Mechanism of Promotion of Iron Fischer-Tropsch Catalysts (Quarterly Report for the Period Ending June 30, 1987)

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FISCHER-TROPSCH SYNTHESIS: COMPARISON OF PRODUCT SELECTIVITY AND ^{14}C LABELED ETHANOL INCORPORATION AT ONE AND SEVEN ATMOSPHERE CONDITIONS

ABSTRACT

^{14}C tracer studies using labeled ethanol indicate that the relative radioactivity/mole in hydrocarbon products is constant to carbon number 20. This result is consistent with (1) the two carbon units of ethanol remaining intact while on the catalyst surface and (2) that an adsorbed ethanol derived species serves to initiate chain growth but that it does not participate in chain propogation. The selectivity data obtained in a one atmosphere plug flow reactor are in excellent agreement with those obtained at seven atmospheres in a stirred tank reactor.

INTRODUCTION

The Fischer-Tropsch Synthesis (FTS) has been widely studied from both commercial and mechanistic viewpoints (for example, 1,2). Even so, many of the details of the reaction remain obscure. One of the features required of nearly all commercial processes is a long catalyst life. This requires either a very long time at process conditions for catalyst screening studies or the development of reliable screening tests at less severe conditions. In this study results obtained at one and seven atmosphere total pressure conditions are compared.

In addition, a considerable amount of the pioneering ^{14}C tracer studies by Emmett and coworkers (3-8) was conducted at atmospheric pressure. It was of interest to verify that these conclusions for tracer incorporation and

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chain initiation by the added alcohol were applicable under the two operating conditions.

EXPERIMENTAL

A C-73 iron catalyst, supplied by United Catalysts, Inc., was used in this study. For the atmospheric-pressure fixed-bed reactor (APFR), the catalyst was reduced for 72 hours in hydrogen at 450°C, the temperature was decreased in flowing hydrogen to 262°C (reaction temperature) and then the syngas feed was initiated. For the slurry reactor (medium pressure slurry reactor, MPSR) the first reduction was the same as for the APFR; then the catalyst was passivated using 1% oxygen in helium. X-ray diffraction showed that the bulk of this passivated catalyst was metallic iron. About 150 grams of this passivated catalyst was charged into a one liter stirred autoclave reactor together with sufficient octacosane solvent to provide about 500 ml of slurry in the reactor. The catalyst-slurry mixture was heated to 300°C in flowing syngas at atmospheric pressure for a 48 hour period; then the pressure was increased to seven atmospheres. This procedure is believed to impart improved catalyst life (1,2). An air driven agitator (650 rpm) was utilized during pretreatment and synthesis to eliminate mass transfer problems (9). Operating conditions for both reactors are detailed in Table 1.

The effluent from the slurry reactor system passed through a hot trap (65°C) and then a cold trap (10°C); finally, three on-line gas chromatographs (g.c.) were utilized to effect analysis of the components (through C_8 hydrocarbons) of the effluent gas from the cold trap. When a radioactive compound was introduced, the g.c. effluent was then passed through a proportional counter to determine ^{14}C activity in each g.c. peak (10). A very similar procedure was used for the APFR system, except that one trap (room temperature) was used rather than two traps. Liquid samples from the traps were also analyzed for individual compounds utilizing a 30 or 60 meter capillary g.c. column. For C-14 activity measurements, a packed g.c. column was utilized so that sufficient sample was in the g.c. effluent to permit analysis by the proportional counter. For higher carbon number components, alkane and alkene fractions were obtained by separation on silica gel. These fractions were separated by carbon number by liquid or gas chromatography, the effluent was collected and the C-14 content of each component obtained with a liquid scintillation counter (10).

RESULTS AND DISCUSSION

CO conversion

The CO conversion at 7 atmospheres remains constant for 150 or more days following an initial break-in period of 6 to 8 days. On the other hand, the activity in the plug-flow reactor declined from about 60% to 30% in about 7 days; treatment in hydrogen for 24 hours at 450°C restored the original activity which again declined with time on-stream (Fig. 1).

It was argued that retention of activity at intermediate pressures (7-15 atm) in the FTS was due to the formation of a liquid oil film, comprised of relatively low molecular weight hydrogen carbons, on the catalyst surface (11). These oils could dissolve wax and high boiling oxygenates to provide a continuous extraction of these from the pores of the catalyst and, consequently, a continuous regeneration of the catalyst activity. In our MPSR, octacosane should serve to do this and may be the reason that the activity of the catalyst was retained for more than 150 days. At SASOL, a fixed-bed reactor is maintained at a constant activity under conditions similar to those in Table 1 by increasing the operating temperature every few months (12). Thus, the difference in the two reactors for retention of activity may be due to a solvent effect.

