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Molecular Weight Distribution of the Heavy Wax Fraction from Fischer–Tropsch Synthesis

Little reliable information is available on the carbon-number distribution of Fischer–Tropsch products above approximately C_{30}, as produced on representative industrial catalysts, for two reasons. First, conventional gas chromatography methods become increasingly less reliable because of the high boiling points and low solubilities of these compounds and second, with fixed-bed reactors heavy products slowly accumulate in the catalyst pores and many hours may be required to elapse before the liquid product leaving the reactor is truly representative of intrinsic kinetics.

We report here on the analysis of the reactor waxes remaining in the liquid phase after several lengthy slurry reactor studies. Analyses were by a high-temperature gas chromatography procedure and by gel permeation chromatography. We will show that the results are similar by the two quite different procedures. The catalysts were a reduced fused magnetite and a precipitated iron oxide promoted with potassium and copper.

Wax Samples

The slurry reactor apparatus and operating procedures are described elsewhere (*1*, *2*). The reactor was initially half-filled with high purity *n*-octacosane (C_{28}). Gas chromatographic analysis showed impurity concentrations that were equivalent to C_{30}, 0.039 wt%; C_{32}, 0.114 wt%; C_{36}, 0.016 wt%; and C_{38}, 0.255 wt%. Most of the products are volatilized overhead. By the use of a pure liquid carrier in the reactor, nonvolatile products can be readily distinguished from the initial material.

Four wax samples were analyzed by a high-temperature GC method and one of these four was also analyzed by a gel permeation method. The wax samples were collected at the conclusion of slurry reactor runs varying in onstream time from 145 to 860 h. Reaction conditions are given in Table 1. During the two longer runs several different combinations of pressure, temperature, and (H_2/CO) inlet ratio were used at different times. The first three runs utilized a fused magnetite catalyst prereduced in pure H_2 in a separate vessel. The fourth run was with a precipitated iron catalyst promoted with copper and potassium. We report elsewhere (*3*) a limited study of that catalyst in our slurry reactor. This catalyst was prereduced with a H_2/CO mixture of 1 : 1 mole ratio, at temperatures rising from 225 to 235°C over the course of 3 days.

GAS-PHASE CHROMATOGRAPHY

The high-temperature gas chromatography procedure utilized a 8-ft. × $\frac{1}{8}$-in. glass-lined stainless-steel column filled with 60/80 mesh dimethyl silicone (Permabond) packing. A flame ionization detector (held at 350°C) was used because of its identical response factor of unity for all hydrocarbons of interest. Hot needle injection was necessary to insure that components were not lost due to condensation prior to entering the column packing. In this technique the wax, in a 10 : 1 solution with carbon disulfide, was drawn into the syringe followed by 0.05 μl of air. The syringe was then inserted through the septum into the injection port until the tip of the needle was within 1 cm of the packing. The needle was held in place for 5 s, the sample was injected and the needle was then held for 10 more seconds before it was withdrawn. The injec-

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TABLE 1

Reaction Conditions for Wax Samples

Time on stream, (h)	H_2/CO Fed	Pressure (kPa)	Temperature (°C)
Run Fe-8			
0–860	0.69 to 1.18	445 to 1480	232 to 263
Run Fe-9			
0–236	0.90	445 to 1480	232 to 263
236–425	1.81	445 to 1480	232 to 263
425–680	0.55	445 to 1480	232 to 263
Run Fe-13			
0–145	1.33	790	263
Run Fe-P-1			
0–206	1.38	1140 to 1480	225 to 250

tion port and entrance of the column were held at 375°C.

The oven temperature had an initial value of 35°C for 8 min, then was programmed at 8°C/min to a final temperature of 320°C and kept there until all detectable components were eluted. The carrier gas was helium (free of oxygen and moisture) used at a flow rate of 30 cm³/min. Septum bleed, which may be considerable at these oven and injector temperatures, was minimized by using a hard black septum (Pyrosep). However, because of its hardness it had to be changed frequently due to leaking. The sample size varied between 0.1 and 0.4 μl, large enough to give identifiable peaks at the chosen attenuation but small enough to allow the baseline to be restored between those peaks where septum bleed caused baseline drift (greater than 31 min). As shown in Fig. 1, this procedure gave good separation of component peaks and good baseline resolution. These waxes are predominantly *n*-paraffins. The small peaks between the main peaks are branched isomers and primary olefins (*2*).

