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The Effect of Water on the  
Iron-Catalyzed Fischer-Tropsch Synthesis

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Abstract

The addition of water vapor to dry synthesis gas to comprise as much as 27 mole% of the feed composition decreased catalyst activity but the effect was completely reversible upon removal of the water vapor. Reversibility was not complete with water addition to comprise 42 mole% of feed. Water vapor decreased methane selectivity, increased oxygenate selectivity and increased the rate of the water gas shift. However these effects did not correlate with the relative  $Fe_5C_2$ ,  $Fe_3O_4$  and Fe content of the bulk catalyst as determined by Mössbauer spectroscopy, although the  $Fe_5C_2$  content did not change greatly. Molecular weight distribution of the  $C_3$ - $C_7$  products was not affected by water.

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**MASTER**

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It is well known that with an iron catalyst containing potassium the rate of the Fischer-Tropsch synthesis is inhibited by water. Water is formed as a primary product which then can react with CO to form CO<sub>2</sub> via the water gas shift. Dry synthesis gas is of itself a reducing gas but as synthesis proceeds the system becomes more oxidizing in character and the iron catalyst surface becomes increasingly converted to an oxide form.

In a recent paper Vogler, et al. (1984) summarize a variety of reports and hypotheses to the effect that an iron oxide surface may have different activity and selectivity characteristics for the Fischer-Tropsch synthesis than a carbided or metallic iron surface. In evaluating the literature it is useful to bear in mind that (1) the presence or absence of potassium in the catalyst has a profound effect on catalyst activity, selectivity and carbon formation, and (2) the course of the synthesis may be considerably different at atmospheric pressure than at pressures of 10 atmospheres or more, typical of industrial conditions. Moreover, it is not clear in several cases whether reported changes in activity were really caused by chemical alteration of the catalyst surface or by a change in surface area of the catalyst.

It is also useful to distinguish between effects occurring during the initial activation period, when the catalyst undergoes considerable reconstruction, and subsequent effects when the catalyst has reached steady-state activity. With an industrial type catalyst prereduced initially to metallic iron, contact with synthesis gas under reaction conditions usually results in a gradual increase in activity until steady-state is approached in typically 20-40 hours.

Water inhibits the synthesis rate much more than does CO<sub>2</sub> (Tramm, 1952; Brötz and Rottig, 1952), so one may speculate that the concentration of H<sub>2</sub>O (or H<sub>2</sub>O/H<sub>2</sub> ratio) is more important than the concentration of CO<sub>2</sub> (or CO<sub>2</sub>/CO

ratio) in affecting the oxidation state of the catalyst under steady-state conditions. The relative concentrations of  $H_2O$  and  $CO_2$ , however, are governed in large part by the rate of the water-gas-shift reaction relative to that of synthesis. On iron catalysts containing potassium this secondary reaction converting  $H_2O$  to  $CO_2$  occurs rapidly and essentially equilibrium may be reached at the higher synthesis temperatures.

In the present studies the synthesis activity and selectivity with a reduced fused magnetite catalyst were observed upon the addition of water vapor to synthesis gas and its removal, after the catalyst had reached steady-state activity. Studies were carried out in a well-mixed slurry phase reactor, continuous with respect to syngas feed and removal of volatile products. Because the reactor contents are uniform, results can thus be interpreted in a more fundamental fashion than can studies with an integral fixed bed reactor, in which catalyst composition may vary from inlet to exit. Samples of catalyst after being subjected to various environments and for different lengths of time were removed and the bulk phases characterized by Mössbauer spectroscopy. It was thus attempted to relate reaction behaviour to catalyst composition. It is, of course, surface composition rather than bulk that determines catalyst behaviour, but there are considerable difficulties in characterizing the surface of a porous catalyst such as this as it exists under reaction conditions.

Our reactor system has been described previously (Huff and Satterfield, 1982; Huff, et al., 1983) and the behaviour of the same catalyst under a variety of conditions has also been described (Satterfield and Huff, 1982; Huff and Satterfield, 1984). Since most of the water formed by the synthesis reaction may disappear by the water gas shift, the addition of water to the synthesis gas in various concentrations made it possible to enhance the effects that it might cause.

We are aware of only two studies in which synthesis rate and selectivity were correlated with addition and removal of water. Karn et al. (1961) used a 6-8 mesh nitrided fused iron catalyst, prereduced and studied at 2.14 MPa and 240°C with feed gas of  $(H_2/CO) = 1$ . Water vapor concentrations in the feed of up to 30 mole% were studied. In the presence of water,  $CH_4$  selectivity in the products increased markedly with percent conversion but increased only slightly with conversion in the absence of water. At conversions of  $H_2+CO$  below about 20%,  $CH_4$  production was less in the presence of water, but at higher conversions was much greater. These methane selectivity effects seem anomalous in light of more recent work. Dry (1981) reports some effects of water addition on reaction selectivity, discussed later, but at a considerably higher temperature.

In the course of a number of studies on a commercial, promoted fused iron catalyst very similar to ours, Raymond, et al. (1980) reported some brief results. Studies were at 0.1 MPa and 250°C using a 9/1 ratio of  $H_2/CO$ . Addition of water greatly reduced hydrocarbon synthesis. Some activity was recovered upon removal of water but the ratio of  $CH_4/C_2H_6/C_3H_8$  seemed to be about the same at the beginning and end of the experiment.

#### Experimental Section

The catalyst was a fused magnetite (United Catalysts, Inc. C-73-1) sold for ammonia synthesis and reported to contain about 2-3 wt%  $Al_2O_3$ , 0.5-0.8%  $K_2O$ , 0.7-1.2%  $CaO$  and <0.4%  $SiO_2$  on an unreduced basis. The sample used here analyzed 64.4 wt% Fe, 0.76 wt% Al and 0.31 wt% K (Galbraith Labs).

In each of two runs, about 69 grams of crushed catalyst (270-325 mesh) were reduced and then slurried with 419 grams of octacosane. After 325 hours of operation in run 1 and 220 hours of operation in run 2, at which times steady-state was clearly achieved, reaction conditions were set at 248°C, 0.92 MPa,  $(H_2/CO)_{in} = 0.96$ , and a feed flow rate of about 11 L (at S.T.P.)

synthesis gas/min-kg catalyst (unreduced basis). Maintaining these base conditions constant, water was injected continuously into a heated 20' x 1/8" stainless steel Supelco GC column, where it was vaporized and fed into the reactor feed gas line at a fixed rate.

After about 4 hours of constant water addition, at which point steady state catalyst activity and selectivity were observed, a 5-8 hour material balance was made. Then the water addition was shut off and, after at least 12 hours of feeding dry synthesis gas, the catalyst activity was measured again. The sequential alternation between feeding dry synthesis gas and addition of water to the syngas was performed for different increasing concentrations of water.

The catalyst sampling system was purged first by removing about 2.5 grams of slurry containing about 0.4 grams of catalyst from the reactor using a slurry sampling tube, and this was discarded. A second slurry sample of the same size was then taken, and once solidified, it was transferred to a plastic container and later analyzed by Mössbauer spectroscopy.

Catalyst samples were taken of the freshly reduced catalyst after it was put into the reactor, of the catalyst after it had reached steady state but before the first addition of water and again at the end of each period of water addition and at the end of each recovery period in contact with dry feed gas. A third brief run was made at the same temperature and pressure but with  $(H_2/CO)_{in} = 0.52$ . No catalyst samples were taken during this run.

Mössbauer Spectroscopy: The catalyst was characterized using a conventional constant acceleration Mössbauer spectrometer operating in time mode. The source was ~100 mCi  $Co^{57}$  in a rhodium matrix. The spectrometer was calibrated with a thin metallic natural iron foil. Measurements were made at room temperature in most cases. Data were collected over long periods of time to assure satisfactory statistics. Typically,  $5-10 \times 10^6$  counts/channel were collected over

512 channels.

The spectra were analyzed by assuming a superposition of iron sites. The Mössbauer parameters for each component spectrum were obtained by least-squares fitting of the experimental points to simulated theoretical Mössbauer spectra. Assuming similar recoil-free fractions (f-factors) for the different spectral components, the relative concentration of the different iron subsites in the sample were calculated from the area under the curve of each component.

### Results and Discussion

A. Phase Composition of Catalyst: Three phases of iron were identified in the catalyst, namely  $\alpha$ -Fe, magnetite ( $\text{Fe}_3\text{O}_4$ ), and iron carbide ( $x\text{-Fe}_5\text{C}_2$ ). The Mössbauer parameters of these phases are shown in Table 1 and agree well with data in the literature.

In addition to these well identified components, a poorly resolved quadrupole doublet at the center of the spectra of about 2% of the total absorption area was observed in the spectra of samples exposed to  $\text{H}_2\text{O}$ . The Mössbauer parameters of the doublet ( $\delta = 0.23$  mm/sec relative to metallic iron at room temperature and  $\Delta E_Q = 1.08$  mm/sec) are typical of ferric high-spin compounds. The quadrupole doublet persisted at low temperatures, indicating that this component remains paramagnetic down to 4.2 K. No identification of this doublet with a unique iron compound was possible. Amelse et al. (1978) also noted the appearance of a central doublet in the Mössbauer spectra of their  $\text{Fe/SiO}_2$  catalyst during Fischer-Tropsch synthesis studies and concluded that the central doublet probably represents superparamagnetic carbide.

