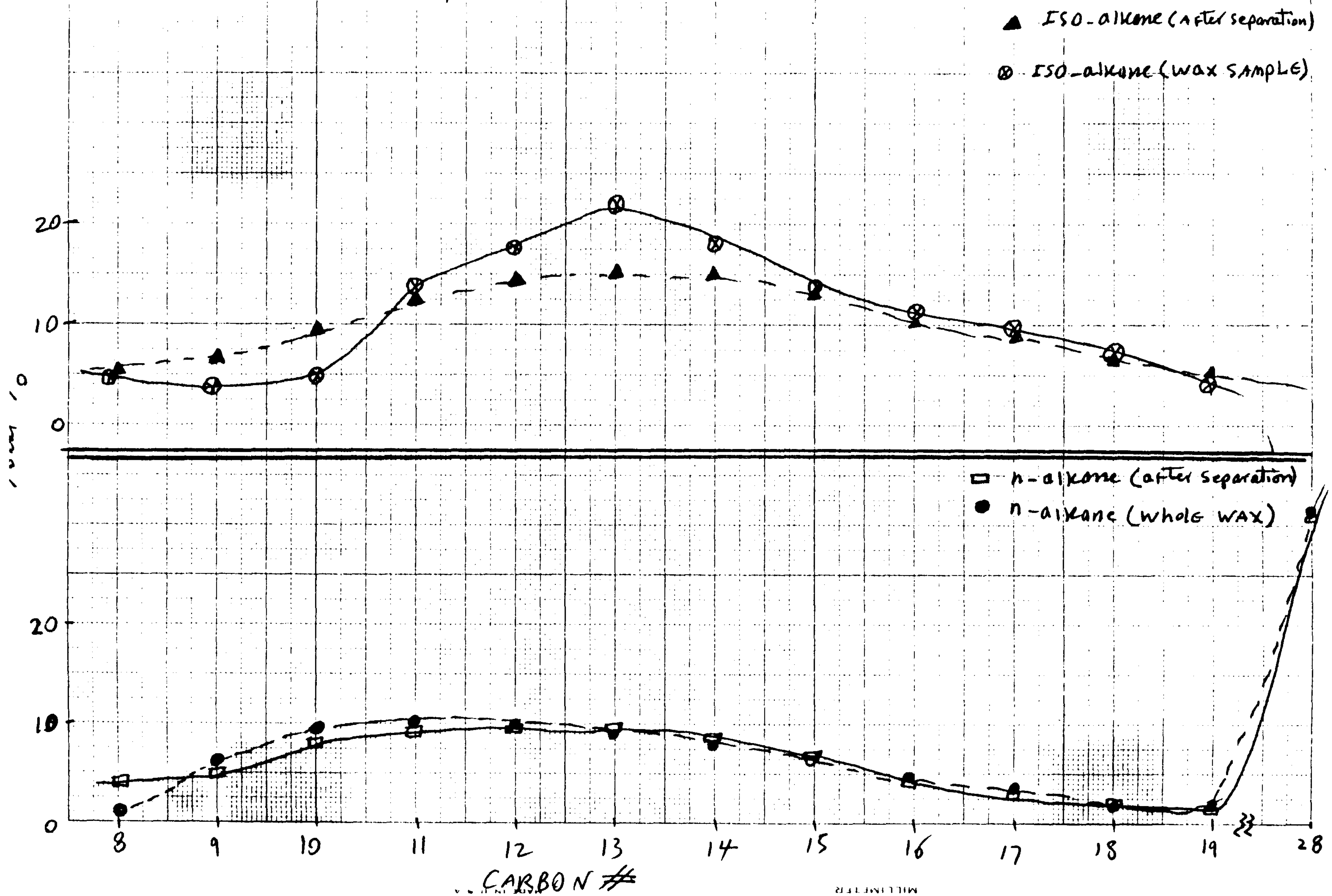

Figure 5. Chromatograms of gas phase products.

a) The CO/H_2 mixture as the reactants, without isotope.
b) Labeled C_2H_5OH has been added into the CO/H_2 gas stream.
c) The p.c. output corresponds to the spectrum of 5b.