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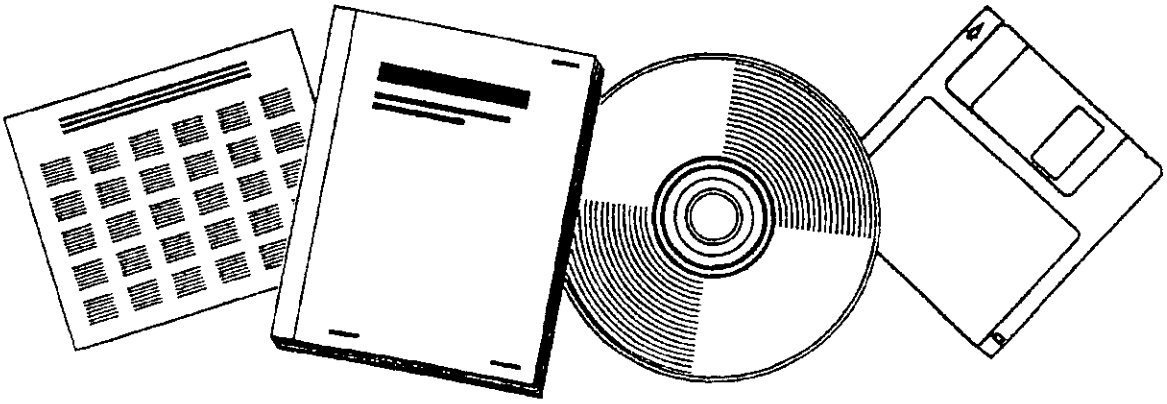

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Fischer-Tropsch Synthesis in Slurry Reactor Systems

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I. SUMMARY

We have now completed and partially analyzed a series of studies on the effect of the nature of the liquid present on activity and selectivity of the Fischer-Tropsch synthesis, and the effects of partial poisoning of the catalyst by H_2S or dibenzothiophene (DBT). We discovered towards the end of our work, quite unexpectedly, that the presence of a small amount of DBT (7.8 mg S per g of Fe in the catalyst) cut methane formation nearly in half under a set of reaction conditions of commercial importance (263°C, 1.48 MPa, H_2/CO feed ratio = 0.69). The selectivity remained constant for at least 200 hours. This is a very important finding since reduction of methane formation is highly desirable. The catalyst activity simultaneously dropped ten-fold but it should be possible to compensate for this in other ways at least in part such as by operation at higher pressure and/or temperature. Alternately, it may develop that lesser levels of catalyst poisoning may be nearly as effective with less loss of activity. These effects are not observed with H_2S. As far as we know the effects caused by DBT are brand new and have not been observed before.

We plan to exploit this lead in several ways, including optimization of DBT level and reaction conditions; study of other heterocyclic sulfur compounds, effects of activation procedures and correlation of methane selectivity with catalyst carbiding as determined by Mossbauer spectroscopy. A detailed proposal is being submitted to D.O.E. for these studies.

Also of some importance was the observation that operation in the presence of an aromatic liquid (phenanthrene) increased

the rate of reaction by a factor of 1.5 to 1.8, everything else being held constant. An extended summary of the studies of effect of liquid composition and poisoning is attached, based on the Sc.D. thesis of Harvey Stenger, completed this quarter.

I.A Activity

Comparing the intrinsic rates between liquid systems requires careful consideration of what units the concentrations should be expressed in. Since solubilities, defined as moles of gas per volume of liquid at a given partial pressure, will vary from liquid to liquid, it may be necessary to compare the intrinsic activities on a liquid phase concentration basis. This is discussed in section I.C.1. The kinetic expression used for comparing activities was (Huff and Satterfield, 1984):

$$-\text{rate of } CO+H_2 = \frac{k\ K\ P_{H_2}^2 P_{CO}}{P_{H_2O} + K\ P_{H_2}\ P_{CO}} \qquad \text{I.1}$$

I.B Experimental

I.B.1 Operation:

Reduction of the catalyst and operation of the slurry reactor followed the procedure of Huff and Satterfield (1983). The slurry reactor procedure was modified to permit the use of more volatile slurry carriers such as phenanthrene and triphenylmethane. Modification was also made to allow the injection of hydrogen sulfide into the slurry reactor.

A schematic diagram of the reactor system is shown in Figure I.1.

I.B.2 Materials:

The catalyst used exclusively in this work was a fused iron ammonia synthesis catalyst purchased from United Catalyst, Inc. and designated C-73-1-101. Its analysis as determined by Galbraith Laboratories of Knoxville, Tennessee was 64.4% Fe, 0.76% Al, 0.31% K, and 0.74% Ca (percents on a weight basis), with the remainder being oxygen and other trace elements.

The carrier liquids chosen to study were phenanthrene, triphenylmethane, Fomblin YR (a polyperfluoroether), and octacosane.

I.B.3 Analytical: The same analytical procedure outlined by Huff et al., (1981) was followed in all the work here.

I.C Results: Slurry Carrier-Catalyst Interaction

I.C.1 Activity: Comparison of the catalyst activity (k in equation I.1) in the various carriers was based on the Langmuir-Hinshelwood expression shown as equation I.1. As an approximation, the value of K in equation I.1 was assumed to be unchanged by the presence of the liquid carrier. K was set equal to the values determined by Huff, who utilized a large data base with the octacosane system.

Two sets of rate constants for the octacosane system are plotted in Figure I.2, those determined by Huff (1982) and those determined here in an independent run. They agree very closely. The octacosane system had an apparent activation energy of 83 kJ/mole.

The phenanthrene carrier system showed an increase in the rate constant at 263°C of approximately 1.8 over the octacosane system. It significantly altered the activation energy from 83 to 105 kJ/mole. The change in the activation energy could be explained by inhibiting adsorption of the phenanthrene carrier on the catalyst surface, since an aromatic compound might be expected to be more strongly adsorbed than a paraffin. Such adsorption would decrease with increased temperature.

The triphenylmethane system was very similar to the octacosane system. The slightly lower rate and slightly higher activation energy indicates some carrier adsorption may be occurring. The free rotation and orientation of the phenyl rings about the central carbon atom reduces the aromaticity of triphenylmethane. Thus its adsorption characteristics are more similar to that of a paraffin than of an aromatic.

The presence of the Fomblin carrier greatly reduced the intrinsic rate and significantly reduced the apparent activation energy (from 83 to 49 kJ/mole). Gas to liquid mass transfer resistances were excluded as a possible explanation because no significant change in rate was observed when varying the stirrer speed from 400 to 850 RPM at 232 degrees Celsius.