A(1). Run 1: The effect of water addition and removal on the Mössbauer spectra of the iron catalyst is shown in Figure 1. The phase compositions corresponding to these Mössbauer spectra are shown in Figure 2, except for

the initial sample (Sample A). This initial sample was taken from the reactor before start-up and found to be 100%  $\alpha$ -Fe, indicating that complete reduction was achieved and that the sampling technique was satisfactory (i.e., no air contamination occurred).

Referring to Figure 2, after 325 hours on stream, the catalyst consisted mostly of  $\chi$ - $\text{Fe}_5\text{C}_2$  (Hägg carbide) and smaller amounts of  $\text{Fe}_3\text{O}_4$  and  $\alpha$ -Fe (Sample A-1). This result is consistent with other Fischer-Tropsch studies by Anderson et al. (1951) and Dry (1981) on potassium promoted fused-iron catalysts that show the used catalyst to contain the same three phases. (In Anderson's study and in some other earlier studies, Hägg carbide was assigned the formula  $\text{Fe}_2\text{C}$ .)

At 325 hours water was added to comprise 12 mole% of the feed and at 338 hours (time B) a catalyst sample was removed and analyzed. This first addition of water caused an increase in the amounts of both  $\alpha$ -Fe and  $\text{Fe}_3\text{O}_4$  in the catalyst at the expense of  $\text{Fe}_5\text{C}_2$  (sample B). Water addition was then stopped and 12 hours later catalyst sample A-2 was taken. The phase change due to water was only partly reversed during this time. While the  $\chi$ - $\text{Fe}_5\text{C}_2$  content increased back towards its base case value and the  $\alpha$ -Fe content decreased below its base case value, the  $\text{Fe}_3\text{O}_4$  content actually increased further away from its base case value.

The second addition of water, starting at 350 hours, caused an additional increase in the  $\text{Fe}_3\text{O}_4$  content while the  $\alpha$ -Fe content decreased and the  $\text{Fe}_5\text{C}_2$  content decreased slightly (sample C). At 360 hours water was removed from the feed, but 37 hours later the catalyst showed no major change in phase composition except for a slight decrease in  $\alpha$ -Fe content (sample A-3).

At 397 hours water addition was commenced to comprise 42 mole% of the feed. Sample D, removed at 406 hours, showed a major increase in  $\text{Fe}_3\text{O}_4$  and



a corresponding decrease in  $\text{Fe}_5\text{C}_2$ , but no change in  $\alpha\text{-Fe}$ . Water addition was then stopped. About 44 hours later, the phase composition of the catalyst (sample A-4) was comparable to the phase composition of the catalyst before the last water addition (sample A-3). This indicates that to some extent the phase changes in this catalyst caused by water are reversible.

A(ii). Run 2: A similar sequence of water addition and removal was repeated in a second run with another sample of the same catalyst, using two lower levels of water content in the feed. The main purpose of these experiments was to see whether, by extending the time period in contact with dry feed after water addition was terminated, the catalyst phase composition would return more closely to its original state. The Mössbauer spectra and corresponding phase compositions are shown in Figures 3 and 4 respectively. After 222 hours on stream (Point A1), the catalyst had a similar composition to the catalyst in run 1 after 325 hours on stream (Figure 2, sample A-1).

Referring to Figure 4, the first addition of water to comprise 7 mole% caused an increase in  $\text{Fe}_3\text{O}_4$  at the expense of  $\alpha\text{-Fe}$  while the  $\chi\text{-Fe}_5\text{C}_2$  content remained constant (Point B). Water was then removed from the feed, and 69 hours later a slight increase in  $\chi\text{-Fe}_5\text{C}_2$  was observed together with a small decrease in  $\text{Fe}_3\text{O}_4$  and a large decrease in  $\alpha\text{-Fe}$  (Sample A-2). Compared with the original catalyst (A-1), the catalyst after water addition and removal (A-2) had a significantly lower  $\alpha\text{-Fe}$  and a correspondingly higher  $\text{Fe}_5\text{C}_2$  and  $\text{Fe}_3\text{O}_4$  content.

At 380 hours water was added to comprise 13 mole% of the feed. Sample C taken at 390 hours showed that the catalyst was further oxidized while both the  $\alpha\text{-Fe}$  and  $\chi\text{-Fe}_5\text{C}_2$  content decreased. Water addition was then discontinued. After 96 hours in contact with dry feed, a slight increase in  $\chi\text{-Fe}_5\text{C}_2$  and  $\alpha\text{-Fe}$  content of the catalyst were observed with a corresponding

decrease in  $\text{Fe}_3\text{O}_4$  (sample A-3). Even after this long period the catalyst did not return to its original phase composition.

B. Reaction Rates: The effects of water on the synthesis rate ( $-r_{\text{CO}+\text{H}_2}$ ), the CO consumption rate, and the  $\text{CO}_2$  formation rate are shown in Figure 5 for run 1. As can be seen, water is for the most part a reversible inhibitor for the synthesis reaction. For each increase in the water content of the feed there was a corresponding decrease in the synthesis rate (compare B, C, D to A-1). After each of the first two water additions and removal, the reaction rate returned to its baseline value (compare A-1, A-2, and A-3). After the final water addition and removal, the Fischer-Tropsch reaction rate (A-4) returned to 85% of its baseline value.

Karn, et al. (1961) likewise showed that the inhibiting effect of water at, e.g. 10 mole%, was reversible while noting that water or  $\text{CO}_2$  at high concentrations over a prolonged period will cause a permanent loss of activity. This is most likely due to sintering. Thus, in the use of fused magnetite catalysts in ammonia synthesis, during reduction the water vapor formed is held below a specified concentration to minimize loss of activity in the subsequent synthesis.

A kinetic expression for the synthesis rate on this catalyst has been recently developed (Huff and Satterfield, 1984):

$$-r_{\text{H}_2+\text{CO}} = \frac{ab' p_{\text{CO}} p_{\text{H}_2}^2}{p_{\text{H}_2\text{O}} + b' p_{\text{CO}} p_{\text{H}_2}} \quad (1)$$

where  $a$  and  $b'$  are functions of temperature.  $\text{H}_2\text{O}$  is a strong inhibitor of the synthesis reaction but it can react with CO present by the water gas shift to generate  $\text{H}_2$  in situ, which is a compensating factor. It is difficult to make meaningful quantitative comparisons between the data here and Eq. 1 because reported low concentrations of  $\text{H}_2\text{O}$  are subject to large

error. Figure 6 gives the actual partial pressures of the permanent gases in the reactor for the various conditions of run 1. The rates observed here are somewhat greater than would be predicted using these partial pressures in Eq. 1, but the observations of decreasing rate with increasing  $H_2O$  fed is the same trend as indicated by Eq. 1.

With run 2, Eq. 1 combined with the observed partial pressures in the reactor predicts about the same activity upon the two additions of water as that observed without  $H_2O$  addition. The increase in activity from A-1 to A-2 (Fig. 7) is anomalous. It possibly is associated with the fact that in run 2 the carbide content of the catalyst increased from A-1 to A-2 whereas it decreased in run 1. Another factor is that even though the catalyst had previously reached steady-state activity, a time-dependency effect may have occurred in these runs upon the sudden introduction of water, reminiscent of some time-dependent effects reported by Frye, et al. (1958).

Iron oxide surfaces are more active for the synthesis than fully reduced metallic iron (Dwyer and Somorjai, 1978; McCartney, et al., 1953). However, metallic iron rapidly disappears upon contact with syngas and the steady-state bulk composition is predominantly oxidic and carbidic. With such a steady-state catalyst an increase in water content decreases catalytic activity, as is indicated by most kinetic expressions that have been developed for the synthesis rate (Tramm, 1952; Brötz and Rottig, 1952; Anderson, 1956; Huff and Satterfield, 1984).

The rate of consumption of CO in run 1 (Figure 5) would appear not to be significantly affected by the concentration of water in the reactor. (The slight decrease in CO consumption under the final set of conditions was most likely caused by the same irreversibility that slightly decreased the synthesis rate.) However, it is likely that this was a happenstance, and that the decrease in the rate of CO consumption in the Fischer-Tropsch

synthesis was approximately equal to the increase in the rate of CO consumption in the water-gas-shift reaction. Thus Figure 5 shows that the rate of CO<sub>2</sub> formation increased proportionately to the increase in water concentration in the feed.

Under other conditions the net rate of CO consumption definitely varies with the amount of water present. For example, in Run 3, some effects of water addition were determined under another set of synthesis conditions, 248°C, 0.92 MPa, (H<sub>2</sub>/CO) feed ratio of 0.52 and SV = 1160 hr<sup>-1</sup> (volume of entering synthesis gas (STP dry basis) per packed volume of catalyst before reduction, per hour). As shown in Table 2, upon the addition of water to cause an eight-fold increase in its concentration, the conversion of CO increased from 67% to 91%. (The degree of conversion of H<sub>2</sub>+CO here happened to remain constant because of two countervailing effects. Inhibition of the reaction by water was offset by the increased H<sub>2</sub> concentration caused by the increased water gas shift.)