Carbon distribution

Anderson-Schulz-Flory (ASF) plots for products from the two reactors are shown in Fig. 2. A very similar distribution is produced in the two reactors. A break in the ASF plot occurs around C10 in both cases; this was reported by others (13-17). The data in Fig. 2 are very similar to those reported by Satterfield and coworkers (15). The APFR products above about C-20 have a lower concentration than those from the MPSR; this is most likely due to the fact that a steady state for these higher carbon number hydrocarbons had not been attained when the sample was collected. It has been shown that such an effect should result for sampling periods following startup (18).

Selectivity

The FTS is believed to be a kinetically controlled reaction; thus, the product distribution rarely reaches the thermodynamic equilibrium values (19,20). The FTS is a very complicated reaction with several parallel and series reaction paths. In this section, the kinetic versus thermodynamic control of products will be considered for some of these reactions. The trans-2-alkene to (trans plus cis-2-alkenes) ratio approaches a constant value at higher carbon numbers; this fraction of ca. 0.7 is the value expected by extrapolation of the equilibrium data in reference 21 (Fig. 3). Even for the lowest carbon number alkenes the value is nearly 0.5, a value that is not that far from the equilibrium value. The results imply that the trans-2-alkene and cis-2-alkene reached a near equilibrium value under our operating conditions; this may result from the mechanism of their formation or by a series of secondary reactions.

For the FTS, the primary product has been viewed, by many, to be an alpha-alkene (reference 23, for example). Thus, the percent of beta alkene, based on alpha plus beta alkene only, is shown in Fig. 4. The same general trend is again obtained for the two reactors; however, it is noted that a constant percentage of beta alkene is attained at a lower carbon number for the fixed-bed reactor than for the stirred-tank reactor. It is also noted that the lower carbon number products approach a value expected if alpha alkenes are the primary synthesis product. The percentage of beta alkenes do not attain the value expected if the ca. 90% beta alkenes calculated from thermodynamic data also represents the equilibrium composition for the higher carbon numbers products. If the beta alkenes result from secondary reactions, then these reaction occur more readily in the AFPR than in the MPSR; this implies that higher carbon number hydrocarbons have a longer residence time in the fixed bed reactor.

An obvious question arises from the apparent limiting percentage of beta alkene. Two reasonable possibilities follow. First, the 1-alkene component, identified by g.c. retention time, may, in fact, contain an impurity component; if this were the case the amount of 1-alkene would be overestimated. This impurity, if present, would become more apparent at higher carbon numbers since the olefins become a progressively smaller fraction for the higher carbon number product. The second possibility is that the thermodynamic data in reference 21 is not accurate; other sources (22) do not exactly agree with the data in reference 21. In view of these uncertainties, it does not appear appropriate to discuss this point further even though its importance in mechanistic considerations cannot be overemphasized.

The fraction of alkene in the alkane plus 1-alkene products is shown as a function of carbon number in Fig. 5. It is apparent that the alkane fraction is at, or near, a minimum at carbon number about 4. Again, hydrogenation appears to be greater for any carbon number above C-4 for the flow reactor. Considering reactor kinetics, the alkene fraction should have been greater in the plug flow reactor than the CSTR slurry reactor if the alkenes are an intermediate in a series of reactions leading to alkanes. Thus, the alkane fraction is also consistent with the higher carbon number products being exposed to a longer reaction time in the catalyst zone in the flow reactor than in the slurry reactor.

This effect is also demonstrated in Fig. 6 by the ratio n-alkane/2-alkene for each carbon number. This ratio is rather constant up to about a carbon number of 12 (or 20); beyond this carbon number the alkane fraction increases rapidly to become the dominant product. If both the alkane and 2-alkenes are viewed as secondary products, the relative contribution of isomerization and hydrogenation are rather constant for lower carbon numbers.