Microscopic examination of samples taken from the reactor after 50 hours on stream showed the Fomblin fluid to be clear, with wax-encapsulated catalyst particles dispersed throughout it. These capsules create an increasing mass transfer resistance between the Fomblin and the catalyst, due to a larger volume to surface ratio. The lower activation energy of approximately half that observed in octacosane is also consistent with a diffusionally limited process.

<u>I.C.1.a Hydrogen Solubility</u>: Figure I.2 showed that the catalyst in phenanthrene was between 1.5 and 1.8 times more active than in the octacosane system. The rate constants in Figure I.2 are based on partial pressures (equivalently, thermodynamic activities) of the reactants. To base these rate constants on concentration the solubility of hydrogen in the liquid carriers must be known.

Peter and Weinert (1955) and Shah et al., (1984) have measured the solubility of hydrogen in paraffin wax mixtures. An independent measurement by Matsumoto (unpublished) in our laboratory agreed with the other two studies. The three are listed in Table I.1.

Table I.1

Hydrogen solubility (micromoles/cm^3 of liquid-MPa of H_2)

	150°C	250°C
Shah et al., 1984(1)	33	44
Peter and Weinert, 1955(2)	37	49
Matsumoto, 1983(3)	36	48

(1) Gulfwax average molecular weight = 380

(2) Gatsch average molecular weight = 345

(3) Octacosane average molecular weight = 394

Data for hydrogen solubility in phenanthrene-like compounds is limited. Sebastian et al., (1979) report solubilities of hydrogen in 9,10 dihydrophenanthrene over the temperature range of Fischer-Tropsch application. At 250°C the solubility of hydrogen in 9,10 dihydrophenanthrene as measured by Sebastian et al., (1979) was 29 micromoles of H_2/cm^3 of liquid-MPa of H_2.

Assuming 9,10 dihydrophenanthrene is similar to phenanthrene, then the solubility of hydrogen is 35 percent less in phenanthrene than in the paraffin solvents. Basing the rate expression on concentration of hydrogen rather than partial pressure makes the rate constants between 2.3 and 2.8 times greater in phenanthrene than in octacosane. Therefore, independent of whether liquid concentrations or partial pressures are used, phenanthrene has an enhancing effect on the activity of the catalyst.

The phenanthrene may possibly alter the configuration of the activated complex and thereby increase its frequency of decomposition. Also 9,10 dihydrophenanthrene, a strong hydrogen donor solvent which is formed during the synthesis reaction, may be involved in modifying the activated complex or acting as a hydrogen transfer solvent. However, its concentration in the carrier was small (1.0 weight percent at the conclusion of the run). It is unlikely that this small amount could effect a 2.5 fold increase in rate constant.

I.C.2 Selectivity

I.C.2.a Light Products: Figures I.3 through I.6 are Schulz-Flory plots for the four carrier systems for the light products. In each figure the mole fraction of total hydrocarbons plus oxygenates is plotted versus carbon number for C_1 to C_7. Alpha denotes the porbability of chain growth based on the C_3 to C_7 fraction. For all four systems, as conversion increases the selectivity to C_2 decreases and to C_3 increases. The value of alpha is also influenced by conversion, with the highest alpha at the lowest conversion. The Fomblin carrier differs with respect to its high methane selectivity and lower value of alpha, but shows similar behavior for C_2, C_3 and variation in alpha.

The variation in the C_2 mole fraction with conversion indicates that reincorporation of a C_2 species is occurring. At high probabilities of C_2 reincorporation the C_3 fraction will be most enhanced since the most abundant monomer species are CH_2 groups. A measure of the extent of this reincorporation is the ratio of the C_3 mole fraction to the C_2 mole fraction. Figure I.7 is a plot of the C_3 to C_2 ratio versus partial pressure of carbon monoxide. Carbon monoxide is strongly adsorbed, and as its partial pressure decreases, the availability of sites for product readsorption increases. Simultaneously, product partial pressures increase which enhances product readsorption and reincorporation. At all temperatures for both systems the C_3 to C_2 ratio increases with decreasing carbon monoxide partial pressure. At 232°C and 248°C the phenanthrene system has lower values of this ratio at a given partial pressure of carbon monoxide. This indicates that the phenanthrene system has a lower probability of reincorporation than the octacosane system. At 263°C no difference exists between the two systems.

At all temperatures the Fomblin system has a significantly higher C_3 to C_2 ratio. The higher C_3 to C_2 ratios indicate a significantly higher probability of reincorporation. This suggests a cage effect in which diffusion of C_2 primary products away from the catalyst is limited by mass transfer.

Olivé and Olivé (1976) present arguments based on the data of Schulz et al. (1970) that ethylene is the most reactive hydrocarbon species for secondary reactions on an iron catalyst. This is borne out by other experimental studies. These reactions can include hydrogenation, chain growth insertion, and decomposition to methane. Krummer et al. (1951) showed that ethanol can also participate in chain growth on an iron catalyst. Based on the selectivity data in Figures I.3 to I.6, reincorporation of C_2 species is very likely. Reincorporation of a C_2 species would increase the production of C_3 most significantly, and less for each subsequent carbon number. Therefore a lower differential value of alpha would be expected from a greater probability of reincorporation, if ethylene and/or ethanol were the major reincorporating species.

The ability of C_2 species to reincorporate was not observed by Huff and Satterfield (1984) in their work on this same subject. This is explained by the lower pressure of 0.79 MPa used in their experiments versus the 1.48 MPa used here. Some data was obtained in the work by Huff (1982) at the higher pressure but not at the higher conversions obtained here. At comparable conversions the data agree very well. Only the higher conversions (>40%) obtained in this work, does the drop in the C_2 mole fraction become significant. Huff did not overlook the phenomena of C_2 reincorporation; instead, he never operated in the regime where it was observable.

I.C.2.b Olefin Formation: Olefin formation is discussed here in terms of olefin to paraffin ratios. The C_5 olefin to paraffin ratio is shown in Figure I.8 for the phenanthrene, Fomblin, and octacosane carriers. At all temperatures the phenanthrene system has higher olefin to paraffin ratios than the octacosane and Fomblin systems. The Fomblin system olefin to paraffin ratios are significantly lower than either of the other two. It is believed that the Fomblin system was strongly limited by mass transfer between the wax encapsulated catalyst particles and the Fomblin fluid. The extent of any secondary reactions in the Fomblin system such as olefin hydrogenation, would also be increased for this same reason.

