C. Catalytic Performance of Bifunctional Catalysts.

1) Metals Which Non-Dissociatively Adsorb CO

Dual-function catalysts containing a methanol synthesis function and a shape selective zeolite hydrocarbon synthesis function are of interest in providing a single step route from synthesis gas to gasoline which is not constrained by the Anderson Shultz-Flory polymerization kinetics of the conventional Fischer-Tropsch synthesis reaction and its inherent non-selective carbon number distribution.[170,171] Palladium, platinum and iridium, which chemisorb carbon monoxide non-dissociatively at 200-300 C [172,173], were recently found to be selective in the synthesis of methanol at low pressures from CO + H_2 [174,175] and from CO_2 + H_2 [176] providing the reaction is carried out in a pressure temperature regime for which methanol formation is thermodynamically favorable.[177,178,179] The activity and selectivity of Pd toward methanol synthesis is strongly affected by the nature of the support.[180,181,182,183,184] The specific activity for methanol synthesis is decreased in the order $Pd/La_2O_3 > Pd/SiO_2 > Pd/ZrO_2 > Pd/ArO > Pd/MgO > Pd/TiO_2 > Pd/Al_2O_3 >$ Pd black. [185] The formation of reaction intermediates such as formates on the oxide surface and the stabilization of active Pd forms by metal support interactions were suggested to explain the enhanced activity of Pd/La_2O_3 over Pd/ThO_2, Pd/Al_2O_3, Pd/SiO_2, Pd/C. [186]. Further, the concentration of Pd^{N+} ions present on Mg and La promoted Pd/SiO_2 were found to vary in parallel with the activity and selectivity toward methanol synthesis.[187] In the presence of acidic supports Pd/Al_2O_3 the methanol produced is dehydrated to dimethyl ether.[189] The overall reaction scheme affected by incorporating ZSM-5 with a methanol synthesis function is given by Chang et al.[190]

$$2H_2 + CO \xleftrightarrow{\text{metal}} (CH_3OH \quad 1/2(CH_3)_2O + 1/2H_2O)$$

$$\xrightarrow{\text{zeolite}} (CH_2) + H_2O$$

The drain-off mechanism exerted by the zeolite in the rapid conversion of methanol to hydrocarbons overcomes limitations imposed by the methanol$\rightleftarrows$CO-$2H_2$ equilibrium.[191,192] The fixed bed conversion of 2:1 H_2/CO at 355 C and 20 kg/cm^2 over a 1:3 wt. mixed Pd/SiO_2-HZSM-5 resulted in a 9.2% yield of hydrocarbons of which 59.2% were aromatic.[193] Since methanol is rapidly converted to hydrocarbons over H-ZSM-5 catalysts, the high pressure and low temperature requirements imposed by the $CO+H_2 \rightleftarrows$ methanol equilibrium on methanol synthesis can be avoided.

The determine the effect of the support on STG conversion over bifunctional Pt or Pd - metal oxide - HZSM-5 a series of catalysts were prepared. Composite catalysts were prepared by the incipient wetness impregnation of La_2O_3,

Al_2O_3, SiO_2 with 4% Pd using a solution of $PdCl_2$ in 0.2μm HCL. Each of these methanol synthesis catalysts were blended with 50 wt.% H-ZSM-5 (SiO_2/Al_2O_3=40). The Al_2O_3 source was Reheis F-2000 gel and the SiO_2 source was Cabosil M-5. The Pd loading of the composite catalysts was therefore 2%. The BET surface areas of 4% Pd/La_2O_3, 4% Pd/Al_2O_3, and 4%Pd/SiO_2 were 13.4, 14.3, 158 M^2/gm, respectively. The catalysts described (2% Pd/La_2O_3 - ZSM-5), (2% Pd/Al_2O_3 - ZSM-5), and (2% Pd/SiO_2 - ZSM-5) will be referred to as catalysts A,B, and C, respectively. Catalyst D was prepared by the incipient wetness impregnation of HZSM-5 (40/1) with 2/% Pd and catalyst E by the incipient wetness impregnation of HZSM-5 with 2% Pt. Catalysts F and G were prepared by the (40/1) direct synthesis impregnation of ZSM-5 with 1.8% Pt and 2% Pd in accordance with the method described earlier.

Each of these catalysts was reduced overnight with flowing H_2 at 300 C. Each catalyst was then reacted with 1:1 CO/H_2, GHSV = 900 hr^{-1} at 300 C 300 PSIG, 350 C 300 HPSIG, 400 C 300 PSIG, 300 C 500 PSIG, 350 C 500 PSIG and 400 C 500 PSIG.

Under the reaction conditions used, the equilibrium conversion to methanol is 1.4 mole % (350 C, 500 lbs H_2/CO = 1). In the absence of the drainoff effect exerted on the $2H_2$ + CO CH_3 OH equilibrium, the conversion of synthesis gas to gasoline range hydrocarbons could not exceed 1.4 mole % of the product. In all catalysts tested, except catalyst B (2% Pd/Al_2O_3 - ZSM-5) the gasoline fraction exceeded that which would have occurred if the drainoff mechanism did not influence the methanol equilibrium. Catalyst B produced no hydrocarbon fraction in the gasoline range and methane was the major hydrocarbon formed. The hydrocarbon product distribution obtained by on-line capillary GC analysis for catalyst A is shown in Figure 101 (350 C; 300 PSIG; GHSV = 900 hr^{-1}; $H_2/CO = 1$). The ethane yield predominated and the majority of the HC product fell in the range C_1 to C_5. The selectivity of this catalyst for gasoline range hydrocarbons was poor.

The product distribution for catalyst C (2% Pd/SiO_2 - ZSM-5) is shown in Figure 102. With this catalyst a significant hydrocarbon fraction formed in the higher end of the C_6 to C_{12} gasoline range. Methane, however, accounted for 37% of the product yield.

Catalyst D produced a hydrocarbon product distribution shown in Figure 103. (2% Pt - HZSM-5 incipient wetness impregnation). This catalyst had poor selectivity toward gasoline range HC synthesis under all temperatures and pressures tested. The product was mainly light gases and the distribution was near Anderson-Shultz-Floryian in appearance.