$CO/H_2/^{14}C$ labeled ethanol

Emmett and his coworkers (3-8) utilized radioactive compounds to study FTS some 30 years ago, and pioneering results were obtained. However, the limitation of the analytical instrumentation restricted the compounds they could analyze. The data in Fig. 7 show the relative radioactivity of gas phase products. Again, the data obtained in these two reactor systems are very similar. There were several aspects of the data in Fig. 7 which should be emphasized. First, the amount of radioactivity/mole in the hydrocarbon products from C_2 to C_6 was essentially the same; this agrees with results of Hall, et al. (6). This implies that ethanol acts primarily as a chain initiator for the reaction. The radioactivity of acetaldehyde was essentially the same as ethanol, indicating that it is derived by dehydrogenation of the added ethanol. It appears, considering the relative activity of ethanol and the C_2 - C_6 hydrocarbons, that a higher fraction of the ethanol was incorporated at atmospheric pressure than at 7 atmospheres. In both cases, however, our results agree with those of Emmett and coworkers (3-8) as well as the later studies by Schulz and coworkers (24-28).

It is surprising that CO, CO_2 and CH_4 contained radioactivity. Furthermore, CO_2 had a much higher radioactivity than CO (Fig. 8). This result indicates that during the course of the synthesis reaction, part of the ethanol dissociated to form a surface intermediate that formed CO_2 directly rather than through CO as an intermediate. If CO had been formed first, the

CO_2 derived from this CO by water-gas shift could not have more radioactivity than CO. Our results further indicate that the water-gas-shift reaction did not attain an equilibrium under our operating conditions; otherwise, CO and CO_2 should have an equal amount of radioactivity rather than the experimental result shown in Fig. 8. A similar conclusion was reached by Kokes, et al. (7) when radioactivity CO_2 was used in their study of the FTS reaction.

A careful examination of Fig. 7 shows that the amount of radioactivity in methane is very close to that of CO_2, but is much higher than CO. This implies that a fraction of the methane was not formed from CO during the tracer study; otherwise, the CO and CH_4 should have the same radioactivity.

In Fig. 9, the relative radioactivity of alkanes in the liquid phase products are shown. For the APFR, the relative radioactivity/mole decreased slightly from C_{14} through C_{23}. However, for the MPSR system, the relative radioactivity decreased much more rapidly with increasing carbon number. One of the reasons for the decline in carbon-14/mole is the accumulation of the heavy hydrocarbons in the slurry reactor. Another reason is that two independent chains, one that produces ^{14}C labeled alkanes, alkenes and alcohols and another that produces only unlabeled alkanes, contribute to produce these products. A more detailed discussion of this is found in reference 10. However, it does appear that the 7 atmosphere conditions produces relatively more of the alkane only products than are produced with the 1 atmosphere conditions.

In summary, the general selectivity patterns obtained at atmospheric pressure are very similar to those obtained at 7 atmospheres. Furthermore, the overall pattern of the selectivity data obtained in the plug flow reactor very closely resembles that obtained in a slurry reactor at 7 atmospheres. Thus, apart from catalytic activity and catalyst aging, the atmospheric pressure plug-flow reactor appears to provide a convenient way to screen iron catalysts. Hydrogenation appears to occur more readily in the flow reactor. While some comparisons have been made at the higher pressure, a more detailed comparison of the two reactors at 7 atmosphere and higher operating pressure is clearly merited.

The data support the overall mechanism advanced some 30 years ago by Emmett and coworkers. Thus, the added alcohol serves as a chain initiator; this applies for products up through carbon number 22. However, it appears that product accumulation must be taken into account when the activity/mole of the higher carbon number products is considered.

ACKNOWLEDGMENT

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TABLE 1

Operating Parameters

	APFR	MPSR
Temperature, ^{o}C	262	262
Pressure, atm.	1.0	7.0
Amount of catalyst, g	60	150
Flow, cc/min.	60	300
CO/H_2	1.0	0.78
C_2H_5OH, molar %	ca. 5	ca. 2

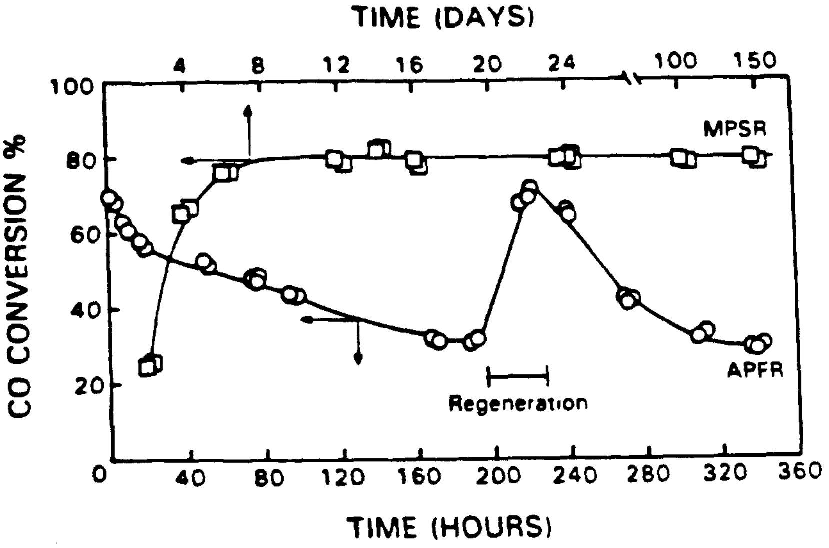

Fig. 1. Carbon monoxide conversion in an atmospheric pressure fixed bed (APFR) and at 7 atmospheres in a stirred autoclave reactor (MPSR).