I.C.2.c Olefin Isomerization: Readsorption and isomerization of alpha olefins occurs significantly on iron catalysts (Schulz et al., 1970). The rate of the isomerization is dependent on the concentration of the readsorbing olefin and the number of available sites. Since carbon monoxide is the most abundant adsorbing species, the concentration of available sites is inversely related to the partial pressure of carbon monoxide. In Figure I.9 the percent of total olefins present as alpha olefins is plotted as a function of carbon monoxide partial pressure. The phenanthrene system produced the greatest fraction of alpha olefins of the three carriers. Presumably phenanthrene is adsorbing on isomerization sites. At 263°C the phenanthrene and the octacosane systems approach one another with regard to isomerization. Adsorption of phenanthrene on both isomerization and hydrogenation sites (which may be identical) may be reduced at 263°C allowing isomerization to proceed at similar rates in the two systems.

The Fomblin system produced a significantly isomerized product with the precent alpha olefins as low as 40 percent. The Fomblin system exhibits a greater extent of secondary reactions, reflecting its diffusional limitations.

I.C.2.d Oxygenate Formation: Figure I.10 compares the oxygenate content at C_2 for the phenanthrene, Fomblin and octacosane systems. Carbon monxoide pressure was chosen as the independent variable. The complexity of the formation of oxygenated products and their subsequent decomposition makes it impossible to choose a single independent variable. Plotting the oxygenate yield versus carbon monoxide partial pressure is an attempt to compare the systems on an equivalent basis since all other concentrations of products and reactants are stoichiometrically dependent.

Figure I.10 shows the phenanthrene system has a greater yield of oxygenates for C_2 at 232 and at 248°C than the octacosane system. At 263°C the two systems are identical. Similar to olefin production and olefin isomerization, the phenanthrene system approaches the octacosane system as temperature is increased. Oxygenated products are susceptible to secondary reactions such as reincorporation, decomposition, and dehydration. The phenanthrene may be occupying sites capable of such secondary reactions resulting in a greater yield of primary products, in this case oxygenates. At 263°C the phenanthrene adsorption is decreased and secondary reactions proceed at comparable rates in the octacosane and the phenanthrene systems.

At all temperatures the phenanthrene system and the octacosane system gave a greater yield of oxygenated products than the Fomblin system. Again the mass transfer resistances imposed by the wax capsule effect result in a greater extent of secondary reactions.

I.D Results: Sulfur-Catalyst Interactions

Bartholomew et al. (1982) present the most recent review on sulfur poisoning of metals. Sulfur poisoning of Fischer-Tropsch catalysts also has been reviewed by Madon and Shaw (1977). In the present study the effect of sulfur poisoning was investigated with respect to a fused magnetite catalyst. Since the slurry reactor is well mixed, sulfur poisoning will be uniform, thus removing the uncertainties caused by poison gradients that occur when studies are made in a fixed bed reactor.

I.D.1 Activity

Hydrogen Sulfide Poisoning: In the first experiments, hydrogen sulfide was added to the feed stream for a short time and the resulting activity noted. This was repeated four times ($T = 263°C$, $P = 0.79$ MPa, $(H_2/CO)_{in} = 1.32$). The catalyst activity

(k) as calculated by equation I.1 is plotted versus sulfur loading in Figure I.11, the latter determined by elemental sulfur analysis. At low sulfur loadings (less than 2 mg S/gm Fe), the catalyst activity sharply increased by 63 percent. This increase in activity also occurred in the work by Karn et al. (1964) for a similar fused iron catalyst.

Experiments were then done at three temperatures (P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69) to determine the effect of sulfur poisoning on the activation energy (Figure I.12). A loading to reduce the catalyst activity to approximately 1/2 of the poisoned level increased the apparent activation energy from 83 to 95 kJ/mole. A further loading to decrease the activity to about 1/10 of the unpoisoned level further increased the apparent activation energy from 95 to 99 kJ/mole.

Dibenzothiophene Poisoning: Phenanthrene with concentrations of 1.0 or 0.01 weight percent dibenzothiophene was used as the slurry carrier. The rate constants calculated using equation I.1 are plotted in Figure I.12. The highest loading of dibenzothiophene decreased the observed activity by a factor of 10, and decreased the apparent activation energy by 21 kJ/mole (from 105 to 81 kJ per mole). The intermediate loading decreased the activity by a factor of 4 and the activation energy by 10 kJ/mole (from 105 to 93).

I.D.2 Selectivity

I.D.2.a Molecular Weight Distribution-Light Products

Hydrogen Sulfide Poisoning: The molecular weight distributions for the hydrogen sulfide poisoning experiments are plotted in Figure I.13 for the light products C_1 to C_6. The first two levels of poisoning had no measurable effect on the light product distributions. The third and fourth sulfur additions lowered the C_3 to C_6 alpha from 0.62 to 0.61 and 0.59 respectively.

Dibenzothiophene (DBT) Poisoning: The influence of dibenz thiophene (DBT) on light product distributions is shown in Figure I.14. In the presence of dibenzothiophene the formation of methane decreased by about 40%. This effect did not occur with H_2S (Fig. 1.13) and it provides an important lead on use of partial poisoning to control methane formation.

I.D.2.b Olefin Formation

Hydrogen Sulfide Poisoning: The C_5 olefin to paraffin ratios for the hydrogen sulfide poisoned catalyst are plotted versus hydrogen partial pressure in Figure I.15. Included in Figure I.15 is the correlation determined by Huff for 263°C (smooth curve). Only at the highest sulfur loading does the olefin to paraffin ratio drop measurably below the correlation.

Dibenzothiophene Poisoning: Figure I.16 plots the C_5 olefin to paraffin ratio versus hydrogen partial pressure for the dibenzothiophene-phenanthrene system and for the pure phenanthrene system. The poisoned system produced significantly higher olefin to paraffin ratios than the unpoisoned system.

I.D.2.c Olefin Isomerization

Hydrogen Sulfide Poisoning: Figure I.17 is a plot of the percent olefins in the alpha form for the C_5 and C_6 fraction versus carbon monoxide partial pressure for the hydrogen sulfide poisoned catalyst (sulfur loadings are in parentheses). As for the unpoisoned catalyst systesm, increasing carbon monoxide pressure reduces the conversion of alpha olefins to beta olefins. The only exception is for the highest level of sulfur poisoning where alpha olefin content decreases slightly.

Dibenzothiophene Poisoning: The dibenzothiophene poisoned system shown in Figure I.18 significantly increased the extent of olefin isomerization. For the data at 263°C and high conversions (low CO partial pressures) up to 80 percent of the C_5 olefins in the dibenzothiophene system were secondary olefins as opposed to 10 to 15 percent in the unpoisoned case at comparable conversions.