Catalyst F (1.8% Pt on HZSM-5 direct synthesis) yielded production shown in Figures 103 (350 C 300 PSIG 6HSV = 900 hr^{-1} $H_2/CO = 1$) and 104 (350 C 500 PSIG 6HSV = 900 hr^{-1} $H_2/CO = 1$). Although the syngas conversion was low, 5-10%, the selectivity toward gasoline range hydrocarbon was excellent. Over 88%

of the hydrocarbon fraction occurred in the gasoline range $C_6 - C_{12}$. This is over twice the maximum theoretical yield possible under ASF kinetics (i.e. 43%). The methane yield was low, 5-9% under all conditions tested. Decreasing the zeolite particle size, increasing the H_2/CO ratio, increasing the pressure, and operating at a high recycle ratio might substantially increase the % conversion and, therefore, produce an economically viable direct route from synthesis gas to gasoline. The BET surface area was 610 M^2/g.

Comparing catalyst C with catalyst F, it can be observed that establishing bifunctionality through physically admixing a methanol synthesis catalyst Pd/SiO_2 with the zeolite function HZSM-5 produced substantially more methane than was formed with catalyst F where the methanol synthesis function was placed in or on the surface of the zeolite. Methanol formed on Pd/SiO_2 must diffuse to the zeolite to be polymerized and, therefore, the drainoff mechanism would not be as effective in reducing the concentration of methanol over the Pt surface. The accumulation of methanol over the Pt surface pushes the equilibrium toward the formation of methane which is the thermodynamically favored product under these reaction conditions.

Although La_2O_3 has been reported by Bell and others as a highly effective support for the synthesis of methanol, its use as the Pd support in bifunctional STG catalysts exhibits low selectivity toward gasoline synthesis under the conditions tested. A possible explanation for the low gasoline yield might be the zeolite effectiveness was reduced by the attack by La cation exchange on the Bronsted acidity of the zeolite HZSM-5.

Of the catalysts tested only catalyst F had excellent selectivity toward gasoline synthesis. Its selectivity was 88% better than twice that theoretically possible under conventional Anderson-Shultz-Flory kinetics.

It has been proven that Cu^{+1} is the active species in the synthesis of methanol over conventional Cu/ZnO catalysts. Recently, Poels et al. demonstrated by acetylacetone extraction of Mg^{+2} and La^{+3} promoted Pd methanol synthesis catalysts that the cation Pd^{N+} is the active species in the synthesis of methanol over Pd. Since PdO_2 is reduced <u>in air</u> to Pd^0 at 200 C, the strong electric fields associated with the zeolite framework might serve to stabilize the Pd^{N+} cation under synthesis temperatures.

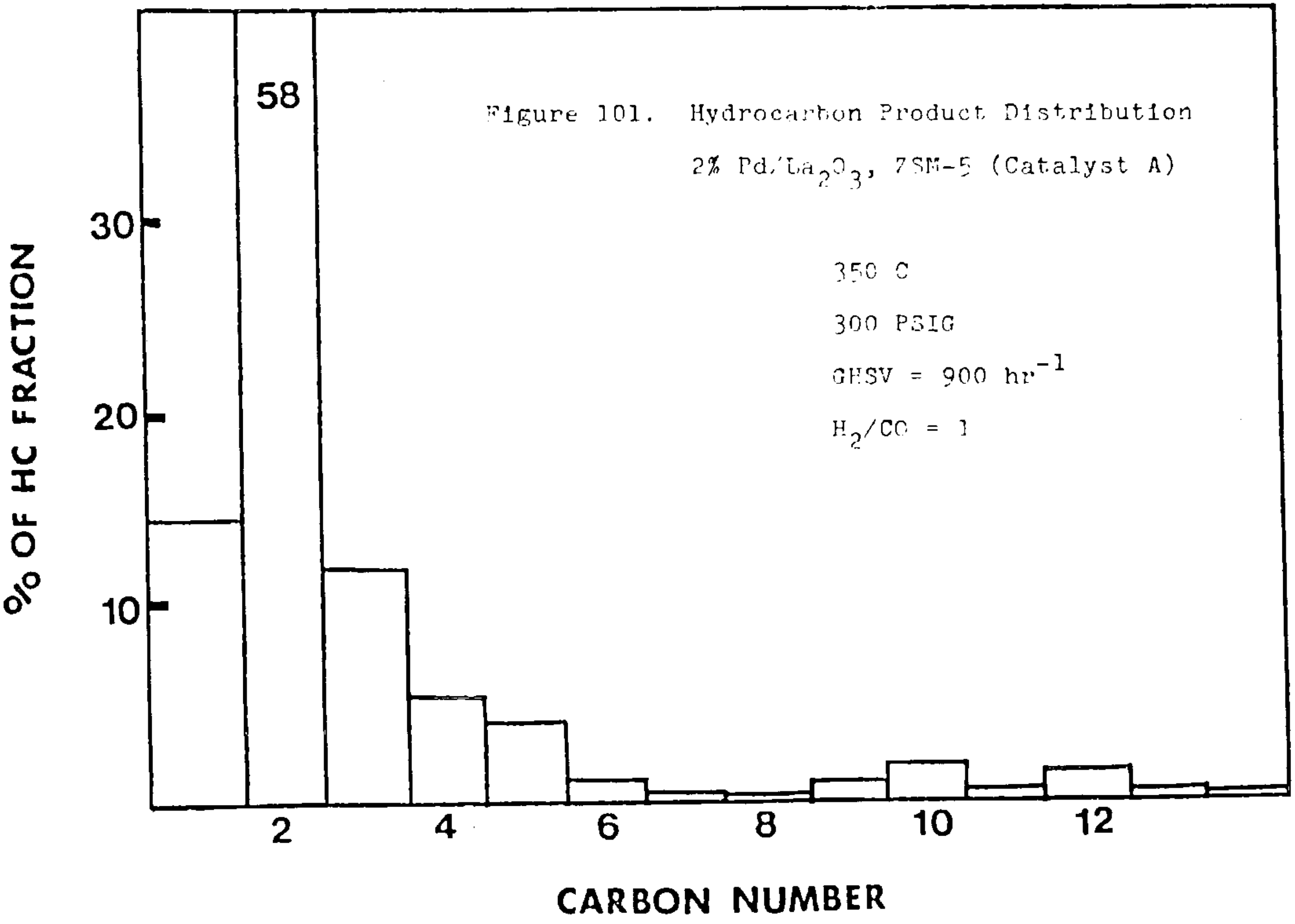


Figure 101. Hydrocarbon Product Distribution
2% Pd/La_2O_3, ZSM-5 (Catalyst A)