B(i). Relationship to Phase Composition: Catalyst samples A-1, A-2, and A-3 in Figure 2 (run 1) all show the same Fischer-Tropsch activity under identical operating conditions despite significant differences in the  $\alpha$ -Fe and Fe<sub>3</sub>O<sub>4</sub> content of the catalyst. Since the  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> content of samples A-1, A-2 and A-3 remained relatively constant, it might be thought that the activity of the catalyst correlates with its iron carbide content. The results of run 2, shown in Figures 4 and 7 are less clear cut. After the first water addition and removal the activity of the catalyst (sample A-2) was 13% greater than before water addition (sample A-1). Correspondingly the Fe<sub>5</sub>C<sub>2</sub> content was about 6% higher for sample A-2 than for sample A-1. However, after the second water addition and removal, the catalyst activity (sample A-3) was approximately equal to the activity before water addition (sample A-2), but the iron carbide content was 13% lower.

A number of previous studies have attempted to relate activity and selectivity to catalyst surface or bulk composition but no clear-cut correlations have as yet emerged. Several studies have attempted to correlate the catalyst activity to bulk phase composition by reporting on the changing catalyst composition and activity during the initial induction period. Other studies, conducted after the initial induction period, have shown the  $\alpha$ -Fe content of a catalyst to decrease with time and the  $\text{Fe}_3\text{O}_4$  to increase but with no accompanying change in activity or selectivity (Anderson, et al., 1951; Loktev, et al., 1973; McCartney, et al., 1953). The more proximate effect may be the nature and amounts of carbon surface intermediates on the surface of the catalyst that can vary from an active but unhydrogenated carbon, to species of the type " $\text{CH}_x$ ", or to relatively unreactive graphitic-type carbon.

C. Water-Gas Shift Activity: Figure 8 shows the effect of water on the ratio of rate of formation of  $\text{CO}_2$  to rate of disappearance of CO. This is a measure of the relative activity for the water-gas-shift reaction, which is seen to increase with increased water content in the feed. The same effect upon water addition is reported by Karn, et al. (1961), for reaction on a nitrated iron catalyst containing K at 2.14 MPa and 240°C, and Raymond, et al. (1980) for reaction on a fused iron catalyst at 250°C and 1 atm. Water-gas-shift activity here remained essentially constant in the presence of dry feed gas after successive additions and removal of water (Samples A-1, A-2, A-3, A-4). Comparison of Figures 8 and 2 shows that the water-gas-shift activity is not correlated to the bulk  $\text{Fe}_3\text{O}_4$  concentration in the catalyst; the latter increased by a factor of four over this series of studies.

The nature of the active form of an iron catalyst for the water-gas-shift is still speculative and much of the evidence is circumstantial.

Moreover, the effects may be significantly different with a catalyst at least partially carbided from contact with syngas and a catalyst in contact with the usual gas compositions encountered in the water gas shift reaction as operated industrially. In the latter case the active catalyst form is reported to be  $\text{Fe}_3\text{O}_4$ , based largely on thermodynamic arguments (Sondergaard, 1969).

Kölbl and Engelhardt (1949) working with a precipitated Fe catalyst promoted with Cu and K at 230-270°C, and 1 atm concluded that oxide played no role and that carbide is less active than reduced iron. Shultz et al. (1955) likewise inferred from their studies on fused iron catalysts that carbides are somewhat less active than totally reduced catalysts. Madon and Taylor (1981) working with a precipitated iron catalyst promoted with Cu and K reported a marked drop in  $\text{CO}_2$  formation in the Fischer-Tropsch synthesis as temperature was increased above 240-250°C. They suggested that the decreased rate of the water-gas-shift at higher temperatures was associated with a higher degree of carbide formation and less  $\text{Fe}_3\text{O}_4$ .

In studies with a fused magnetite catalyst at 232°C to 263°C and 790 kPa, however, we observed that the higher the temperature, the closer the approach to equilibrium with no unusual effects in the 240-250°C temperature range (Huff and Satterfield, 1984). Furthermore, in other studies with this catalyst at 232 and 248°C (Satterfield, et al., 1985), we observed that the catalyst attains a steady-state water-gas-shift activity quickly during the induction period ( $t < 15$  hours). No magnetite is observed; only  $\alpha$ -Fe and iron carbide are present.

D. Reactor Gas Composition: In Figure 6 the partial pressures of  $\text{H}_2$ , CO,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the reactor are shown as a function of the water content in the feed, for the various conditions in run 1. The addition of  $\text{H}_2\text{O}$  to

comprise 12 mol% in the feed caused the partial pressure of  $H_2$  to increase, the partial pressure of CO to decrease, and the partial pressure of  $H_2O$  to increase slightly. Subsequent additions of water did not significantly change the partial pressures of  $H_2$  and CO but they did significantly increase the partial pressure of  $H_2O$ . Thus, the effects of water on the Fischer-Tropsch selectivity data and the iron phase composition data were essentially isolated in the three water addition experiments, since the partial pressure of  $H_2O$  changed while the partial pressures of  $H_2$  and CO remained essentially constant. (The observed decrease in  $CO_2$  partial pressure caused by  $H_2O$  addition to the feed is not believed to have affected the synthesis or the phase composition of the catalyst for reasons discussed earlier.)

E. Carbon Number Distribution: Figure 9 is a Flory plot of the  $C_1$ - $C_6$  molar product distributions for run 1, for the base case with no water addition and for each of three subsequent water additions. The anomalies that sometimes occur in the selectivities of the  $C_1$  and  $C_2$  fractions are evident. There is little effect on the  $C_3$ - $C_6$  product distribution of the large increase in the partial pressure of water. The value of  $\alpha$  as determined from the product distribution changed only slightly, increasing from a value of 0.60 in the absence of added water to a value of 0.62 with the addition of the maximum amount of water.

#### F. Product Selectivity

F(1). Methane: In Figure 10, the methane selectivity, defined as the molar ratio of methane to the  $C_1$ - $C_6$  fraction, is shown as a function of the water content in the feed, from the data of run 1. The first level of water addition caused the methane selectivity to increase very slightly while the two subsequent water additions caused the methane selectivity to decrease significantly. The initial slight increase in methane selectivity was accompanied by a more reducing atmosphere in the reactor, as the  $p_{H_2}/p_{CO}$

ratio increased from 3.2 to 8.6 while the partial pressure of water increased only slightly. The decrease in methane selectivity with subsequent water additions is associated with an increase in  $p_{H_2O}$  at essentially constant  $p_{H_2}$  and  $p_{CO}$ .

In Run 3 (Table 2) addition of water to cause a substantial increase in the ratios of both  $H_2O/H_2$  and  $CO_2/CO$  still produced no drop in  $CH_4$  selectivity. However, the  $(H_2/CO)$  ratio in the syngas feed was unusually low, below the consumption ratio, and a substantial deposit of carbon could have previously occurred. The doubling of  $H_2$  partial pressure upon addition of water could then have caused increased formation of  $CH_4$ .

There is little other information on methane selectivity with which to compare these results. The early studies of Karn, et al. (1961) are difficult to interpret. Dry (1981, p. 225) reported no significant change in methane selectivity in studies of water addition to comprise up to 17% using a promoted, fused-iron catalyst in a fluidized bed at 320°C, and 2.1 MPa and  $(H_2/CO)_{in}$  of about 5.5. However the Fischer-Tropsch synthesis seems to proceed in a substantially different way at 320°C than at the temperatures of 232 to 263°C which we have used in our various studies on this catalyst. In this lower temperature range and at pressures up to 1.5 MPa, the highest studied, we saw no significant effect of degree of conversion on methane selectivity, for CO conversions up to 90% or more.

F(ii). Oxygenate Selectivity: In Figure 11, the mole fraction of oxygenated compounds formed at each of 3 carbon numbers (run 1) is seen to increase with water content in the feed, and especially for the  $C_2$  fraction. Since the  $Fe_3O_4$  content of the catalyst presumably increased with increased water partial pressure, selectivity could be favored by the presence of magnetite. However, in run 2, there was no trend in the ratio of  $C_2$  oxygenates to  $C_2$  hydrocarbons with the change in bulk composition corresponding to A-1, A-2 and A-3.



F(1ii). Olefin/Paraffin Selectivity. In Figure 12 the effect of the mole fraction of water in the feed on the olefin ( $\alpha+\beta$ )/paraffin ratio for three carbon species is shown. An increase in water significantly increases the olefin/paraffin ratio for the  $C_2$  fraction and increases, but to a lesser extent, the ratio for the  $C_3$  and  $C_5$  fraction. Dry (1981) likewise noted an increase in the ethylene/ethane ratio upon addition of water, on a fused iron catalyst. Plausibly the change in catalyst composition inhibited the readsorption and hydrogenation of the primary  $\alpha$ -olefin products. However, the partial pressures of the olefins also decreased. That of  $C_2H_4$ , for example, decreased from 6.2 kPa atm with dry syngas feed to 1.2 kPa at the highest  $H_2O$  concentration. This large decrease in olefin concentration could have reduced secondary hydrogenation.