I.F.1 Conclusions: Sulfur Poisoning

(1) Hydrogen sulfide added as such to a catalyst after a period of unpoisoned reaction does not significantly change the product selectivity. At sulfur levels sufficient to cause a 10 fold decrease in activity, there occurred a slight increase in the extent of secondary reactions and a slight decrease in alpha.

(2) Dibenzothiophene, present in the carrier fluid initially, is more effective at reducing the catalyst activity than hydrogen sulfide on a mg-of-S-per-gm-of-Fe basis. Most noteworthy is the marked decrease in methane formation that it caused. DBT also increased olefin to paraffin ratios and increased alpha olefin to beta olefin isomerization.

I.F.2 Conclusions: Carrier Interactions

(1) Secondary reactions occur significantly on this fused iron catalyst. These secondary reactions include alpha to beta olefin isomerization, C_2 reincorporation, most likely olefin hydrogenation, and possibly alcohol dehydration. All the secondary reactions increase with increasing conversion and increasing temperature.

(2) Secondary reactions are all decreased by the presence of an aromatic slurry carrier (phenanthrene). This is presumably due to adsorption of the phenanthrene on secondary reaction sites.

(3) The presence of a slurry carrier (Fomblin) which has a low solubility of Fischer-Tropsch products in it causes a capsule of products to form that surrounds the catalyst particle. This capsule lowers the observed activity and the apparent activation energy of the reaction indicating diffusional limitations. Secondary reactions also occur to a greater extent in this system due to the capsule creating a cage effect preventing the primary products from escaping.

(4) Phenanthrene increases the catalyst activity compared to octacosane even though it seems to be significantly adsorbed onto the catalyst. Most likely the phenanthrene has altered the configuration of the activated complex in a way to increase its frequency of decomposition.

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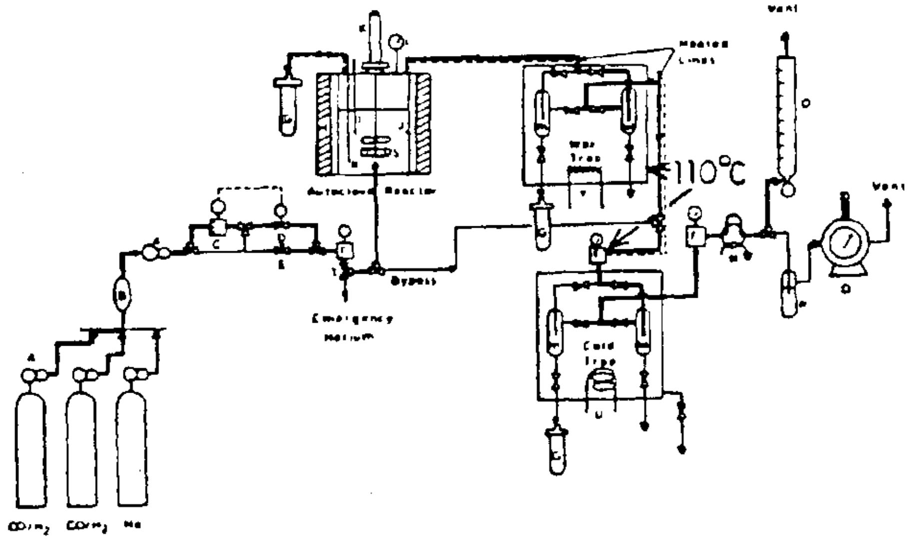

Figure 1.1 Slurry-Bed Reaction Unit: A Pressure Regulator; B Filter Drier; C Differential-Pressure Cell; D Pneumatic Control Valve; E Manually-Operated Needle Control Valve; F Dome-loaded, Back-Pressure Regulator; G Condensed Products; H Electric Furnace; I Thermocouple Well; J Baffle; K Magnedrive Stirrer; L Pressure Gauge, M 300 cc Trap, M 1.0 l Trap; N Gas Sample Valve; O Soap-film Flowmeter; P Water Saturator; Q Wet-Test Meter; R Slurry Sample Tube; S Agitator; T Three-way, Air-Operated Valve; U Mechanical Refrigeration Unit; V Strip Heater (Huff and Satterfield, 1981).

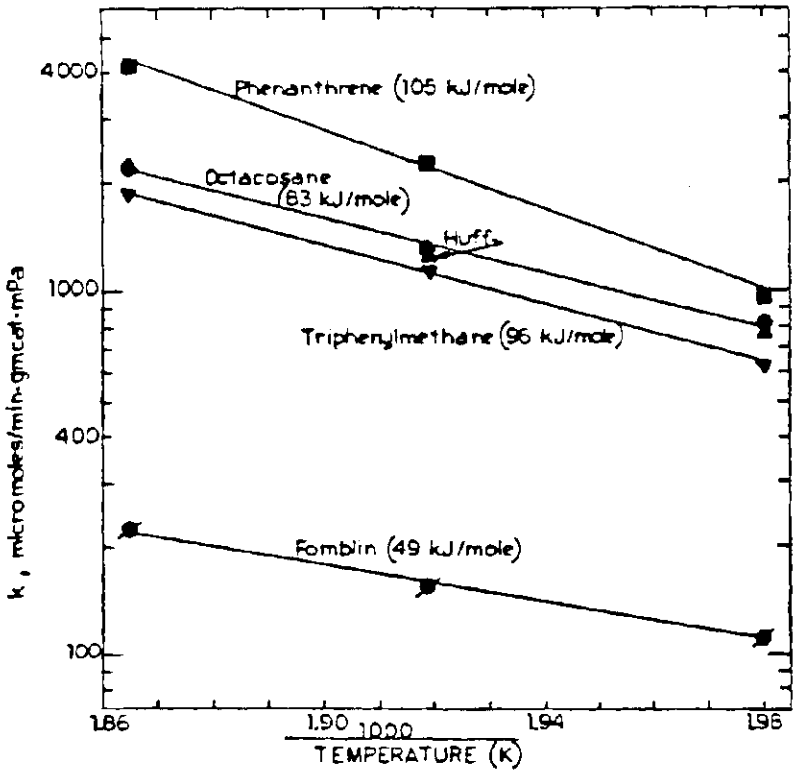

Figure 1.2 Rate constants calculated by equation 1.1 for the four carrier systems versus reciprocal temperature.

