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**Mössbauer Spectroscopy Studies of Iron Catalysts Used in
Slurry Phase Fischer-Tropsch Synthesis**

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Mössbauer Spectroscopy Investigation of the Structure of Iron-Based Fischer-Tropsch Catalysts

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Introduction

Iron and cobalt are the two principal choices as catalysts for Fischer-Tropsch (F-T) synthesis. As discussed in a recent review by Wender,⁽¹⁾ each metal has certain advantages and disadvantages. Davis and co-workers⁽²⁾ have recently discussed the advantages of iron-based F-T catalysts in some detail.

In order to understand the catalytic reaction mechanisms of iron during F-T synthesis, it is critical to identify the active catalytic phases. Moreover, from a practical point of view, it is equally important to identify the reactions and transformations that deactivate the catalysts. ⁵⁷Fe Mössbauer spectroscopy is perhaps the best technique available for quantitative characterization of the iron phases in complex samples. For the past several years, our group has been using Mössbauer spectroscopy to characterize the iron-based catalysts prepared and tested for F-T synthesis in a number of DOE-sponsored programs. These include F-T research programs supervised by Dragomir Bukur at Texas A & M University, Burtron Davis at the University of Kentucky, Davindar Mahajan at Brookhaven National Laboratory, and the F-T pilot plant program at La Porte, Texas.

The results of this investigation have been summarized in detail in DOE reports and in a number of publications released over the past few years. A list of the principal publications resulting from this work is given in references 3 - 13. A brief summary of the highlights of the results presented in these papers is presented in the current report.

Experimental Procedure

The preparation and testing of the catalysts examined in this work has been described in detail elsewhere^(2, 13, 14) and will not be repeated here.

The Mössbauer spectroscopy apparatus and spectral fitting procedures are fairly standard.^(15, 16) Briefly, the Mössbauer laboratory uses constant acceleration spectrometers of standard design manufactured by Halder Elektronik, GmbH. The radioactive Mössbauer sources consisted of from 25 to 50 milliCuries of ^{57}Co in a Pd matrix. ^{57}Co decays to an excited state of ^{57}Fe , which then emits the 14.4 keV gamma ray that can be resonantly absorbed by a second ^{57}Fe nucleus in its ground state. As discussed in earlier review articles,^(15,16) magnetic, electric quadrupole, and electrostatic interactions between the electrons and the nucleus give rise to nuclear level splittings and shifts that cause every solid iron-bearing phase to exhibit a distinctive Mössbauer absorption spectrum.

In order to enhance the nuclear level splittings and better distinguish between different iron-bearing phases, it is sometimes advantageous to cool the sample to cryogenic temperatures. In the current experiments, this was done for some samples using a Displex system, which is capable of achieving sample temperatures of 10 K. For most samples, however, the room temperature spectra were sufficient.

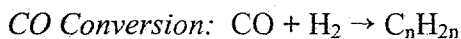
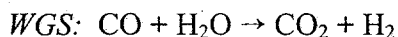
Analysis of the spectra was carried out by performing least squares analysis in which the spectra were fitted to a series of Lorentzian peaks. As discussed elsewhere,^(15,16,17) the percentages of iron contained in different iron-bearing phases can be determined from the peak areas. It is worth emphasizing that this method normally gives quantitative iron phase analyses that are considerably more accurate than can be obtained by competing techniques, such as x-ray diffraction (XRD) or x-ray photoelectron spectroscopy (XPS).

Results and Discussion

Prior to F-T synthesis reaction, the catalysts are in the form of superparamagnetic, ferric oxyhydroxides. During reaction, they are converted principally into magnetite and

carbide phases. Typical Mössbauer spectra obtained from two used catalysts, one reacted in an autoclave, and the other reacted in the La Porte pilot plant, are shown in Figure 1. The peaks derived from magnetite (Fe_3O_4), χ -carbide (Fe_5C_2) and ε -carbide ($\text{Fe}_{2.2}\text{C}$) are appropriately labeled.

One goal of the current work is to identify the iron phases that are active for the water-gas shift (WGS) reaction and for F-T hydrocarbon synthesis.