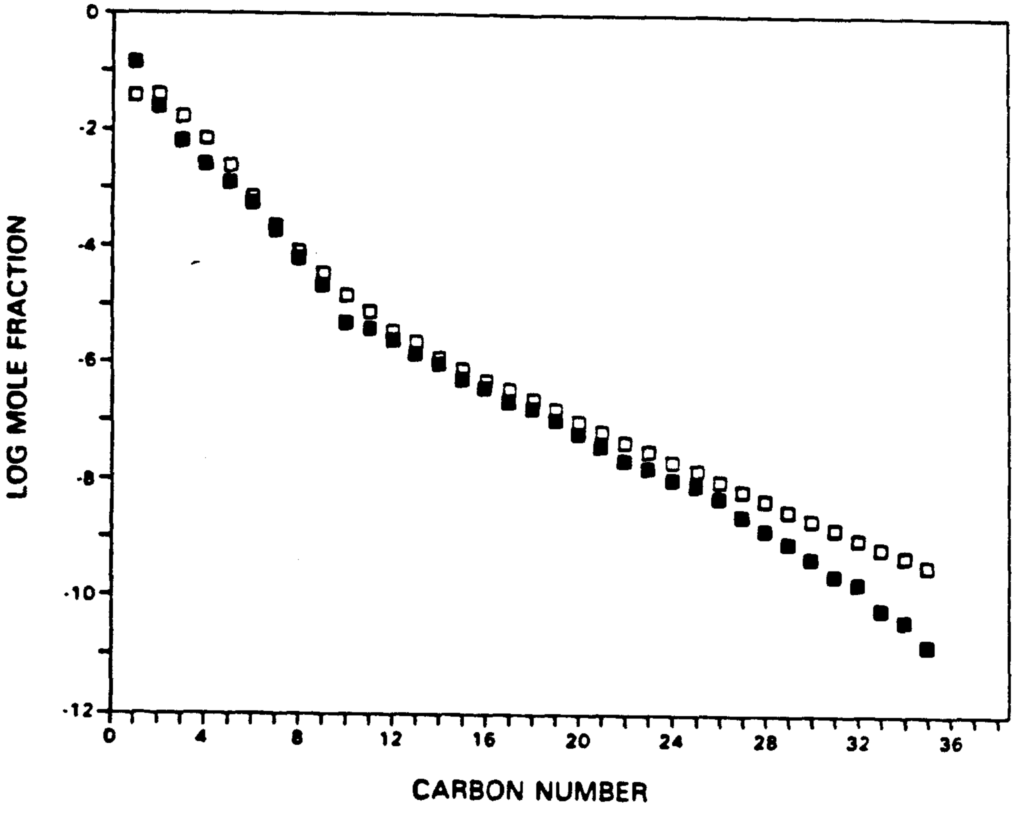

Fig. 2. Anderson-Schulz-Flory plots for the products from Fischer-Tropsch synthesis at 1 (■) and 7 (□) atmosphere conditions.