350 C
300 PSIG
GHSV = 900 hr^{-1}
H_2/CO = 1

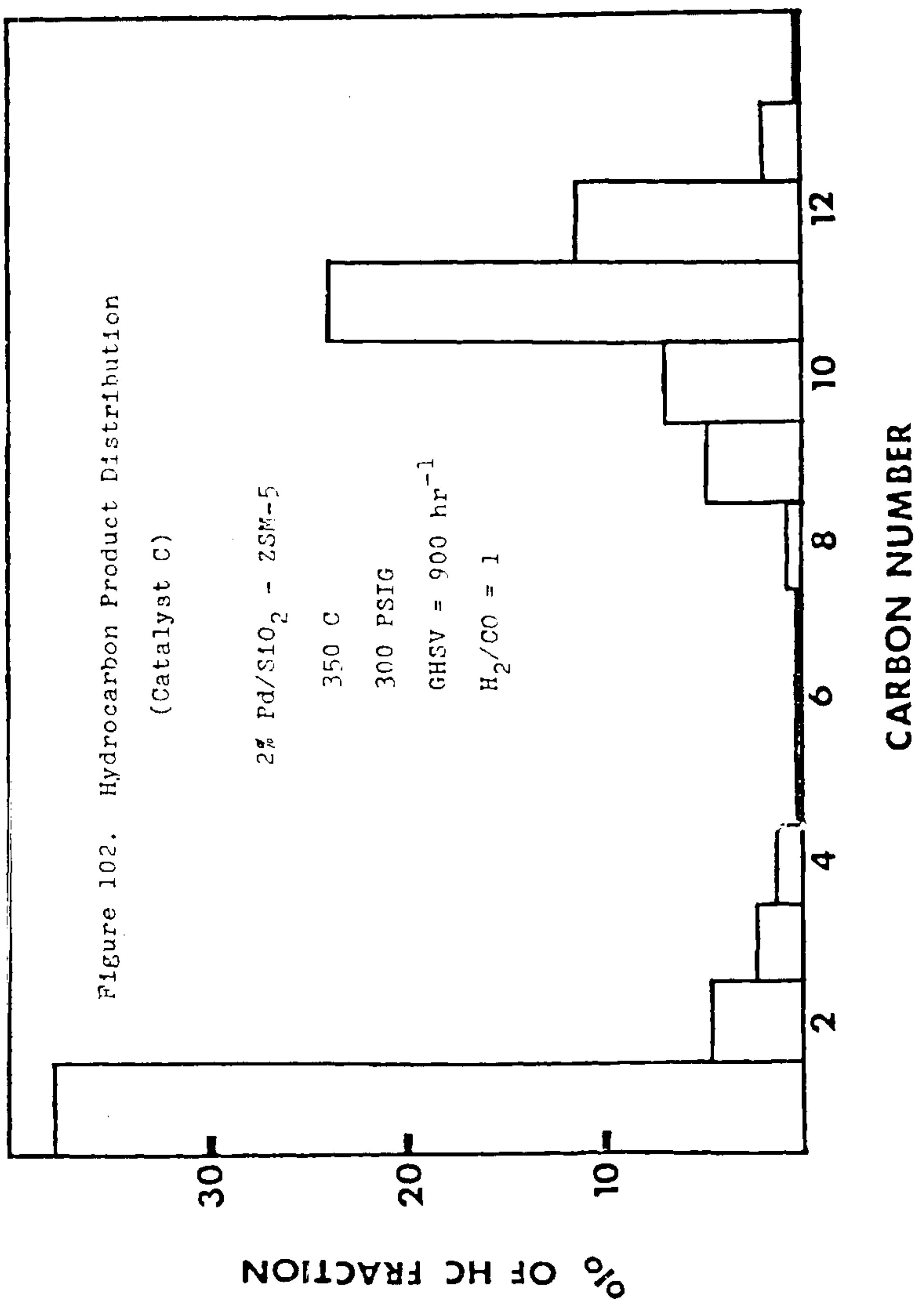


Figure 102. Hydrocarbon Product Distribution

(Catalyst C)