Gas Chromatography Results

Figure 2 presents the hydrocarbon distribution (essentially normal paraffins) for run Fe-8. The plot is of W_n/n on a log scale versus carbon number n, where W_n is the weight fraction of product of carbon number n. Excluded are the C_{28} paraffin, initially present in the reactor and C_{32} and C_{38}, the two principal impurities in the C_{28}. Below about C_{25} significant amounts of product are volatilized out of the slurry reactor. The slope of the curve at the higher carbon numbers gives the chain growth probability, α, in the Flory distribution, which is 0.89 for this run. Figure 3, for run Fe-9 gives α = 0.90. The point for C_{29} is high because of interference with C_{28}, which

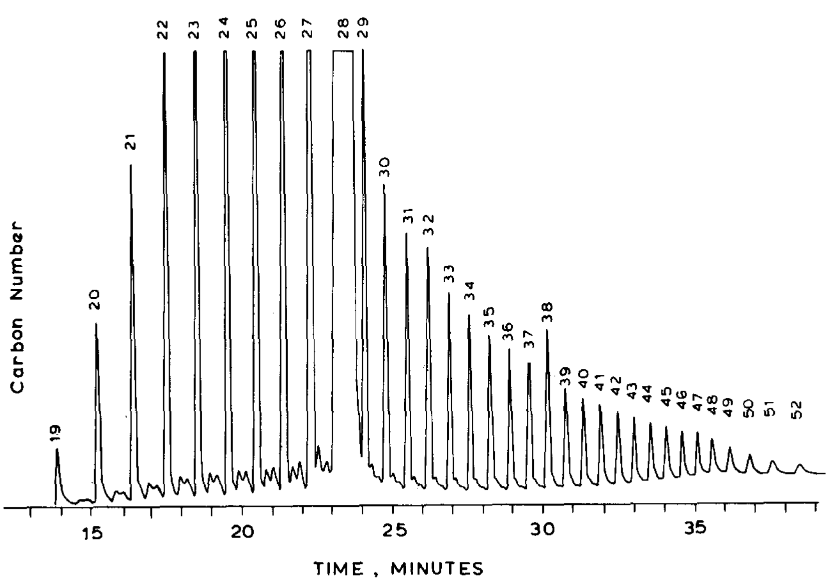

FIG. 1. Representative high-temperature gas chromatogram.

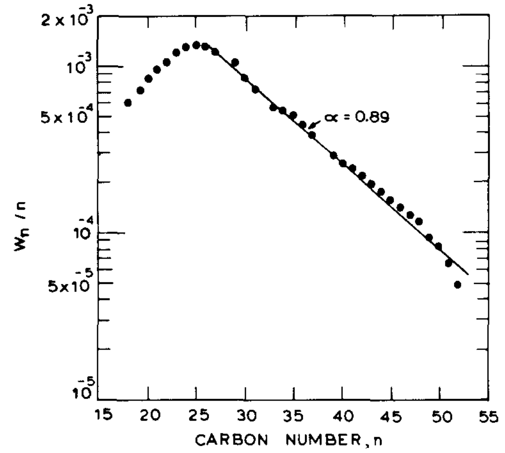

FIG. 2. GC analysis of slurry wax from run Fe-8.

dominates. A similar plot for run Fe-13 (not shown) gave $\alpha = 0.89$. Figure 4, for the wax formed by the precipitated Fe catalyst promoted with Cu and K shows $\alpha = 0.92$.

GEL PERMEATION CHROMATOGRAPHY

Samples were analyzed at 50°C using a Waters Associates 150 ALC/GPC apparatus utilizing a refractive index detector. This is a fully automated, microprocessor-controlled system with precise temperature control. Columns containing 100 and 500 Å Ultrastyragel were used in series. The solvent was HPLC grade 1,2,4-trichlorobenzene filtered through a 0.5-μm Teflon filter under vacuum to degas the liquid. A Data Module M 730 was used to record and automatically compute molecular weight distributions.

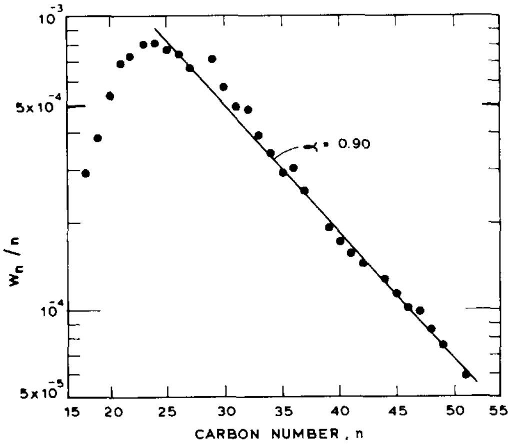

FIG. 3. GC analysis of slurry wax from run Fe-9.