F(1v).  $\beta$ -olefin/ $\alpha$ -olefin Selectivity: In Figure 13, the effect of water on the  $\beta$ -olefin/ $\alpha$ -olefin ratio is shown for the  $C_4$  and  $C_6$  species. An increase in water significantly decreased the ratio at both carbon numbers. As with olefin hydrogenation water inhibits the readsorption and isomerization of the  $\alpha$ -olefins, which are the primary product, but again the effect could have been caused at least in part by the decreased  $\alpha$ -olefin concentration.

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Table 1. Mössbauer Parameters of Catalyst Components at Room Temperature

Catalyst Component	Fe site	This Study		Literature Data		ref.
		I.S. (mm/s) <sup>a</sup>	H <sub>eff</sub> (kOe)	I.S. (mm/s) <sup>a</sup>	H <sub>eff</sub> (kOe)	
α-Fe		0	330	0	330	d
X-Fe <sub>5</sub> C <sub>2</sub>	I	0.21 ± 0.03	187 ± 3	0.18 ± 0.03 <sup>b</sup>	189 ± 2	e
	II	0.30 ± 0.03	216 ± 3	0.26 ± 0.03 <sup>b</sup>	218 ± 2	
	III	0.25 ± 0.03	107 ± 3	0.22 ± 0.03 <sup>b</sup>	110 ± 5	
ε'-Fe <sub>2.2</sub> C(g)		0.28 ± 0.03	170 ± 3	0.25 ± 0.03 <sup>b</sup>	173 ± 2	a
Fe <sub>3</sub> O <sub>4</sub>	I	0.32 ± 0.03	504 ± 3	0.36 ± 0.01 <sup>c</sup>	500 ± 20	f
	II	0.68 ± 0.03	470 ± 3	0.61 ± 0.01 <sup>c</sup>	450 ± 20	

<sup>a</sup> reference to α-Fe

<sup>b</sup> isomer shifts referenced from sodium nitroprusside (SNP) to metallic iron

<sup>c</sup> isomer shifts referenced from stainless steel to metallic iron

<sup>d</sup> Greenwood and Gibb (1971)

<sup>e</sup> Niemantsverdriet et al. (1980)

<sup>f</sup> Bauminger et al. (1961)

<sup>g</sup> This component was identified in a study described in an accompanying paper (Satterfield, et al., 1985).

TABLE 2

EFFECT OF WATER ADDITION ON CONVERSION  
AND METHANE SELECTIVITY. RUN 3(T = 248°C, P = 0.916 MPa,  $(\text{H}_2/\text{CO})_{\text{in}} = 0.52$ , SV = 1160 hr<sup>-1</sup>)

Mole Fraction H <sub>2</sub> O in Feed	Conversion			Reactor composition, MPa				$\frac{\text{CH}_4}{\text{C}_1-\text{C}_6}$
	$x_{\text{H}_2+\text{CO}}$	$x_{\text{H}_2}$	$x_{\text{CO}}$	$P_{\text{H}_2}$	$P_{\text{CO}}$	$P_{\text{H}_2\text{O}}$	$P_{\text{CO}_2}$	
0	69	72	67	0.15	0.34	0.009	0.35	0.32
20	69	28	91	0.31	0.077	0.080	0.38	0.31

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### Figure Captions

- Figure 1 Mossbauer spectra of Run 1 catalyst samples:  
A - After reduction before reaction; A-1, A-2, A-3, A-4, no water in feed; B - 12 mole% H<sub>2</sub>O in feed; C - 27 mole% H<sub>2</sub>O in feed; D - 42 mole% H<sub>2</sub>O in feed. The six identifications shown for the A-1 spectrum represent, from top down, the Fe sites I and II in Fe<sub>3</sub>O<sub>4</sub>, α-Fe, and the Fe sites II, I and III in Fe<sub>5</sub>C<sub>2</sub>.
- Figure 2 Effect of H<sub>2</sub>O on Bulk Catalyst Phase Composition (Run 1) (SV = 1860 hr<sup>-1</sup>)
- Figure 3 Mossbauer spectra of Run 2 catalyst samples:  
A-1, A-2, A-3, no water in feed; B - 7 mole% H<sub>2</sub>O in feed; C - 13 mole% H<sub>2</sub>O in feed.
- Figure 4 Effect of H<sub>2</sub>O on Bulk Catalyst Phase Composition (Run 2) (SV = 2000 hr<sup>-1</sup>)
- Figure 5 Effect of H<sub>2</sub>O on Reaction Rate, Run 1
- Figure 6 Effect of H<sub>2</sub>O in Feed on Partial Pressures of Permanent Gases in Reactor, Run 1
- Figure 7 Effect of H<sub>2</sub>O on Synthesis Rate, (Run 2)
- Figure 8 Effect of H<sub>2</sub>O on Water Gas Shift, Run 1
- Figure 9 Effect of H<sub>2</sub>O on the Carbon Number Product Distribution, Run 1.
- Figure 10 Methane Selectivity Drops with Increased Water Concentration, Run 1.
- Figure 11 Oxygenate Concentrations Increase with Increased Water Concentration, Run 1.
- Figure 12 Olefin Hydrogenation Decreases Upon Addition of Water; C<sub>5</sub> is sum of α and β olefins, Run 1.

Figure 13

$\alpha$ -Olefin Isomerization Decreases with Increased  
Water Concentration, Run 1.