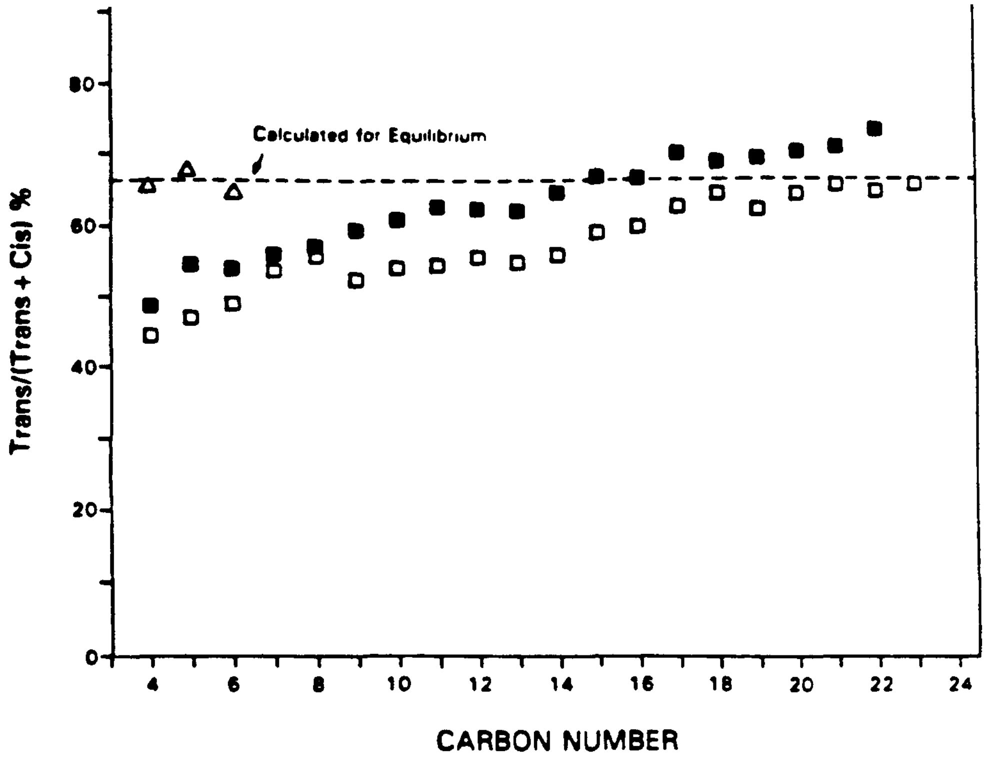

Fig. 3. Percent trans-2-alkene in the 2-alkene fraction of the products from Fischer-Tropsch synthesis at 1 (APFR; (■)) and 7 (MPSR; (□)) atmosphere conditions (equilibrium values calculated using data in reference 21).

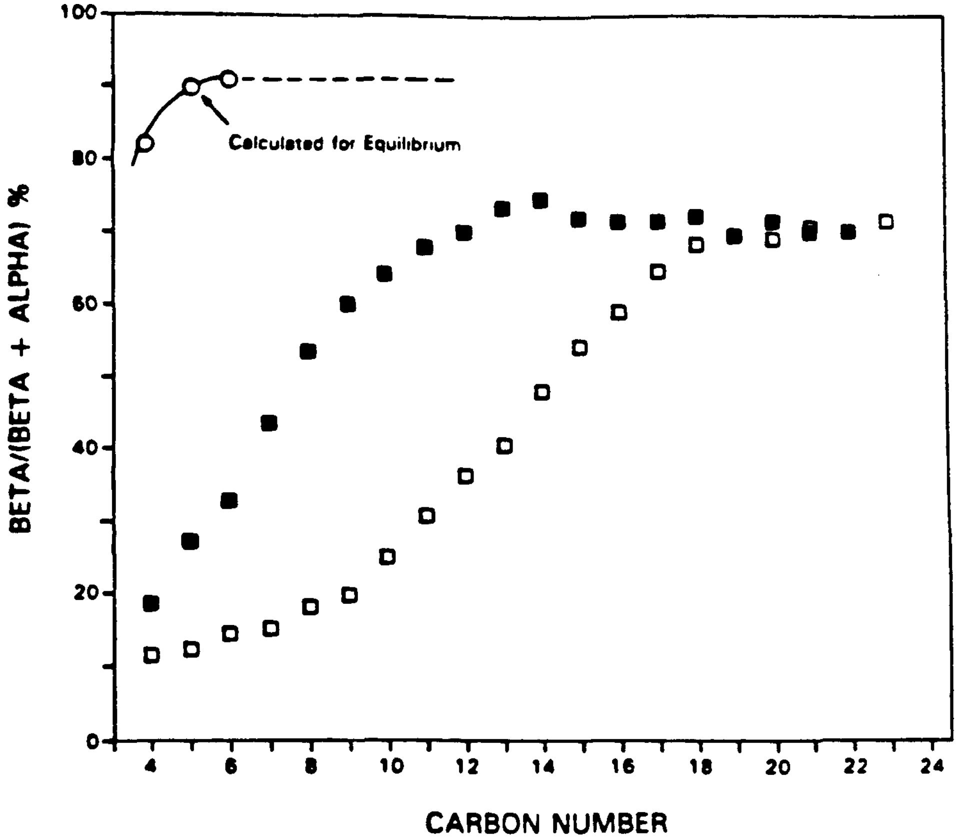

Fig. 4. Percent beta-alkene in the alpha plus beta-alkene products from Fischer-Tropsch synthesis at 1 (APFR; (■)) and 7 (MPSR; (□)) atmosphere conditions (equilibrium values calculated using data in reference 21).