2% Pd/SiO$_2$ - ZSM-5

350 C

300 PSIG

GHSV = 900 hr^{-1}

H$_2$/CO = 1

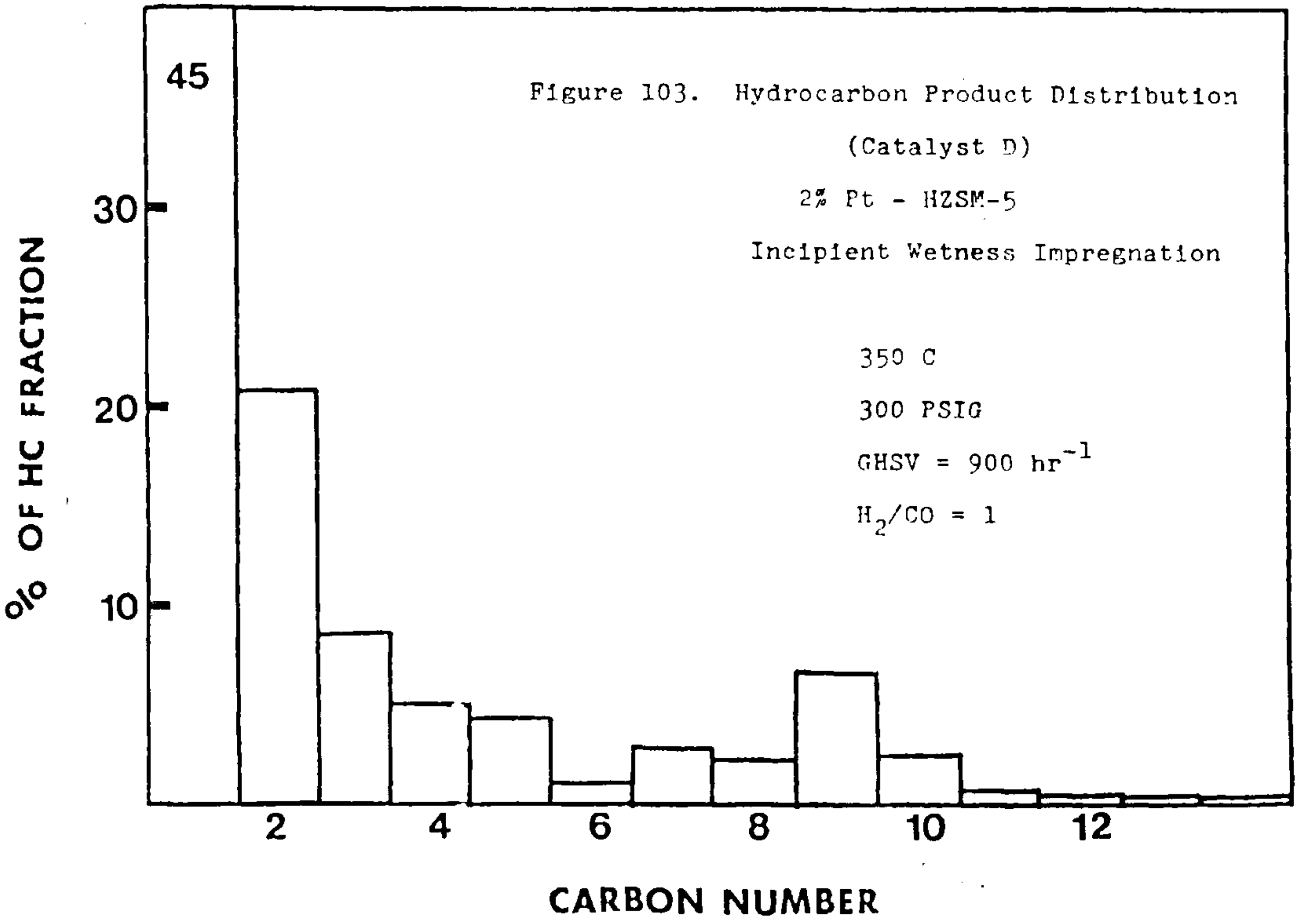


Figure 103. Hydrocarbon Product Distribution (Catalyst D)

2% Pt - HZSM-5

Incipient Wetness Impregnation

350 C

300 PSIG

GHSV = 900 hr^{-1}

H_2/CO = 1

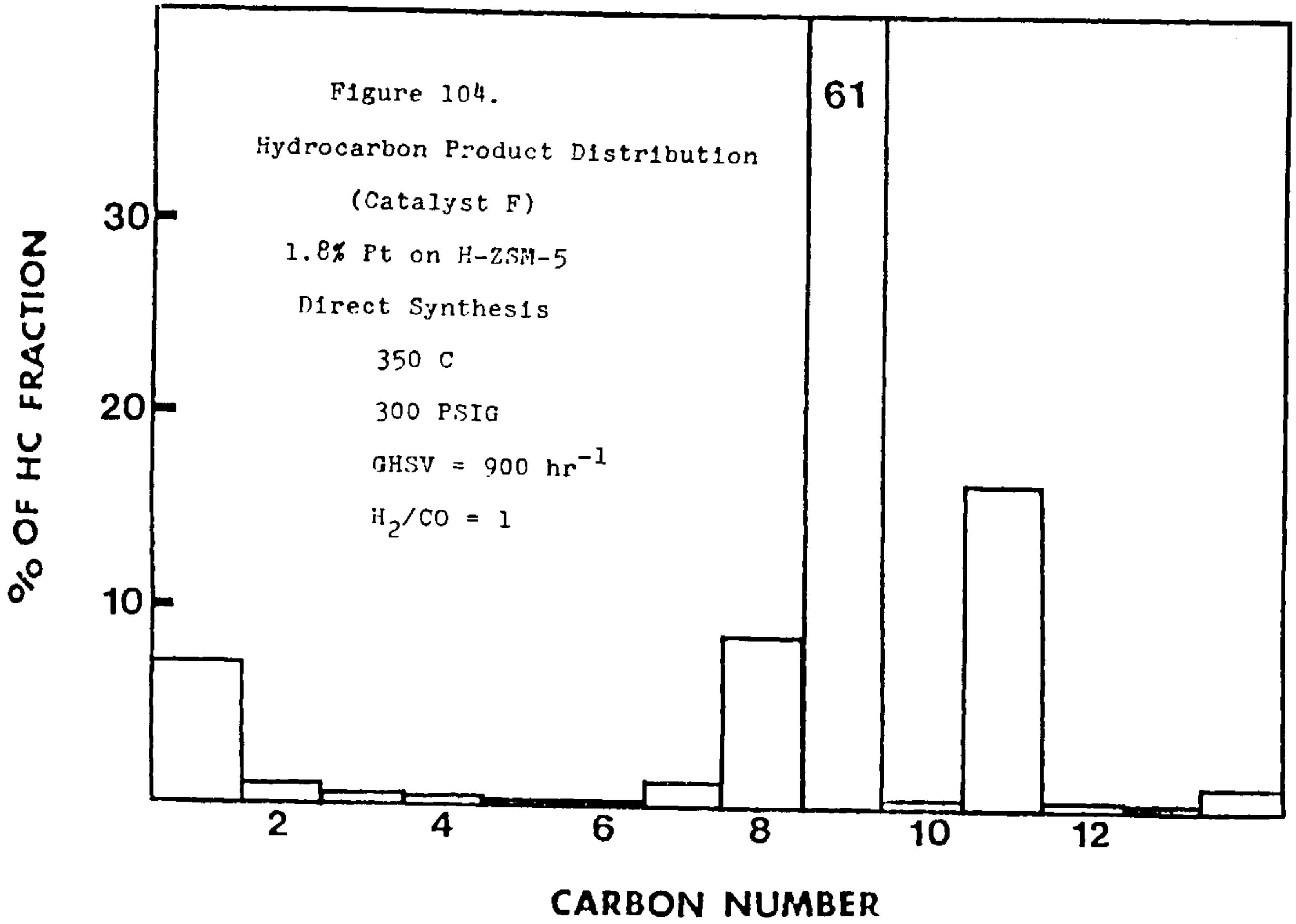


Figure 104.
Hydrocarbon Product Distribution
(Catalyst F)
1.8% Pt on H-ZSM-5
Direct Synthesis
350 C
300 PSIG
GHSV = 900 hr^{-1}
H_2/CO = 1