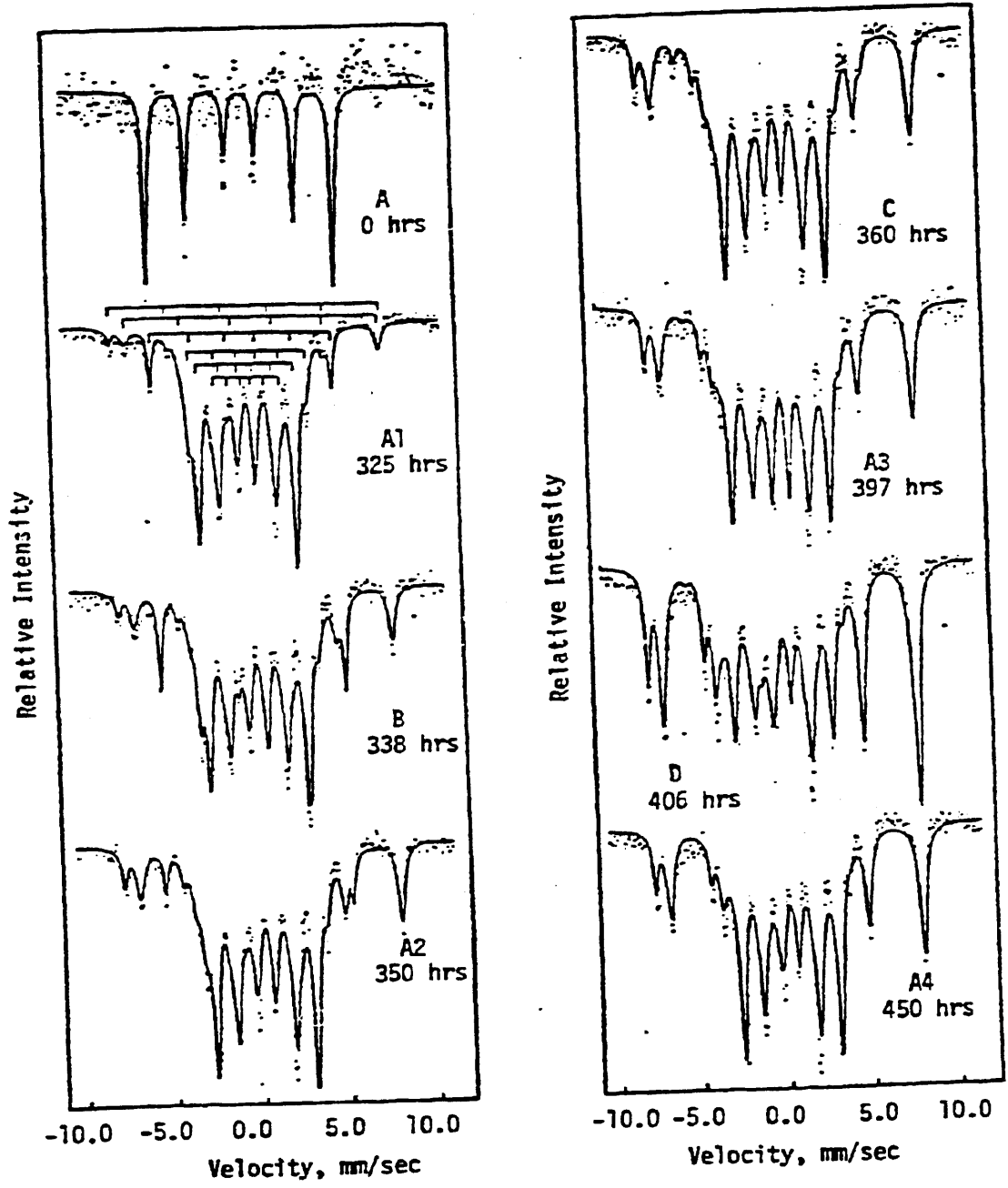


FIG. 1

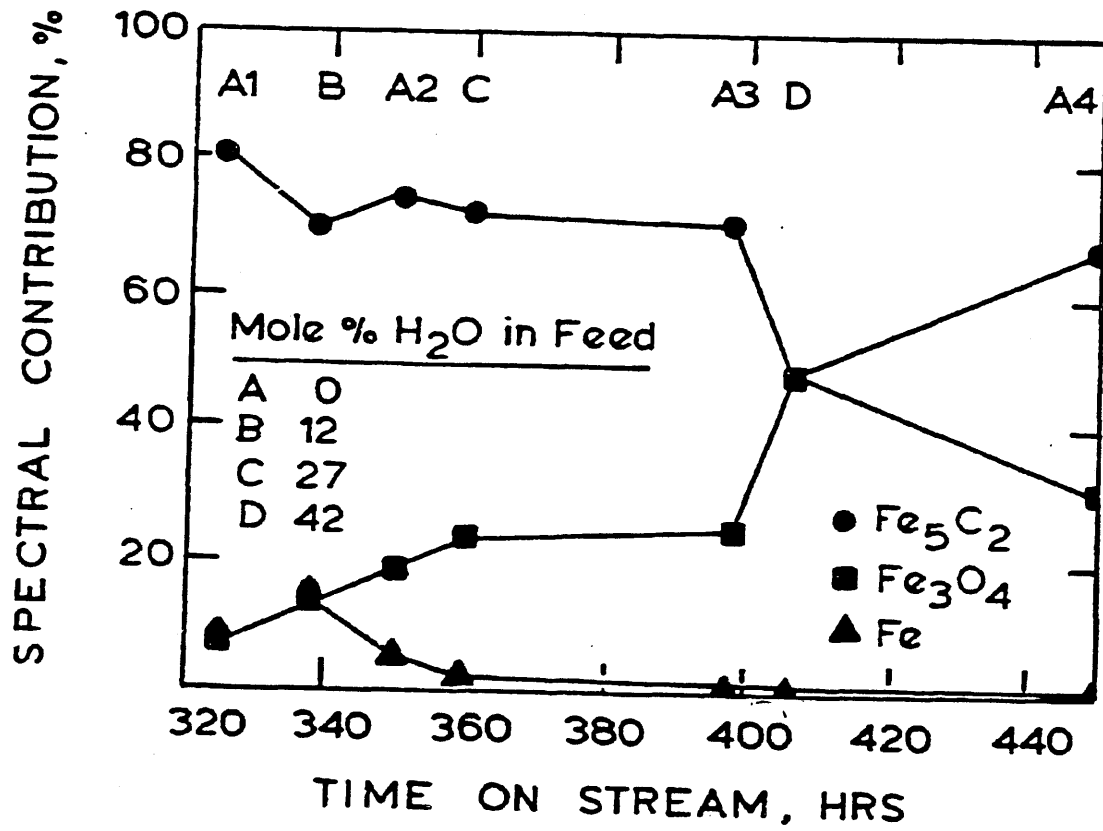


FIG. 2

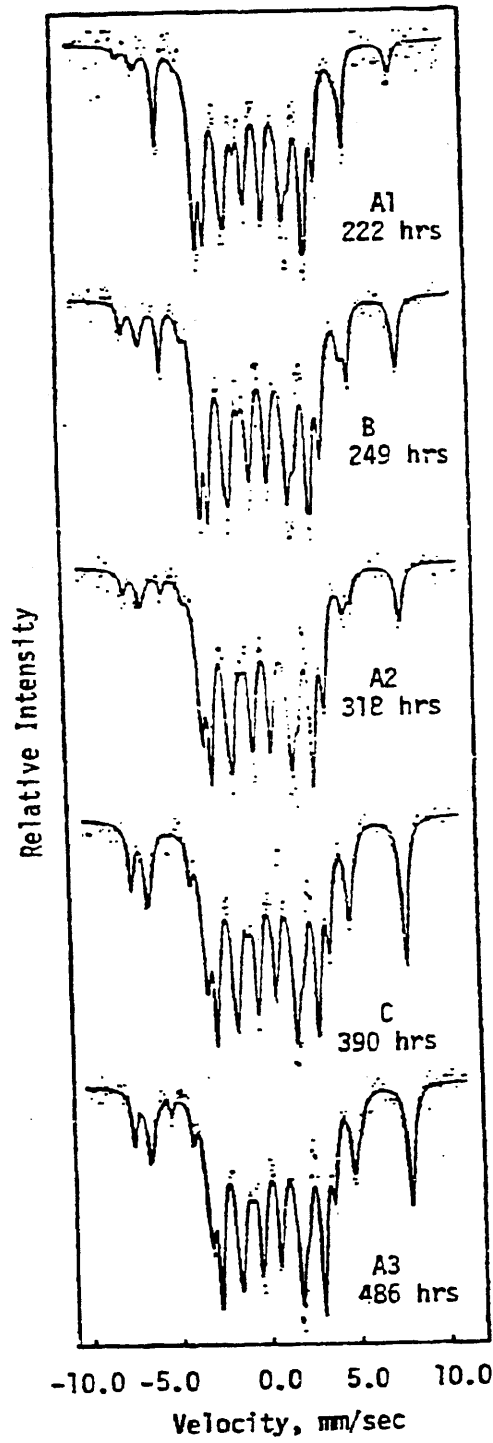


FIG. 3

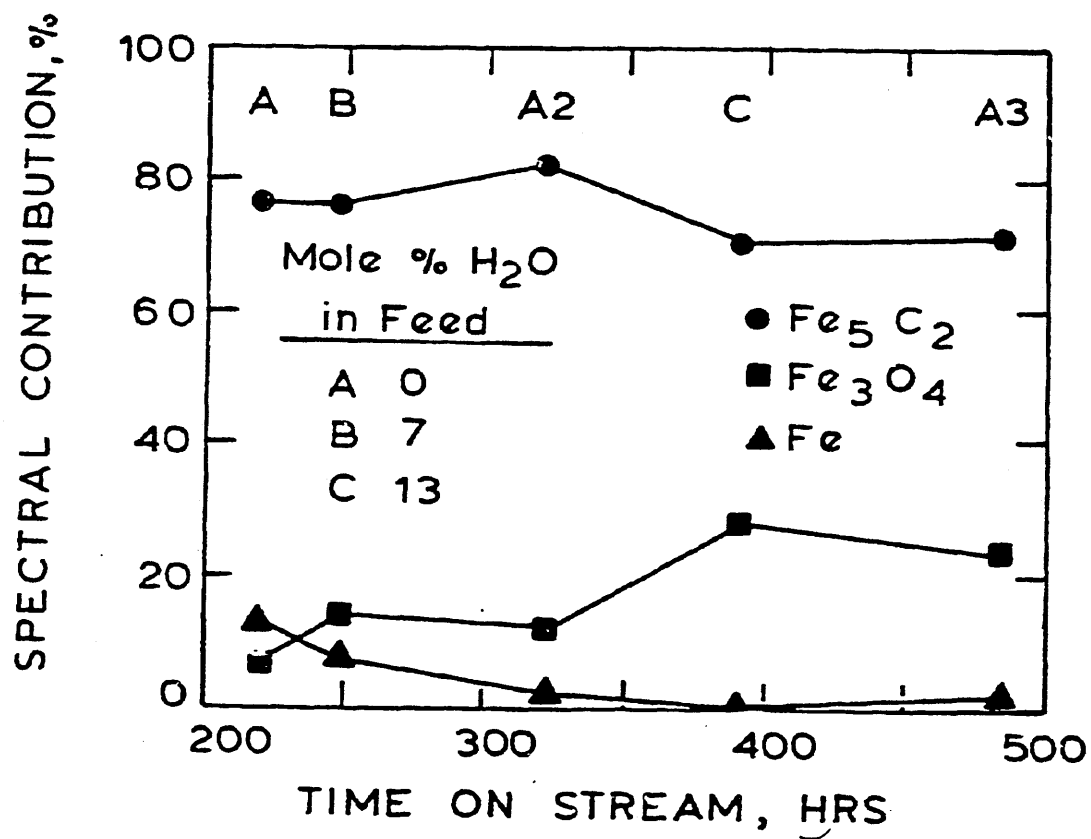