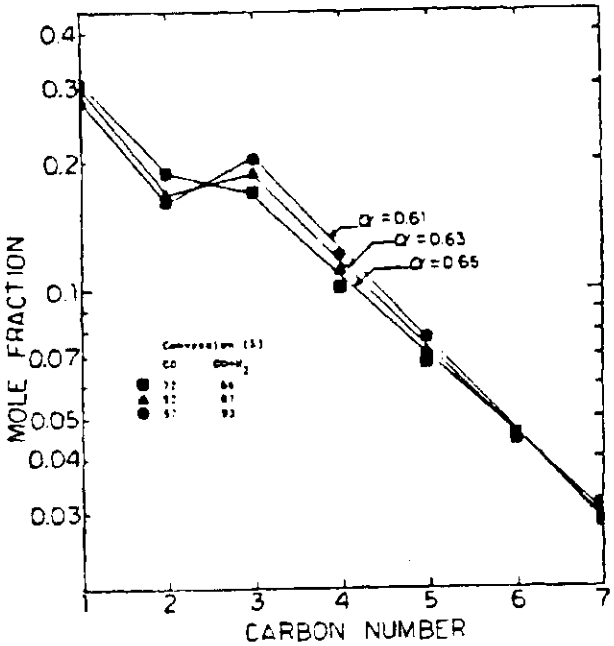

Figure I.3. Light product distribution for the octacosane carrier system. T = 263°C, P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

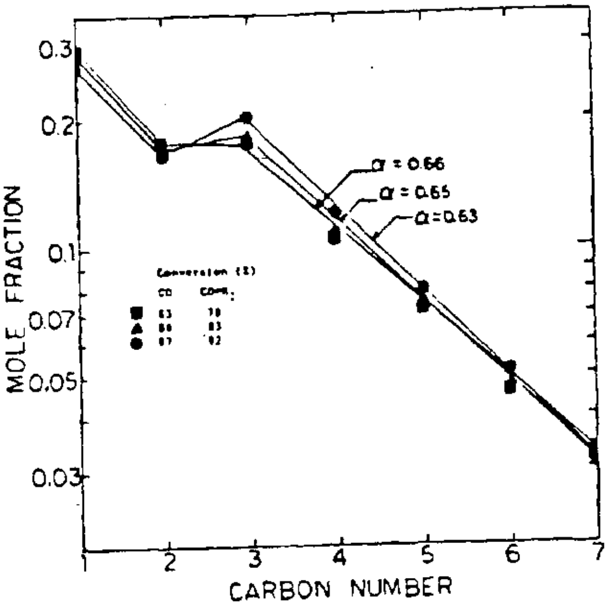

Figure I.4. Light product distribution for the phenanthrene carrier system. T = 263°C, P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

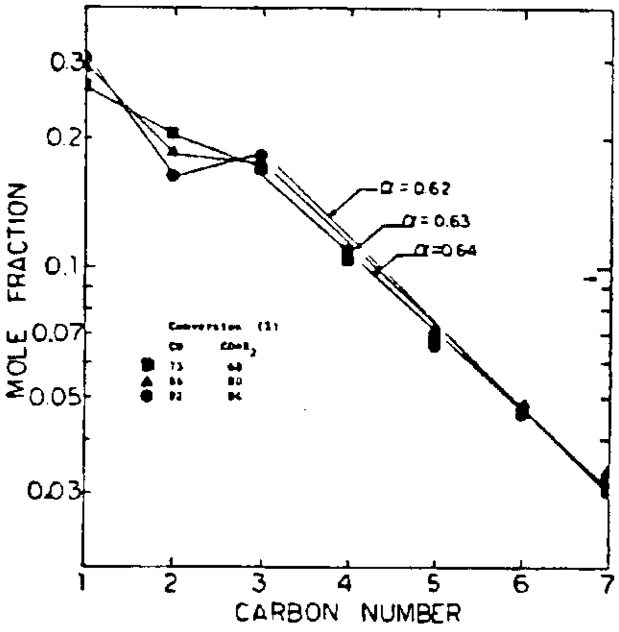

Figure I.5. Light product distribution for the triphenylmethane carrier system. T = 263°C, P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

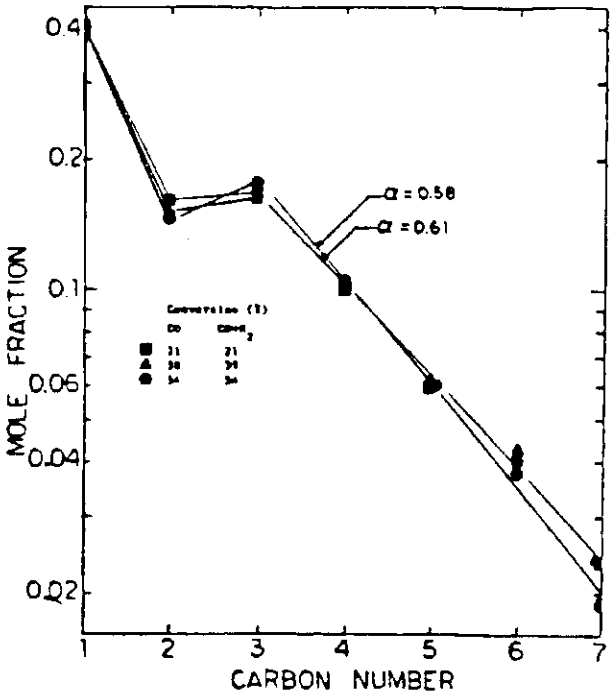

Figure I.6. Light product distribution for the Fomblin carrier system. T = 263°C, P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

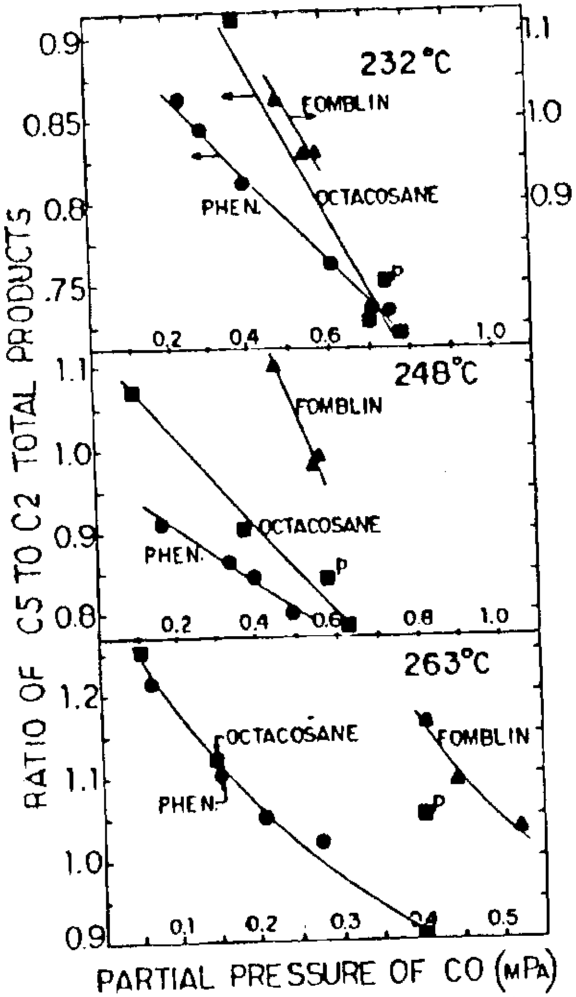

Figure 1.7 C2 reincorporation for the octacosane, phenanthrene, and Fomblin systems. Points labelled with p are for the H_2S poisoned catalyst. P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