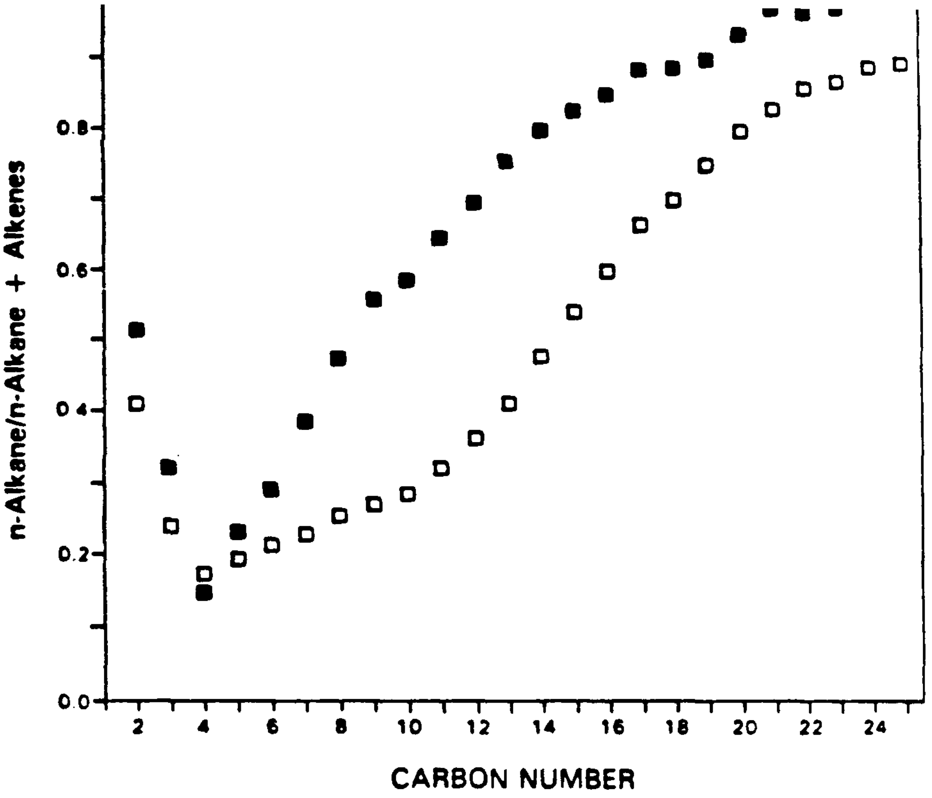

Fig. 5. Fraction of n-alkane in the n-alkane plus 1- + 2-alkene products (from Fischer-Tropsch synthesis at 1 (APFR; (■)) and 7 (MPSR; (□)) atmosphere conditions.