FIG. 7

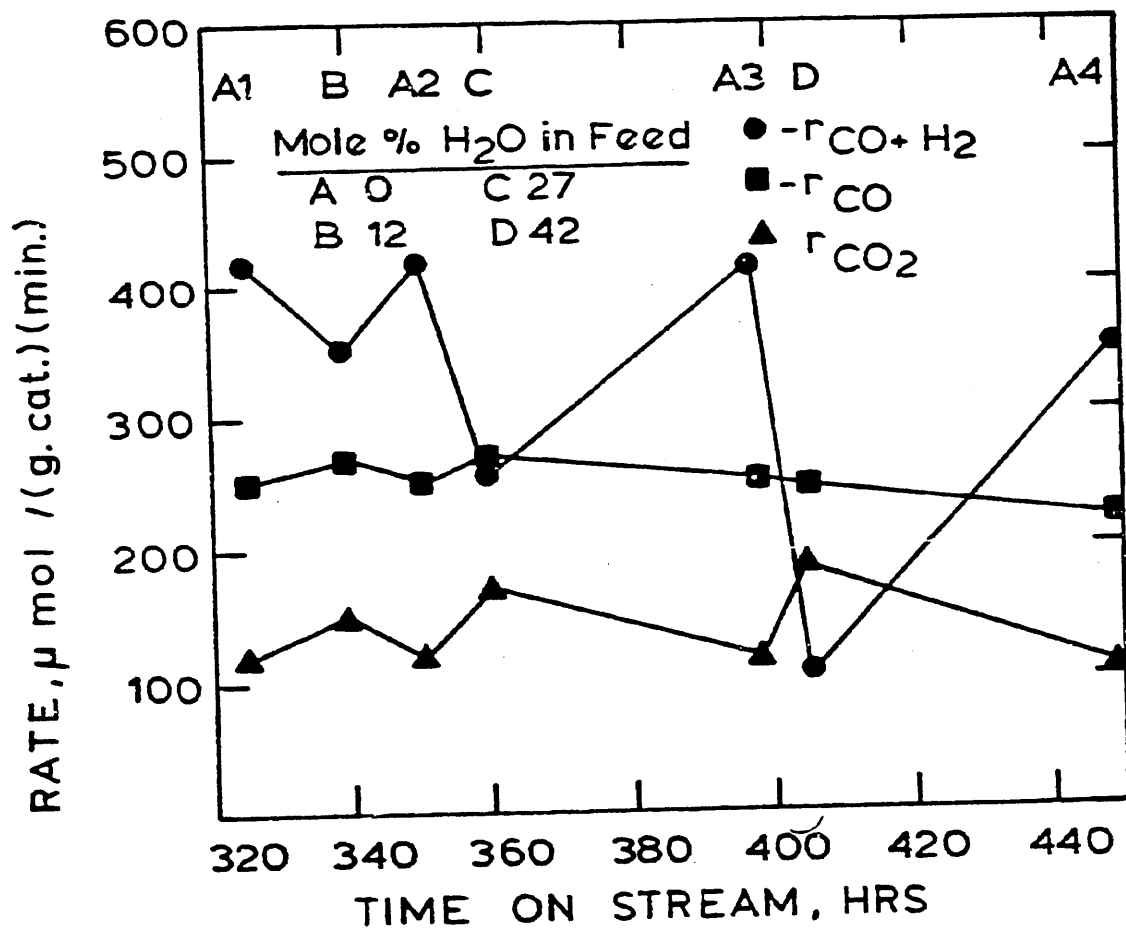


FIG. 5

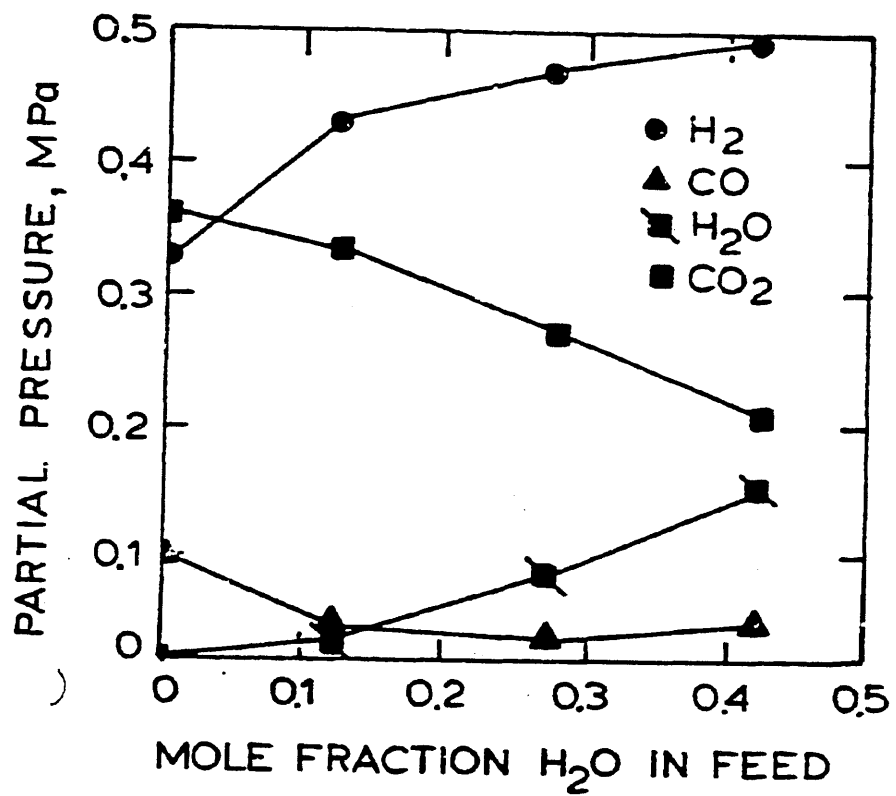


FIG. 6

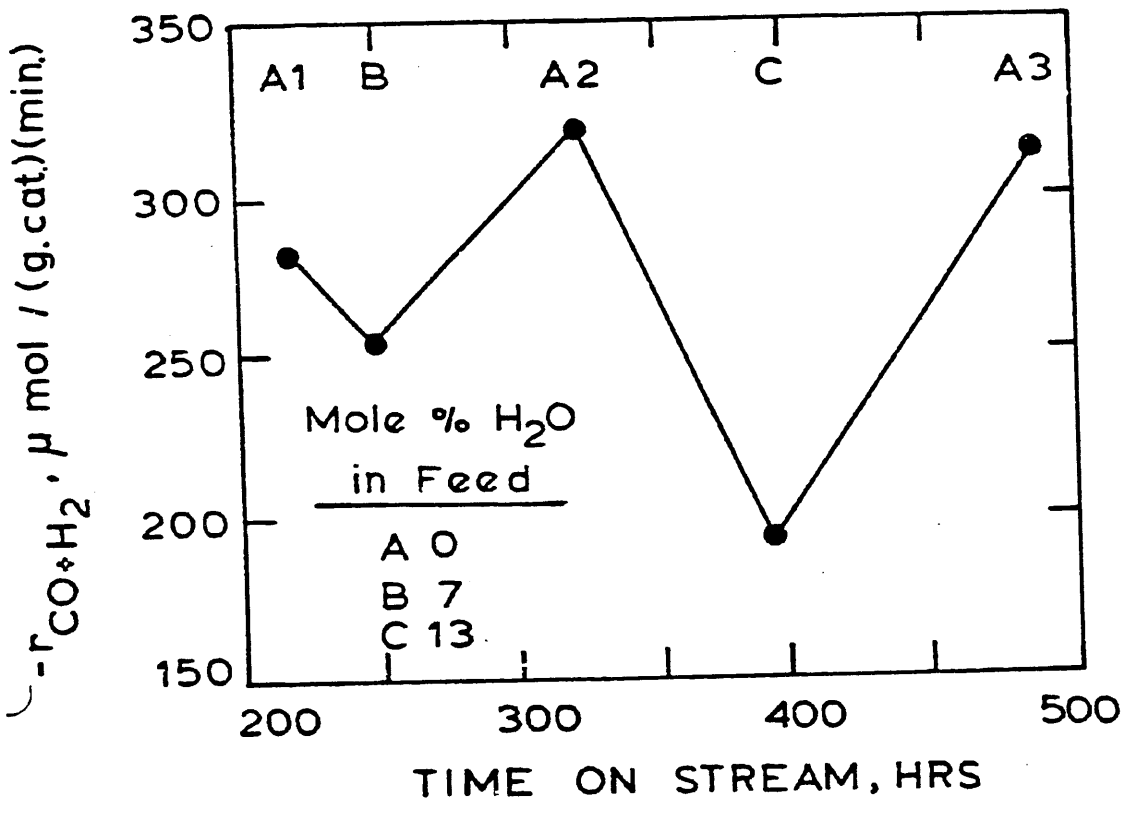


FIG. 7