2) Metals Which Dissociatively Adsorb CO

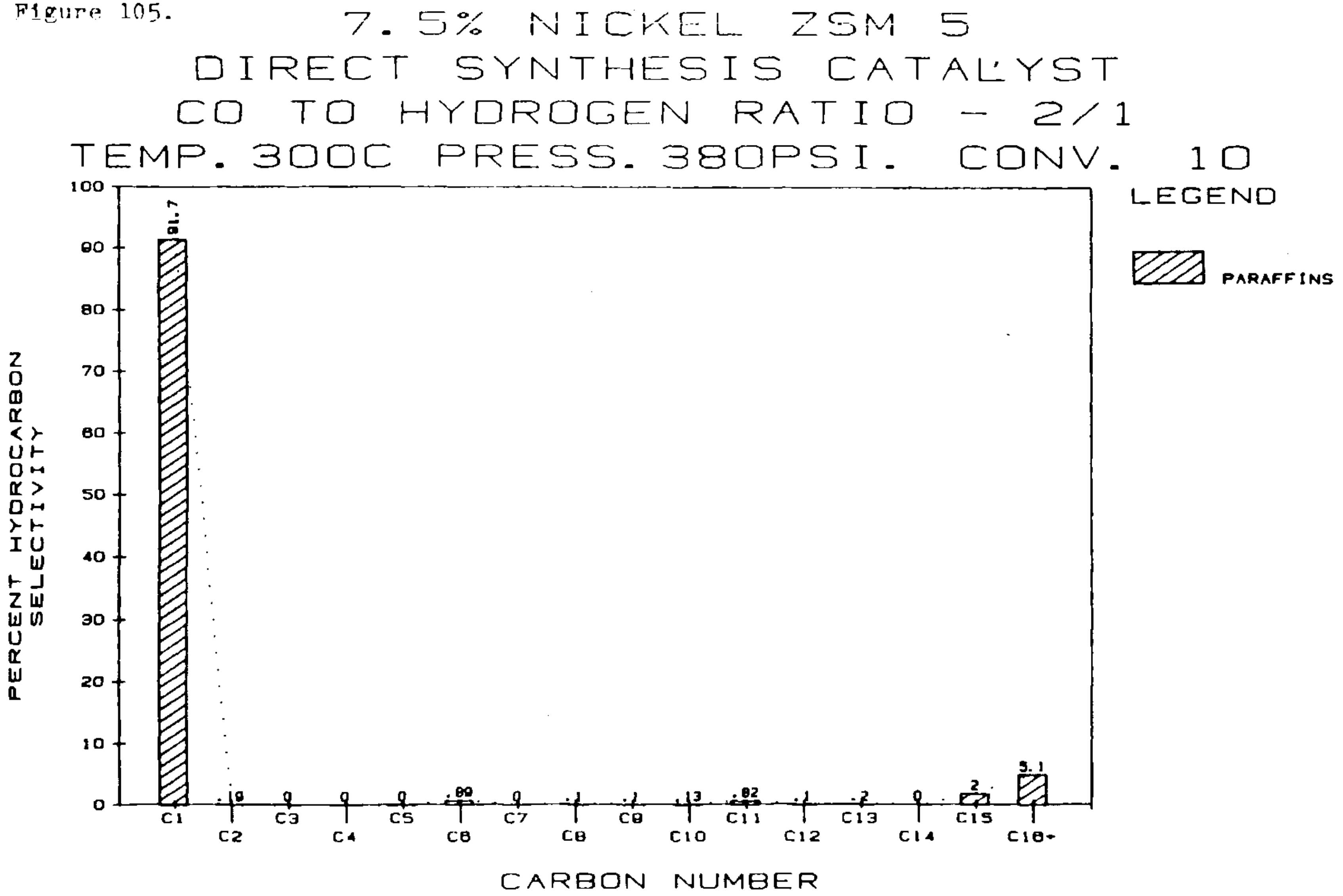
At the reaction temperatures employed for the conversion of synthesis gas to gasoline all transition metals except Pt, Pd, and Ir dissociatively adsorb CO. The product formed is not methanol therefore, but the complex distribution of products for which Fischer-Tropsch metals are notable. Shape selective zeolites have been used to upgrade the product distribution from Fischer-Tropsch synthesis both in a subsequent reaction step and during synthesis gas conversion. If HZSM-5 is used to upgrade the Fischer-Tropsch product in a separate reactor it can be used in its pure form. If, however, the zeolite is to perform its function in the same reactor in which CO reduction is taking place, bifunctional catalysts must be used. In bifunctional catalysts many techniques can be used to incorporate the CO reduction function (transition metal) with the zeolite function (ZSM-5). These include ion-exchange, impregnation, co-deposition, adsorbtion from the gas phase, using metal carbeneles, hydrocarboneles, acetylacetonates, halogenides, and alkyl derivatives. The metals can also be incorporated by introduction during synthesis and by adsorption of the metal vapor. The majority of the literature concerning the preparation of bifunctional catalysts for synthesis gas to gasoline conversion involves impregnation and adsorption from the gas phase as the chosen method of introducing the transition metals. Little work has been done on bifunctional syngas catalysts wherein the transition metal is introduced during the synthesis of the Pentasil Zeolite. There are certain advantages for attempting to occlude the CO reduction function within the zeolite pore system. These include the maintenance of high dispersion, the prevention of wax production while operating under high polymerization probability, the prevention of polyaromatic ring formation leading to the deposition of coke, the proximity of the reduction function to the Bronsted acid sites, the substantially increased reaction pressure caused by the interaction of the adsorbed molecules with the crystal field (approaching liquid density), and the potential for this crystal field to hold the metal in a high spin electron configuration.

The disadvantages of this approach include the increased diffusional resistence to the metal surface and the increased diffusional resistence to the Bronsted acid sites resulting from the partial obstruction or decrease in the effect of pore diameter. As previously discussed in Section IV B.6., success was achieved in the first direct synthesis of bifunctional STG catalysts for a wide variety of transition metals on ZSM-5. Preliminary evidence suggest these metals are being occluded within the zeolite pore system. To investigate the effect of this method of preparation on the selectivity in the conversion of synthesis gas to gasoline, the micropilot plant reactor system was employed. The nickel catalyst, DOD Ni-ZSM-5-1 was reduced in flowing hydrogen at 300 C and 100 PSIG for several hours. It was then carbided at 300 C and 300 PSIG for 1 hour using 2:1 syngas and reacted under these conditions at a GHSV = 900 hr^{-1}. The product distribution obtained is shown in Figure 105. The product yield was 92% methane and the CO conversion 10%. This catalyst was green in color and changed to steel gray after reduction. The product selectivity was typical to conventional nickel based catalysts. The Ru-ZSM-5 catalyst, DOD-Ru-ZSM-5-1-11-29, was reduced and carbided by the same procedure. The product distribution obtained in the conversion of 2:1 synthesis gas at 300 C 380 PSIG and GHSV = 900 hr^{-1} is shown in Figure 106. The product distribution was bimodal and appeared to consist of a conventional Shultz-Flory distribution however, a peak occurred at C_{10} which is probably attributable to the zeolite function.