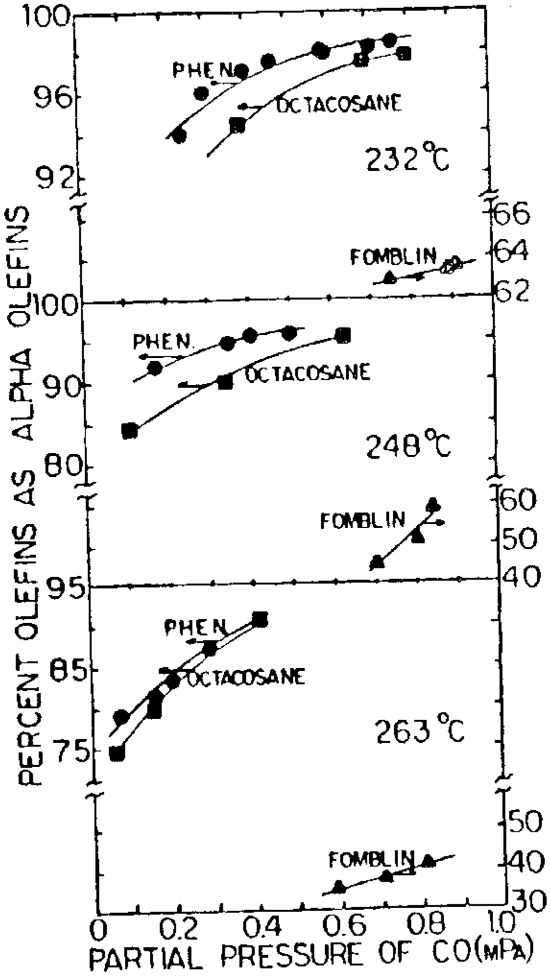

Figure 1.9 Percent C5 olefins in alpha form for the three carrier systems: octacosane, phenanthrene, Fomblin. P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

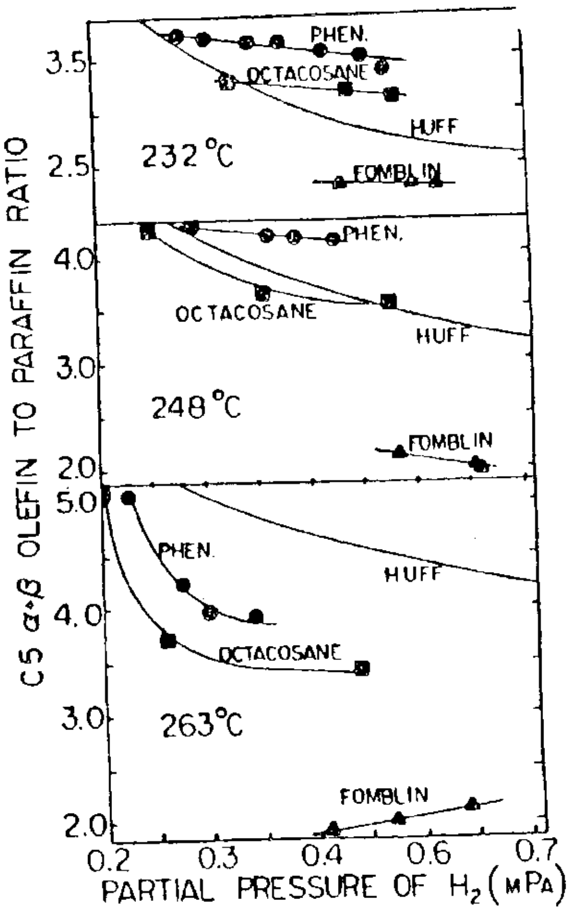

Figure 1.8 C5 olefin to paraffin ratios versus H_2 partial pressure for the three carrier systems: octacosane, phenanthrene, and Fomblin. Smooth curves are correlations by Huff(1982). P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

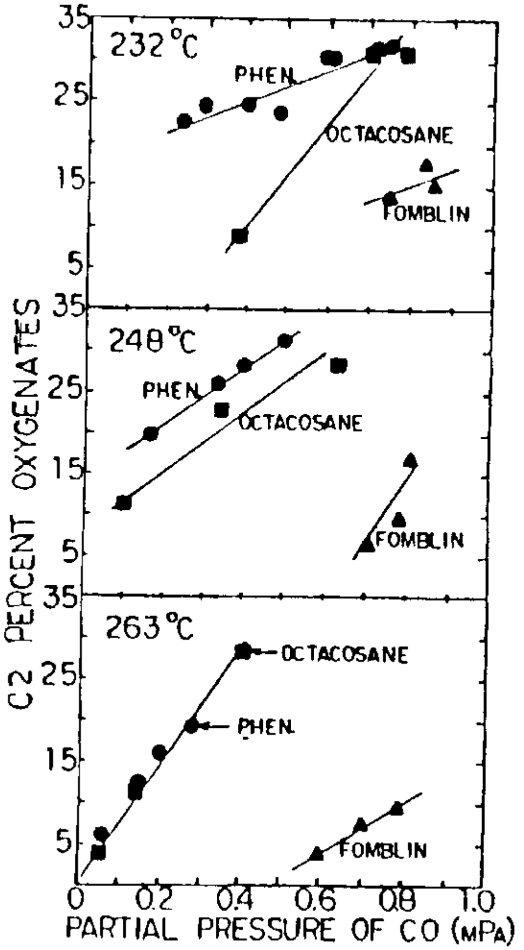

Figure 1.10 Percent C2 oxygenates versus CO partial pressure for the three carrier systems: Octacosane, phenanthrene, and Fomblin. P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

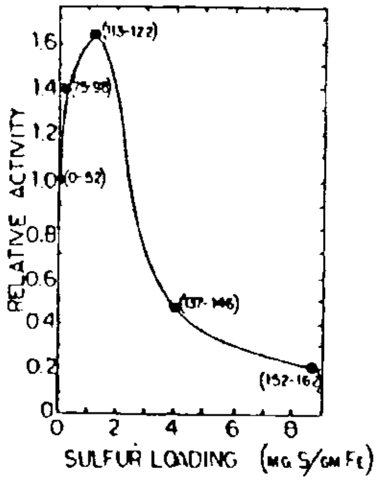

Figure 1.11 Relative activity as a function of sulfur loading for the H_2S poisoned catalyst. T = 263°C, P = 0.79 MPa, $(H_2/CO)_{in}$ = 0.90. Numbers in parentheses are hours on stream.