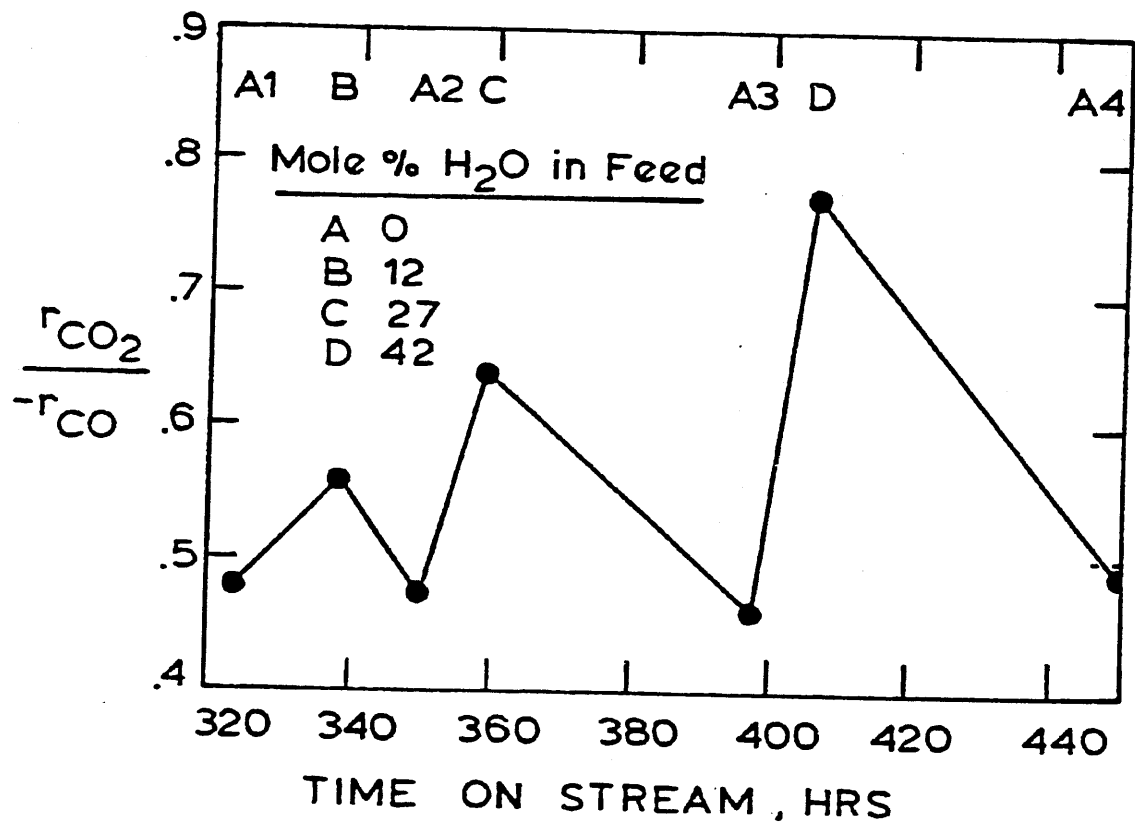


FIG. 8



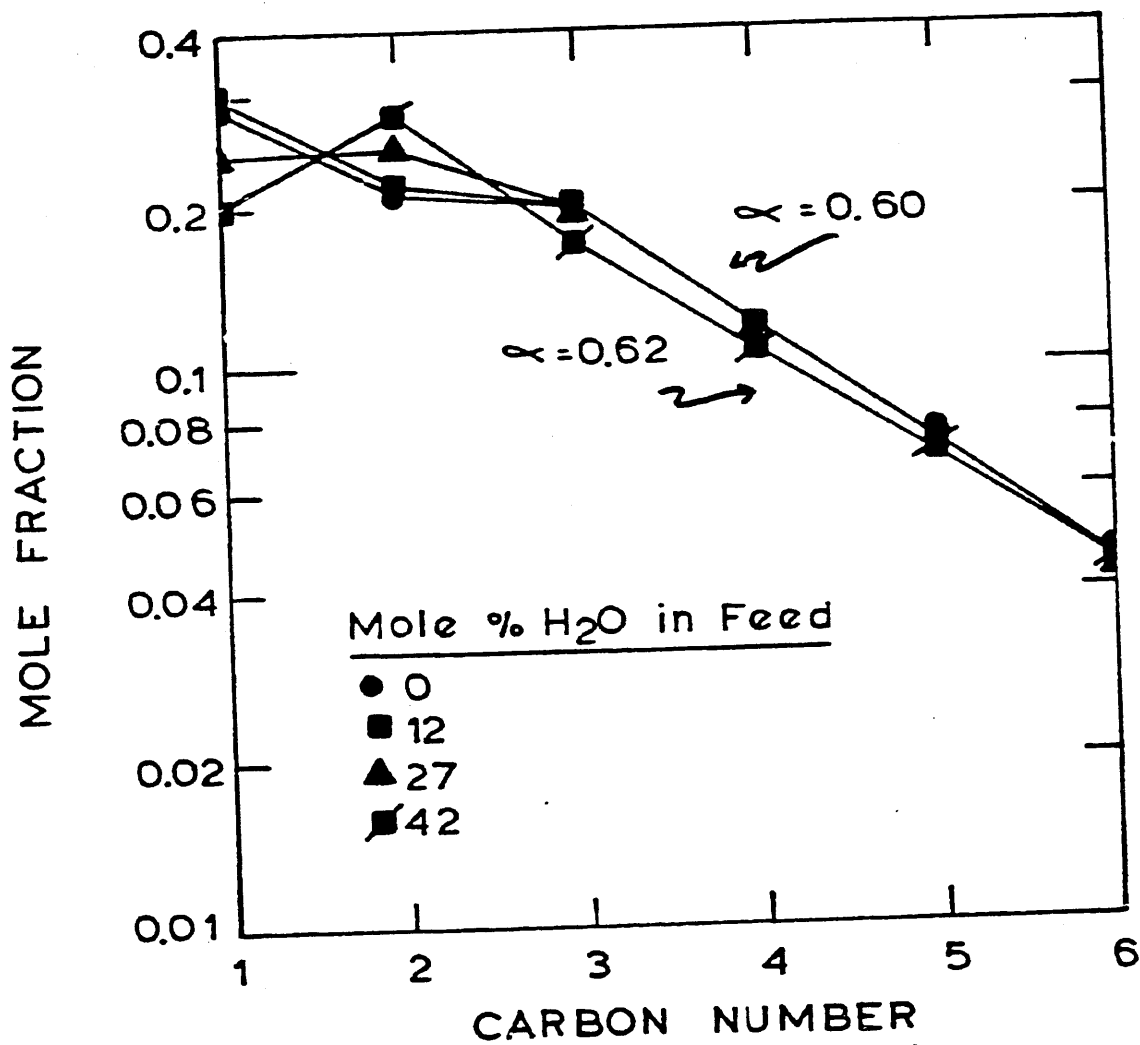


FIG. 9

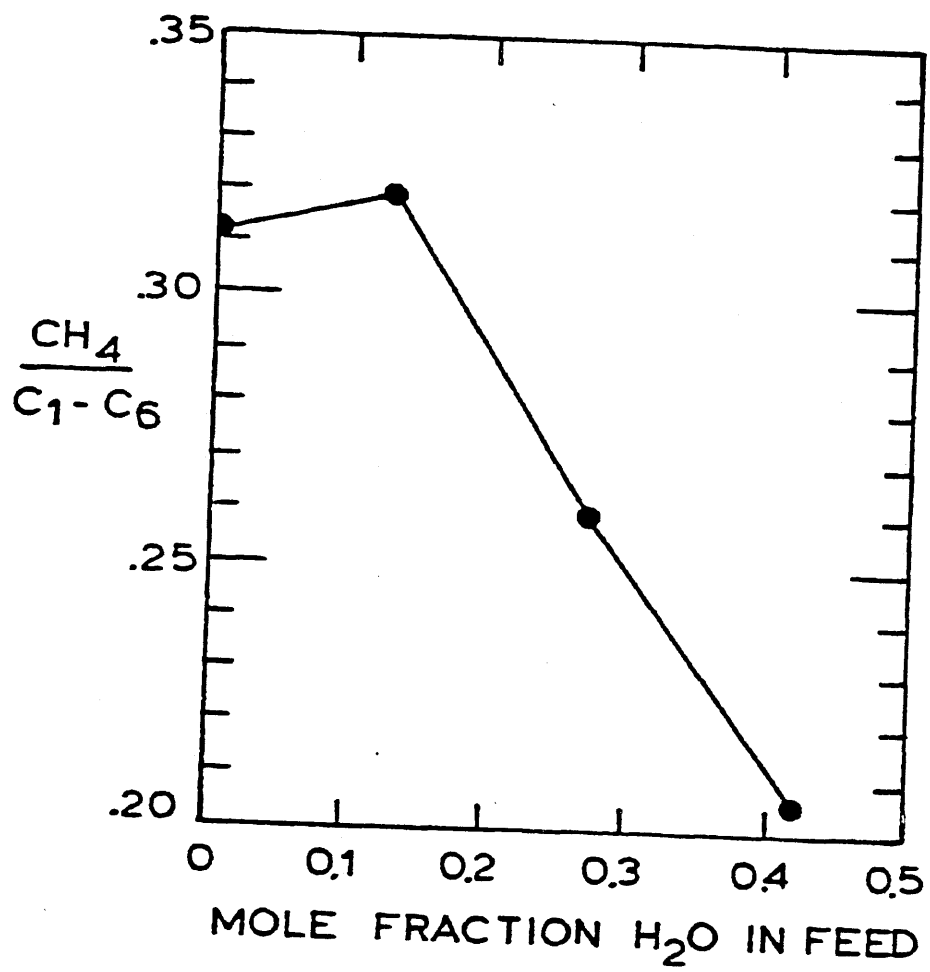


FIG. 10

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