A somewhat similar result was obtained on the iron catalyst, DOD-Fe-ZSM-5-5(300 C 300 PSIG and GHSV = 900 hr^{-1}) which is shown in Figure 107. This catalyst consisted of 2 phases. The well crystalline ZSM-5 phase was purple in color. The amorphous phase was rust in color. It was desired to separate the ZSM-5 phase from the rust colored phase for the latter was producing conventional non-selective Shultz-Floryian product distributions. The vast difference in the particle size of the amorphous phase from that of the zeolite phase made this separation relatively easy. The crystals were gently mulled by hand in a Buckner funnel. The smaller amorphous particles adhered to the filter paper changing its color to rust. The crystalline phase was brushed off after the filter paper was dried. After reduction and carbiding this catalyst was run under 2:1 syngas at 300 C 300 PSIG GHSV = 900 hr^{-1}. The results obtained for the product distribution are shown in Figure 108. The CO conversion was 97.5% and the selectivity to the gasoline range outstanding. The catalyst showed no tendency to follow Shultz-Floryian kinetics and the C_1 to C_5 yield was very low. The sharp cut-off at C_{11} was typical of Pentasil catalysts. This same catalyst when operated under 1:1 syngas at the same temperature, pressure and space velocity, showed a shift in the product distribution toward higher carbon numbers (Figure 109). Using 2:1 syngas the product was centered at C_9 and using 1:1 syngas it was centered at C_{11}. With 1.5:1 synthesis gas, the product distribution was Gaussian in appearance and was centered at C_9 (Figure 110). The selectivity to the gasoline range was outstanding 92%, as was the extent of CO conversion 99.3%. This catalyst under these conditions was by far the most attractive catalyst we tested for the conversion of synthesis gas to gasoline.

The aforementioned diffusional disadvantages of occluding a transition metal did not impede a good CO conversion at a space velocity of 900 hr^{-1}. As previously discussed in Section IV. B. 6., Mossbauer results indicated the iron contained in this sample was 85% superparamagnetic. It is believed that the iron is in its high spin state and has 5 unpaired electrons. The increase in activity of the iron atom in this state more than makes up for lowering the concentration of iron by removing the extracrystalline iron.

Figure 105.



7.5% NICKEL ZSM 5
DIRECT SYNTHESIS CATALYST
CO TO HYDROGEN RATIO - 2/1
TEMP. 300C PRESS. 380PSI. CONV. 10
PERCENT HYDROCARBON SELECTIVITY
100
90
80
70
60
50
40
30
20
10
0
91.7
.19
0
0
0
.09
0
.1
.1
.13
.02
.1
.2
0
2
5.1
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16+
CARBON NUMBER
LEGEND
▨ PARAFFINS

Figure 106. 5.2% RUTHENIUM ZSM-5 DIRECT SYNTHESIS CATALYST CO TO HYDROGEN RATIO - 2/1 TEMP. 300C PRESS. 380 PSI. CONV. 15%

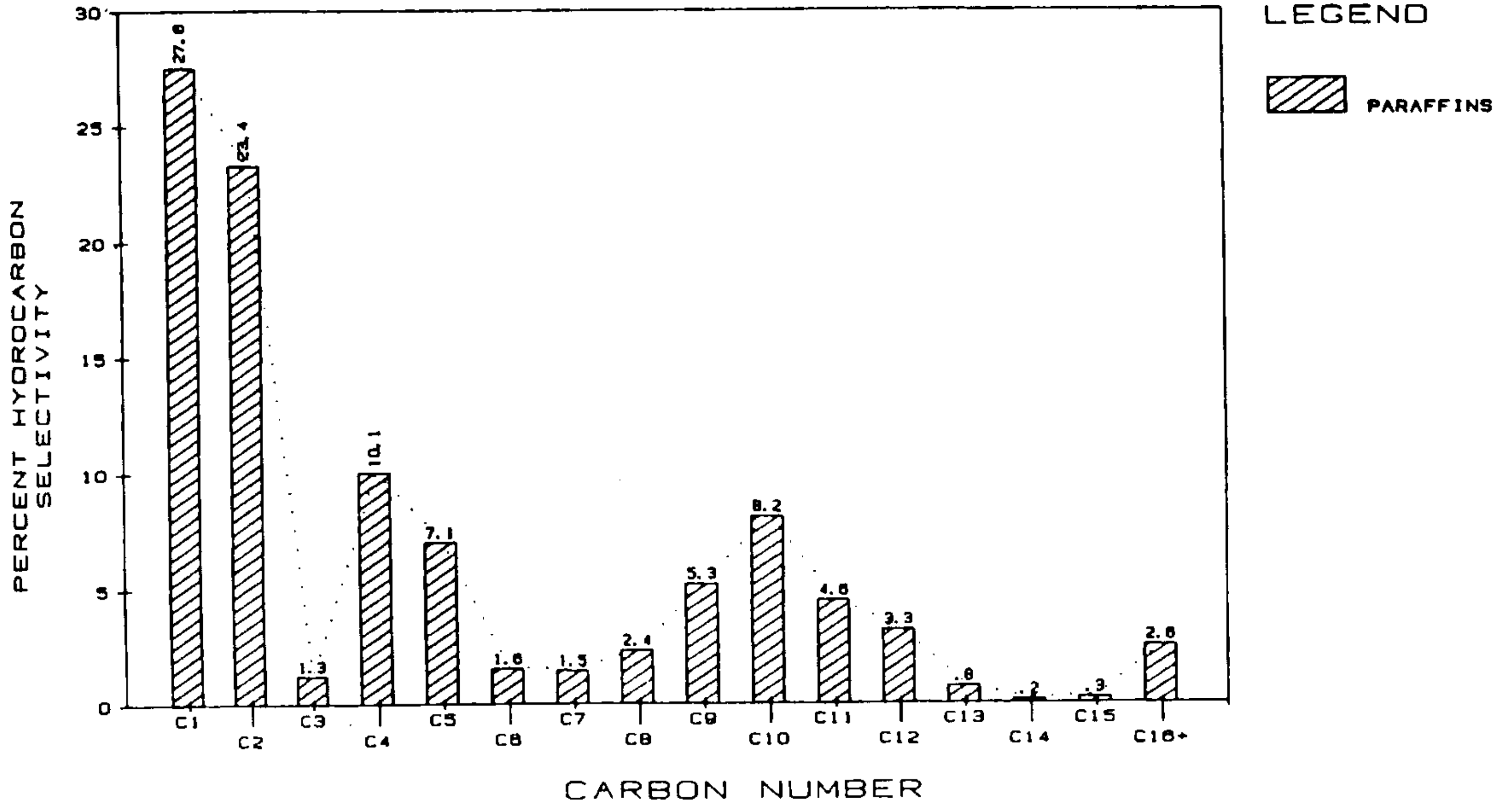


Figure 107.