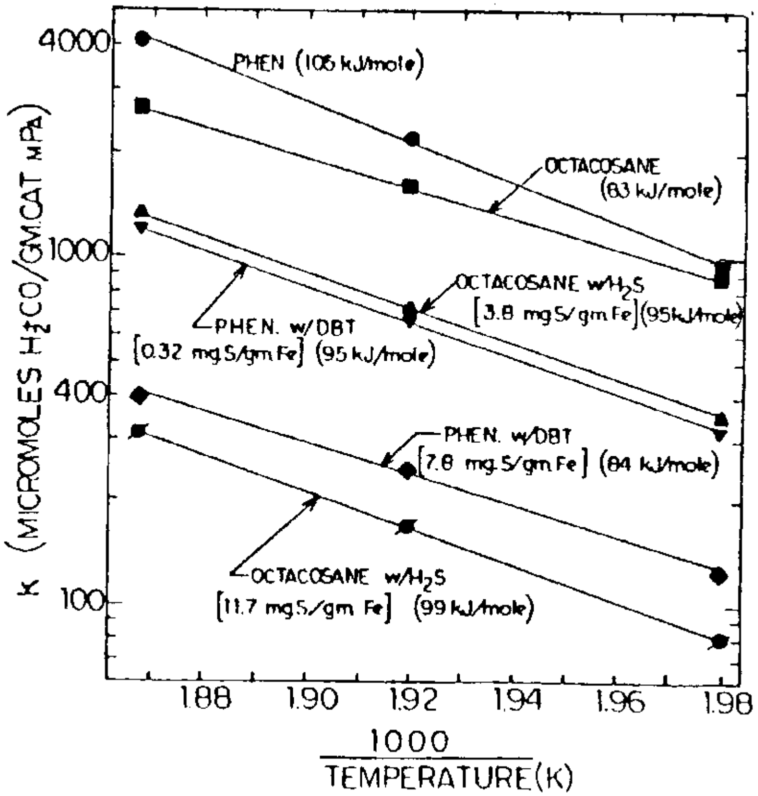

Figure 1.12 Rate constants for poisoned catalyst systems versus reciprocal temperature.

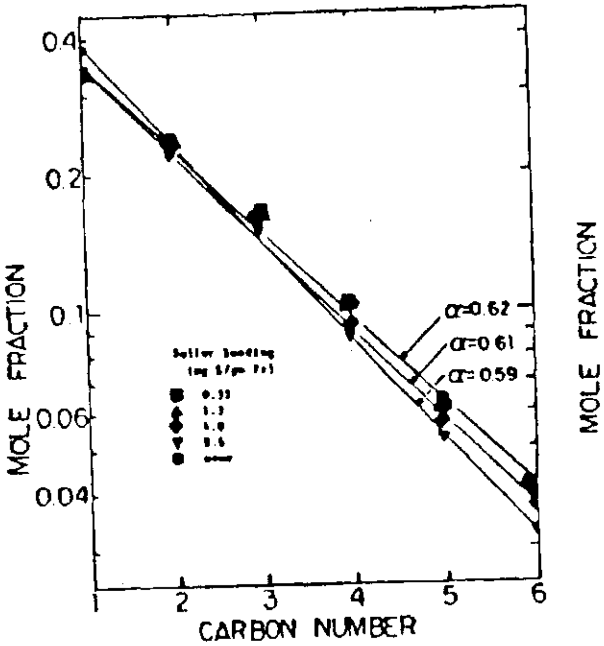

Figure I.13. Influence of H_2S on light product distributions. T = 263°C, P = 0.79 MPa, $(H_2/CO)_{in}$ = 0.69.

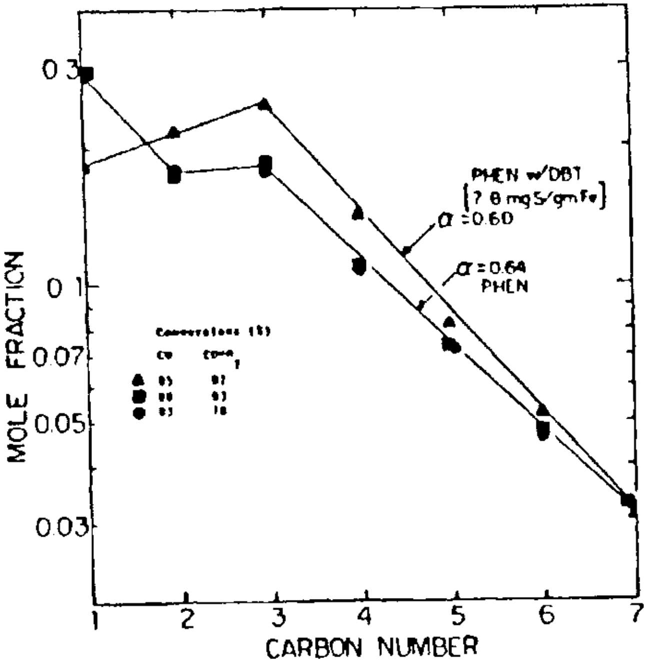

Figure I.14. Light product distributions for DBT catalyst compared to pure phenanthrene system. T = 263°C, P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

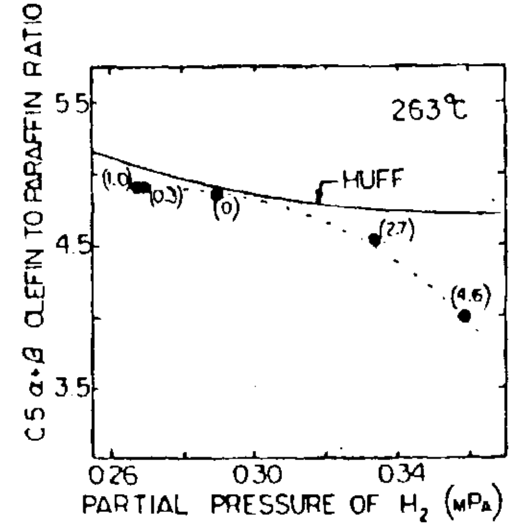

Figure I.15. C_5 olefin to paraffin ratios versus H_2 partial pressure for the H_2S poisoned catalyst. Numbers in parentheses are sulfur loadings in mg S/gm Fe. P = 0.79 MPa, $(H_2/CO)_{in}$ = 0.90.