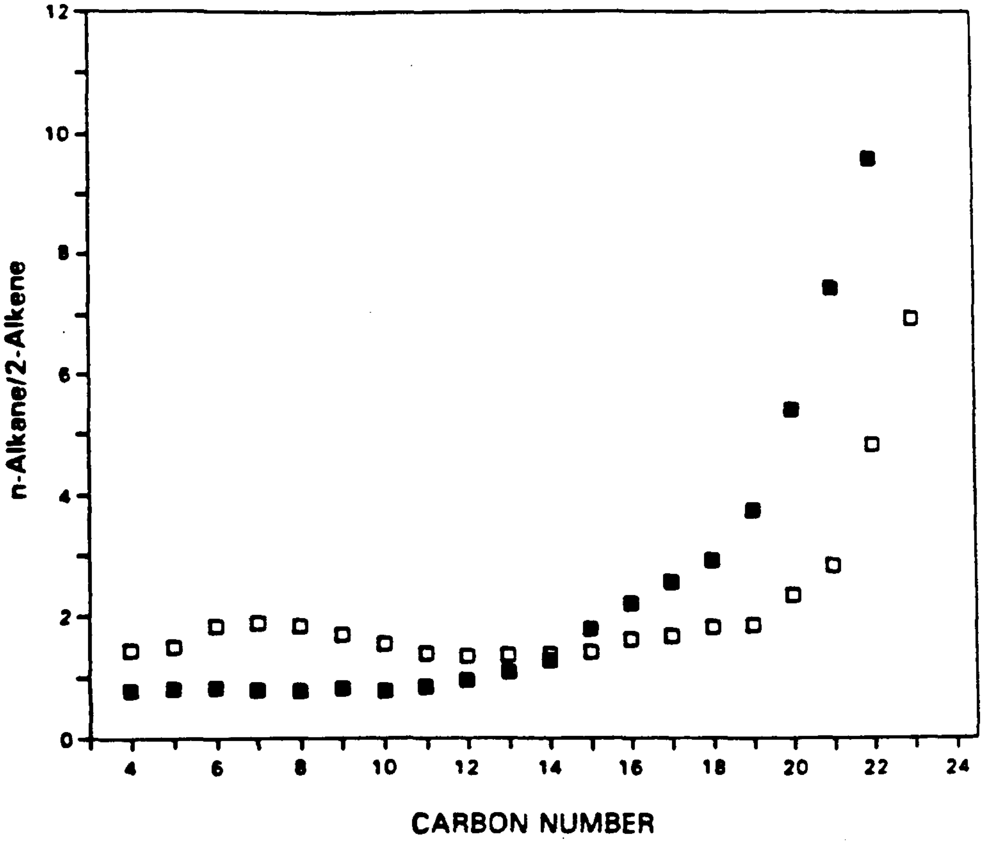

Fig. 6. Ratio of n-alkane/2-alkene for products from the fixed bed (1 atmosphere, (■)) and stirred tank (7 atmosphere, (□)) reactor.

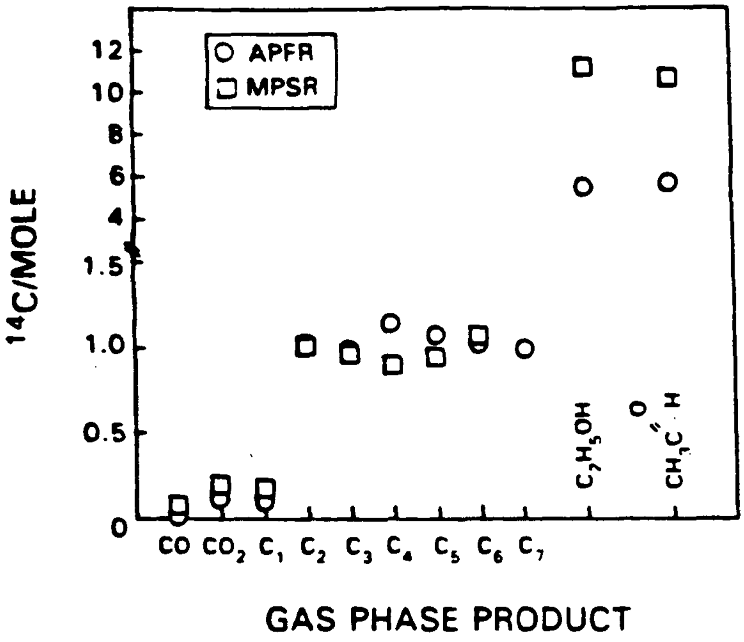

Fig. 7. Relative ^{14}C/mole in the Fischer-Tropsch products in the gas effluent from the fixed bed (○) and stirred tank (□) reactors when ^{14}C labeled ethanol was added to the synthesis gas.

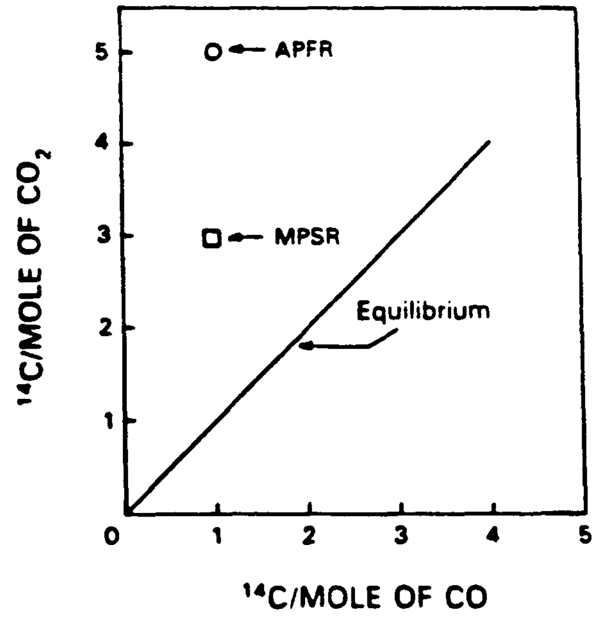

Fig. 8. The ^{14}C activity in the CO and CO_2 from Fischer-Tropsch synthesis at 1 (APFR) and 7 (MPSR) where ^{14}C labeled ethanol was added to the synthesis gas.