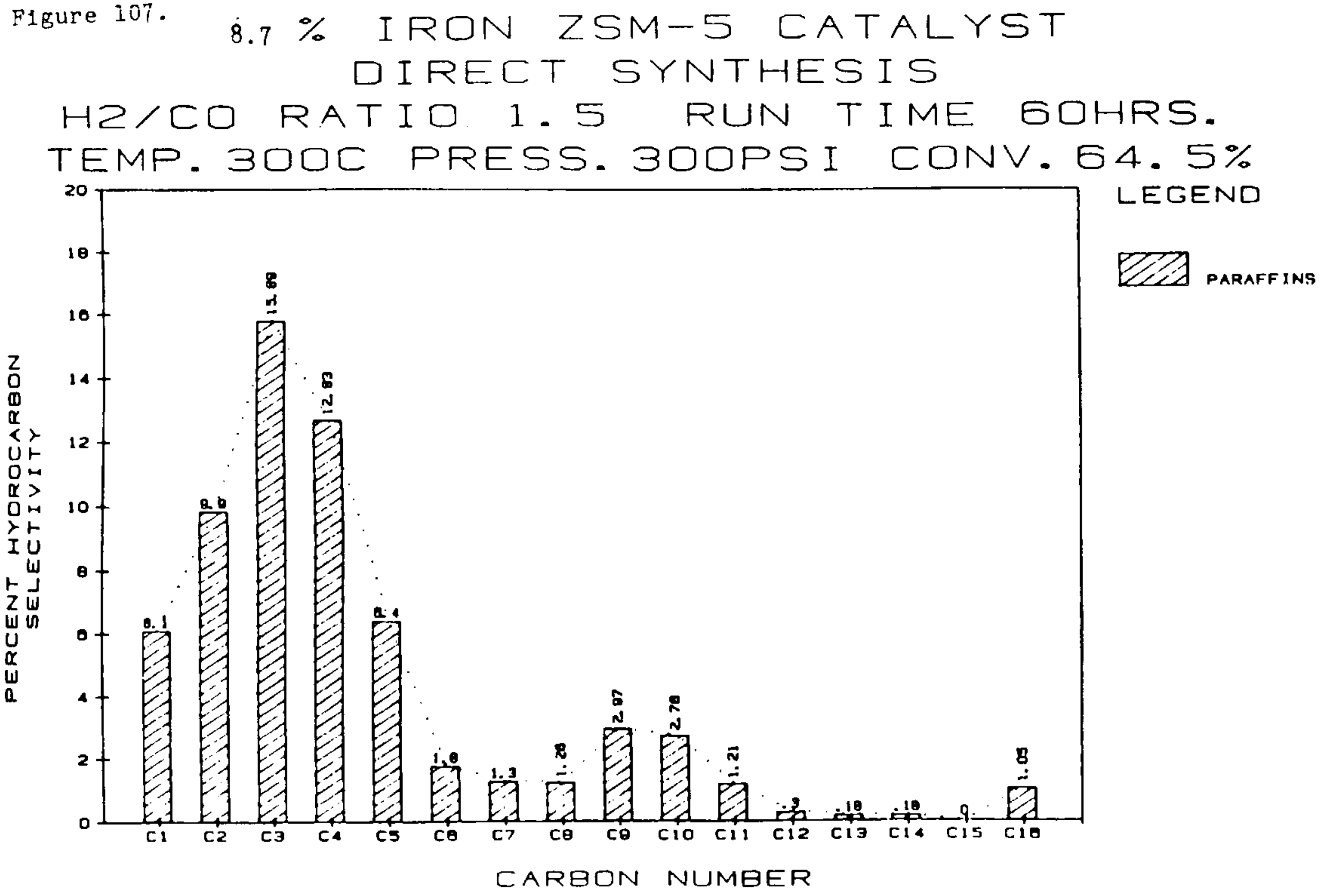
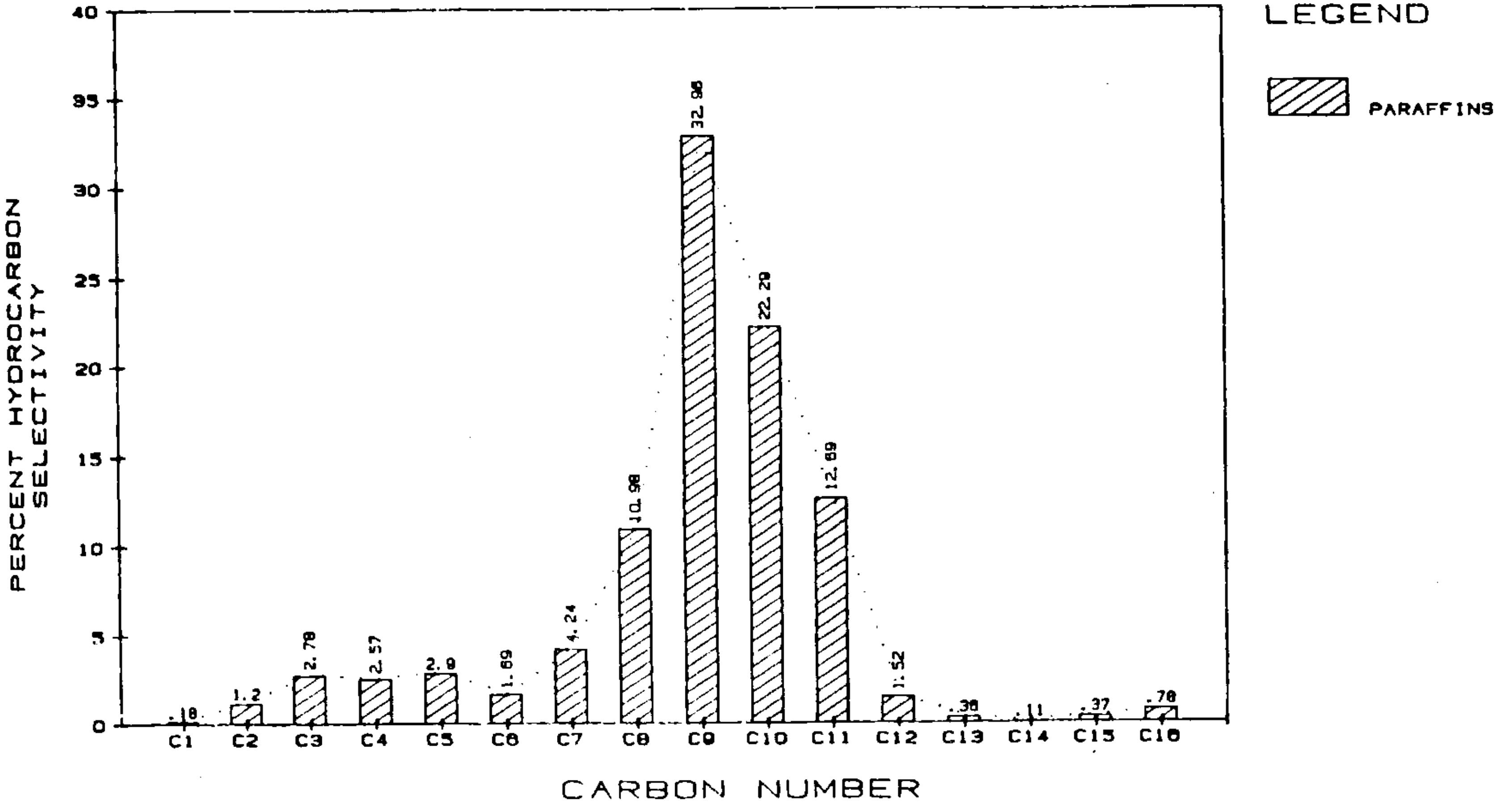