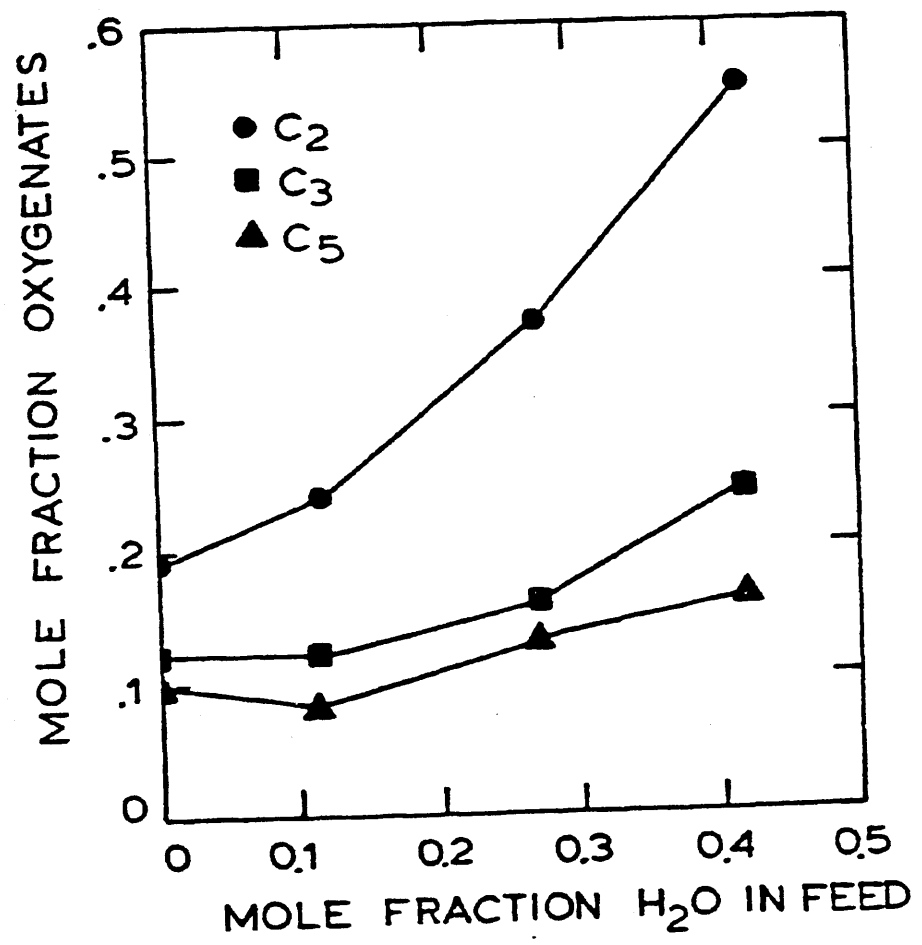


FIG. 11

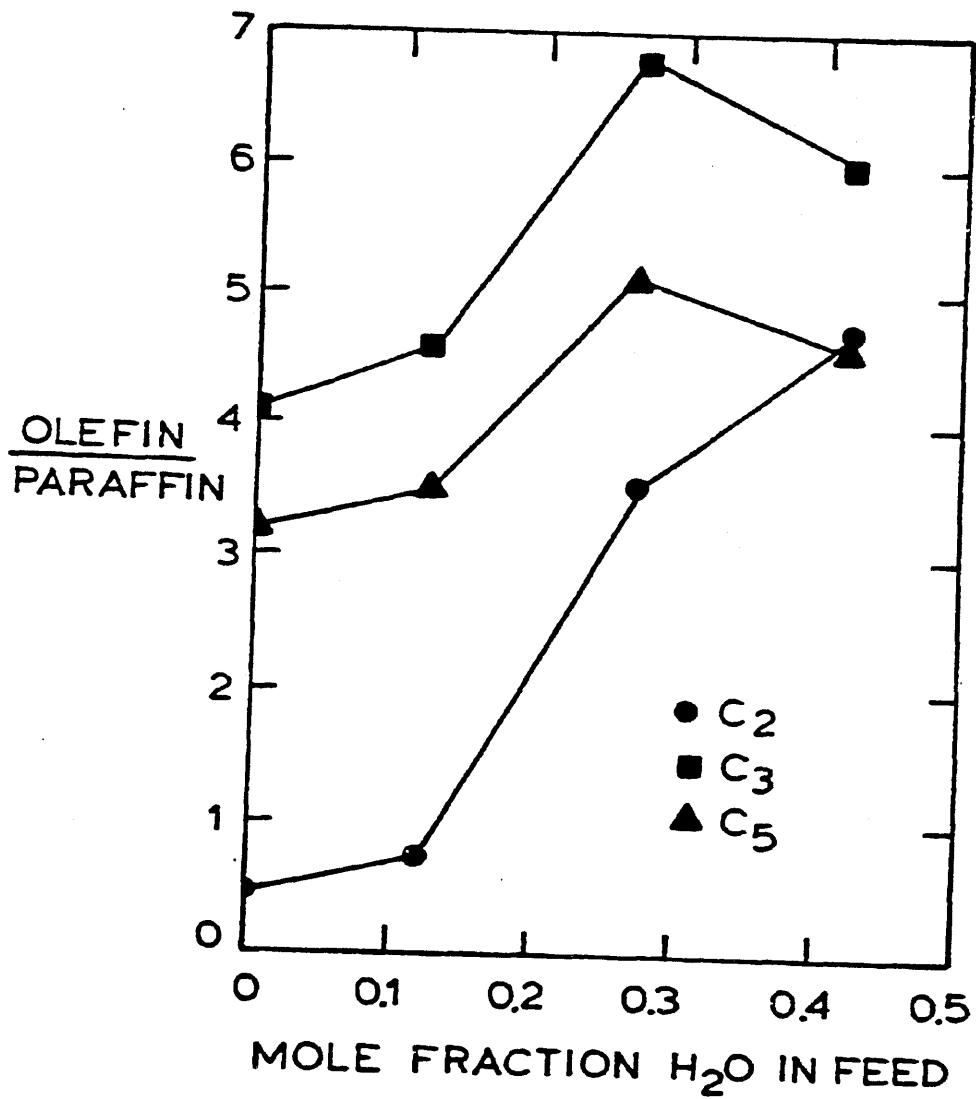


FIG. 12.

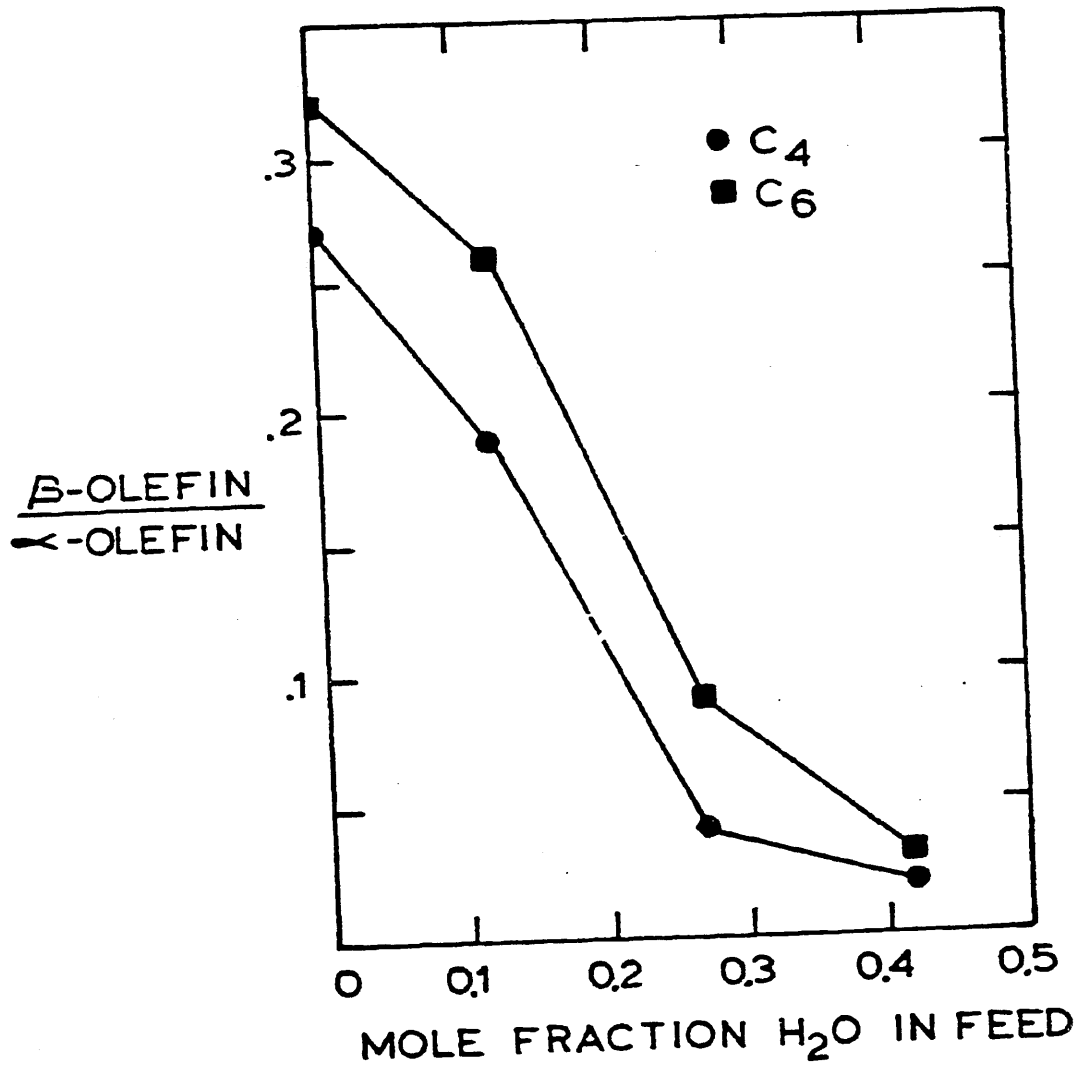


FIG. 13