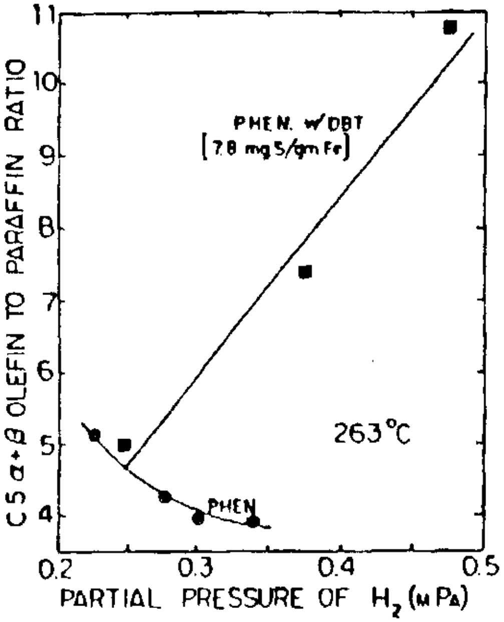

Figure I.16a. Influence of DBT poisoning on the C_5 olefin to paraffin ratio. P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

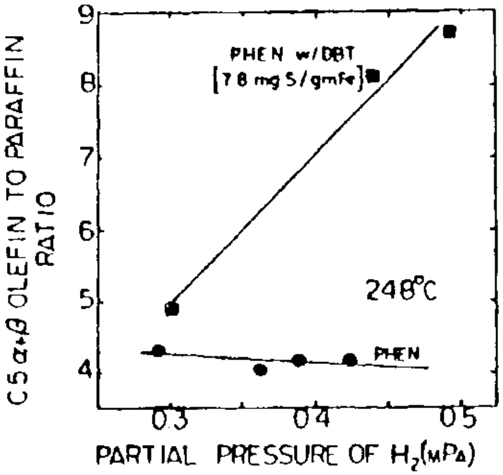

Figure I.16b. Influence of DBT poisoning on the C_5 olefin to paraffin ratio. P = 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.

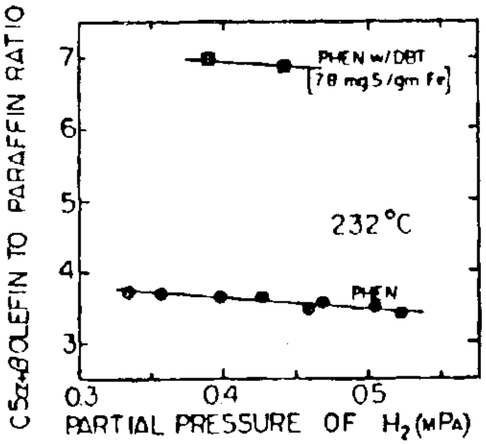

Figure I.16c. C_5 olefin to paraffin ratios versus H_2 partial pressure. Influence of DBT poisoning. P = 1.48 MPa. $(H_2/CO)_{in}$ = 0.69.

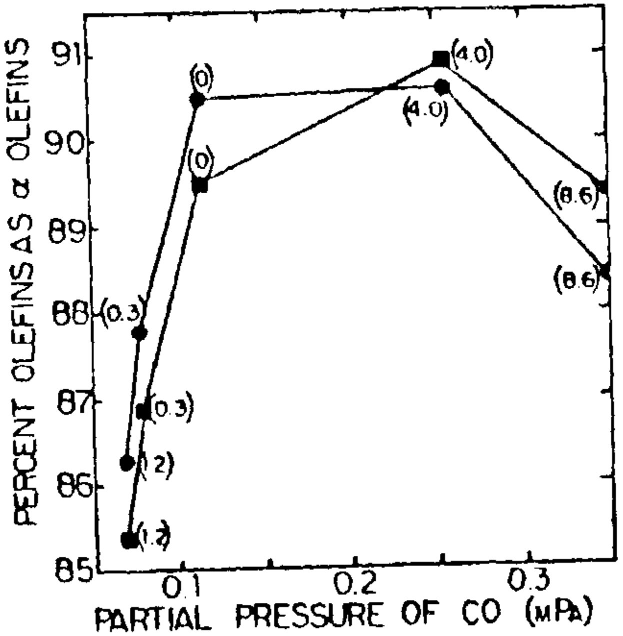

Figure 1.17 Influence of H_2S poisoning on olefin isomerization. Values in parentheses are sulfur loadings in mg S/gm Fe. P=0.79 MPa, T=263°C, $(H_2/CO)_{in}$ =0.90.

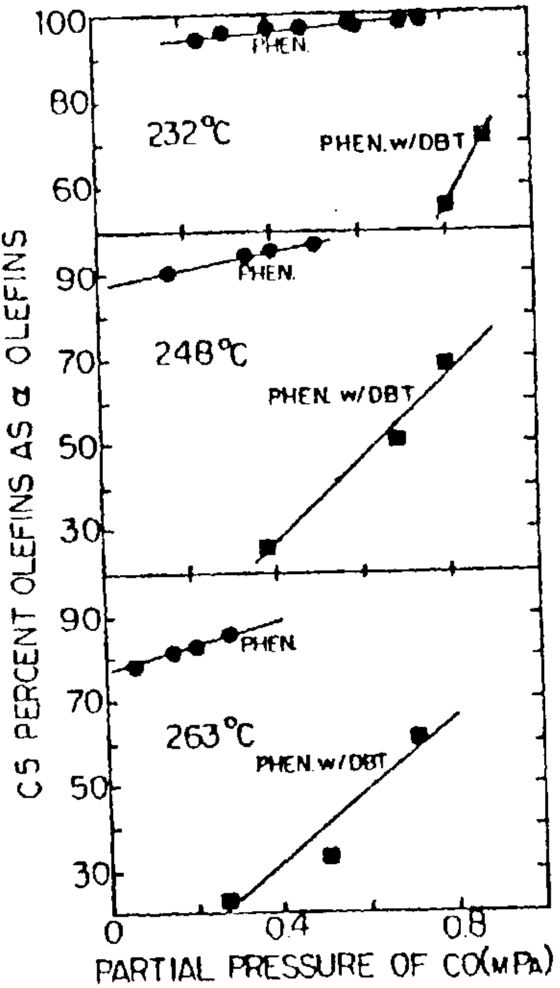

Figure 1.19 Percent C5 olefins as alpha olefins versus CO partial pressure for the unpoisoned phenanthrene system and the DBT poisoned system (w/ 7.8 mg S/gm Fe). P= 1.48 MPa, $(H_2/CO)_{in}$ = 0.69.