8.7 % IRON ZSM-5 CATALYST
DIRECT SYNTHESIS
H2/CO RATIO 1.5 RUN TIME 60HRS.
TEMP. 300C PRESS. 300PSI CONV. 64.5%
LEGEND
PARAFFINS
PERCENT HYDROCARBON SELECTIVITY
0
2
4
6
8
10
12
14
16
18
20
6.1
9.8
15.88
12.83
6.4
1.8
1.3
1.28
2.97
2.78
1.21
.3
.18
.18
0
1.05
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
CARBON NUMBER

Figure 108. 78.7% IRON ZSM-5 CATALYST DIRECT SYNTHESIS HYDROGEN TO CO-2.0 TEMP. 300C PRESS. 300PSI CONV. 97.5%



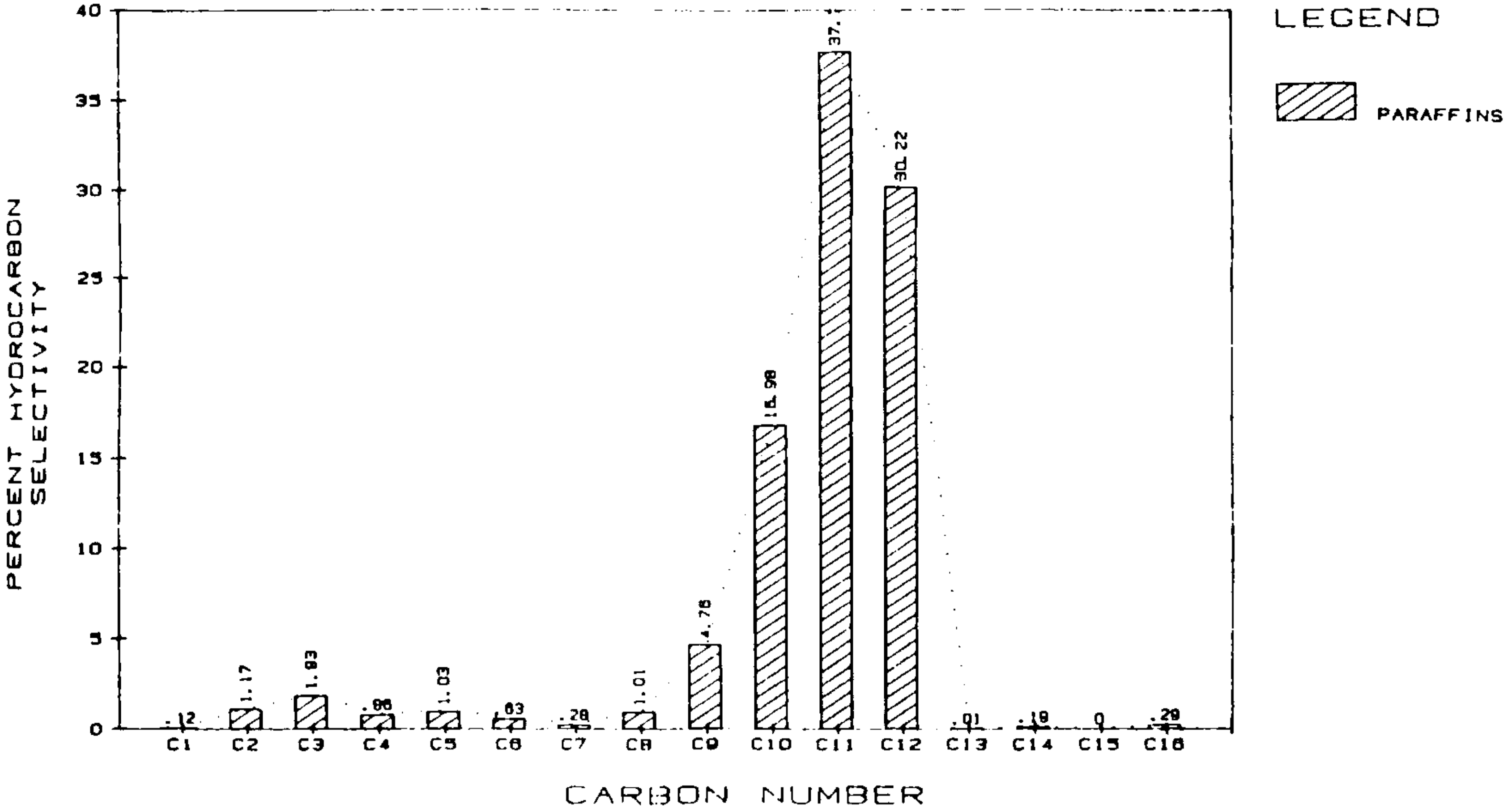


Figure 109. 78.7 % IRON ZSM-5 CATALYST
DIRECT SYNTHESIS PREPARATION
HYDROGEN TO CO RATIO - 1.0
TEMP. 300 C PRESS 300 PSI CONV. 97%

Figure 110. 78.7 % IRON ZSM--5 CATALYST
DIRECT SYNTHESIS
HYDROGEN/CO RATIO 1.5
TEMP. 300C PRESS. 300PSI CONV. 99.3%