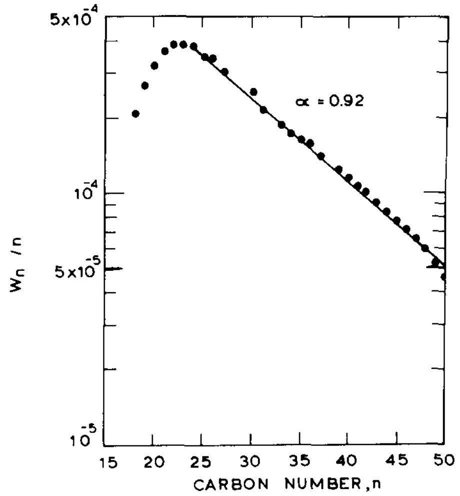

FIG. 4. GC analysis of slurry wax from run Fe-P-1.

The column system was calibrated by injecting samples of *n*-paraffin standards from C_{20} to C_{40}, to determine retention time as a function of molecular weight. The calibration curve was

$$\log(MW) = 4.82 - 0.0824\,(RT) \quad (1)$$

where RT is retention time. This linear relationship holds through C_{116}, as shown by injecting a standard sample of linear polyethylene of molecular weight 1635. The refractive index increases with molecular weight but then flattens out above about C_{30}–C_{35}. The DRI response was therefore assumed to be independent of molecular weight for the region of interest. The calculation procedure was similar to that of Sosa *et al.* (*4*) who found good agreement between GC and GPC analysis of paraffin waxes they studied. Further details of the apparatus, procedures and results are given in the thesis of Johnson (*5*).

Gel Permeation Results

Figure 5 shows representative results from the analysis of the wax from run Fe-9, plotted as the log of the differential number fraction, N_i, versus carbon number. These

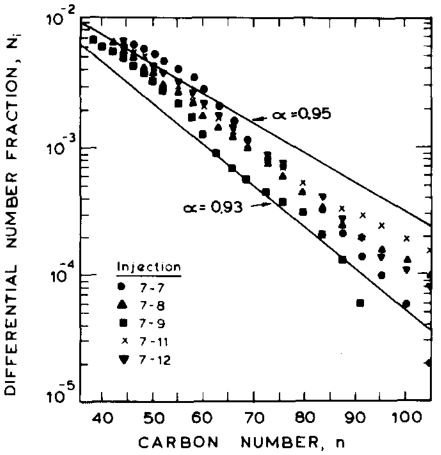

FIG. 5. Gel permeation analysis of slurry wax from run Fe-9.

can be matched against the theoretical carbon number distributions for various values of α as calculated from the Flory equation to determine α for the sample studied. Two of these theoretical lines are shown. Comparison indicates that the values of α here are about 0.93 to 0.95, compared to $\alpha = 0.90$ from the GC method.

Some preliminary measurements were also made with a different apparatus operated at ambient temperature (24°C). The lowest molecular weight material that could be analyzed was about C_{40} and the exclusion limit was about C_{60}–C_{70}. Calculated values of α were about 0.92 to 0.94, based on approximately the C_{40}–C_{60} range.

SUMMARY AND CONCLUSIONS

The molecular weight distribution for wax from the reduced fused magnetite catalyst corresponded to α in the Flory distribution of 0.89–0.90, as determined by a high-temperature GC method. That for wax from a precipitated Fe–K–Cu catalyst corresponded to $\alpha = 0.92$. Gel permeation chromatography gave results that essentially agree within the accuracy of the two methods. Product as high as C_{105}, near the exclusion limit of the gel permeation apparatus, was detected.

Elsewhere (*6*) we show that new data and reexamination of several previous studies in either fixed-bed or slurry reactors with iron catalysts indicate that the products consist of the sum of two distinct distributions corresponding to two values of α, with a marked break at about C_{10}. The value of α is much higher for the C_{10}^{+} fraction. The present studies show no clear evidence for any other change in α at higher C numbers such as that encountered near C_{10}; indeed there is no evidence for any limit on the maximum molecular weight product produced by Fischer–Tropsch synthesis on a conventional iron catalyst.

ACKNOWLEDGMENT

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