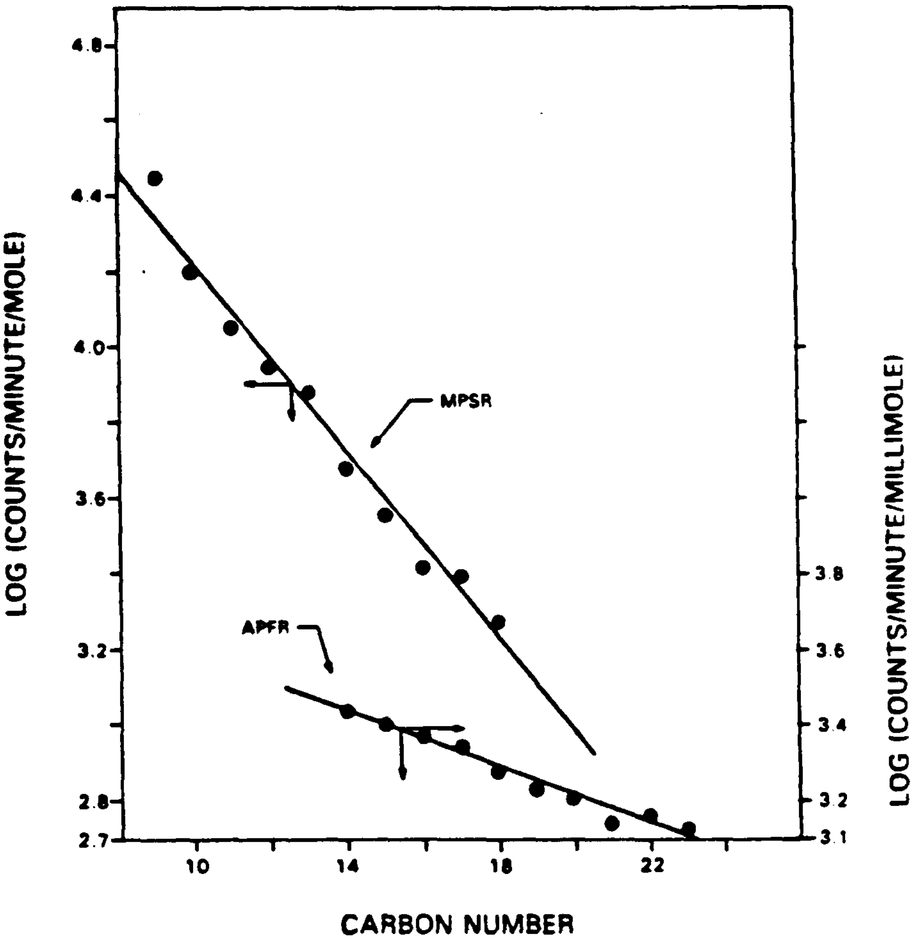

Fig. 9. Relative ^{14}C/mole for higher carbon number alkanes produced during the Fischer-Tropsch synthesis at 1 (APFR) and 7 (MPSR) atmospheres when ^{14}C labeled ethanol was added to the synthesis gas (note the activity of the products from the APFR is on a millimolar basis while those from the MPSR are on a molar basis).

The stirred tank reactor (CSTR) operation presents a number of operational problems for our tracer studies that introduce questions that require answers. One of these is the length of time required to attain a steady state. Data generated at 1 atm. in a plug-flow reactor were compared with those obtained at 7 atm. The data indicate that similar alkene selectivities and carbon number distributions are obtained at 1 atm. and 7 atm. Hence, 1 atm. screening studies are adequate to define the catalyst composition for further isotopic tracer studies. The comparison of ^{14}C in the higher carbon number liquid products (C_{10} to C_{23}) show a similar trend for both the 1 atm. plug flow reactor and the 7 atm. CSTR.

During the quarter runs were made with a FE-ThO_2 catalyst in a fixed-bed reactor at both 1 atm. and 7 atm. as well as in the CSTR at 7 atm. Product analyses are in grogress. Runs for the structural promoter survey have been completed using iron plus silica, alumina,thoria or zirconia and analyses-data reduction is underway. In addition, preliminary runs have been made with iron-potassium and with iron-ThO_2-K catalysts.

Emphasis during the next quarter will be on tracer studies needed to complete the work with the C-73 catalyst and to incorporate tracer compounds to provide data to answer some questions raised by the data generated in our study and literature data.