Because all of the samples examined exhibited a number of phases, it is difficult to reach hard conclusions regarding active phases and deactivation mechanisms. Nevertheless, a number of interesting trends have been observed.

Figure 2 illustrates the behavior of the iron phase percentages as a function of time on stream (TOS) for reacted catalyst samples obtained at the LaPorte plant. The first sample examined was obtained after 50 hours on stream. At that point, the catalyst is a mixture of magnetite, χ -carbide and ε -carbide and ferric oxide. With increasing TOS, ε -carbide gradually increases while the other phases.

Figure 3 shows the variation of a number of parameters with TOS for the same La Porte run. The usage ratio is defined as the number of hydrogen atoms consumed per molecule of CO converted. An increase in the WGS yields a decrease in the usage ratio. The general increase in the usage ratio shown in Figure 3b occurs while the amount of magnetite is decreasing (Figure 1). This appears to support the proposal of Dumesic and Rethwisch that magnetite is the active phase for the WGS. We have also observed an increase of the B site to A site ratio (Figure 3a) in the magnetite phase with increasing usage ratio (or decreasing WGS activity). This suggests that cation deficient magnetite is a better catalyst for WGS.

Finally, there appears to be a general increase in F-T synthesis (Figure 3c) with increasing carbide percentage (Figure 2).

Unfortunately, although these trends can be seen in the La Porte data, they are somewhat obscured by the fact that several parameters were being varied during the run for various reasons. As indicated by the insets in Figure 2, these included space velocity, pressure and syngas composition. This is the origin of the sizeable fluctuations in conversion, useage ratio, and B/A ratio seen in Figure 3. The correlation between CO conversion and carbide percentage is seen more clearly in the better controlled autoclave data of Figure 4, obtained in Bukur's laboratory. Both the F-T conversion and the χ -carbide percentage are seen to decrease with increasing SiO₂ content.

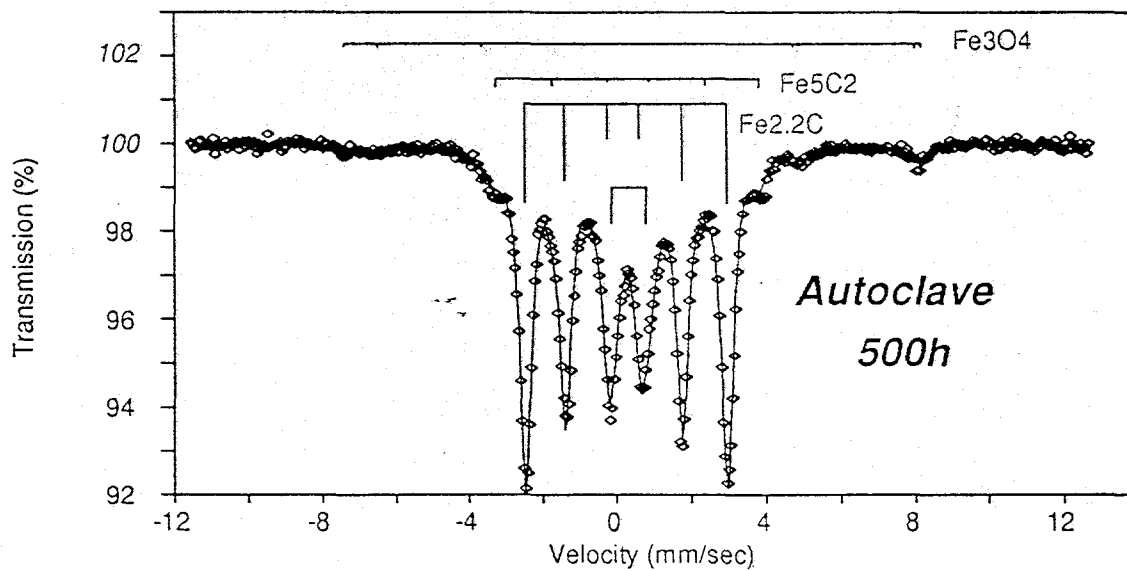
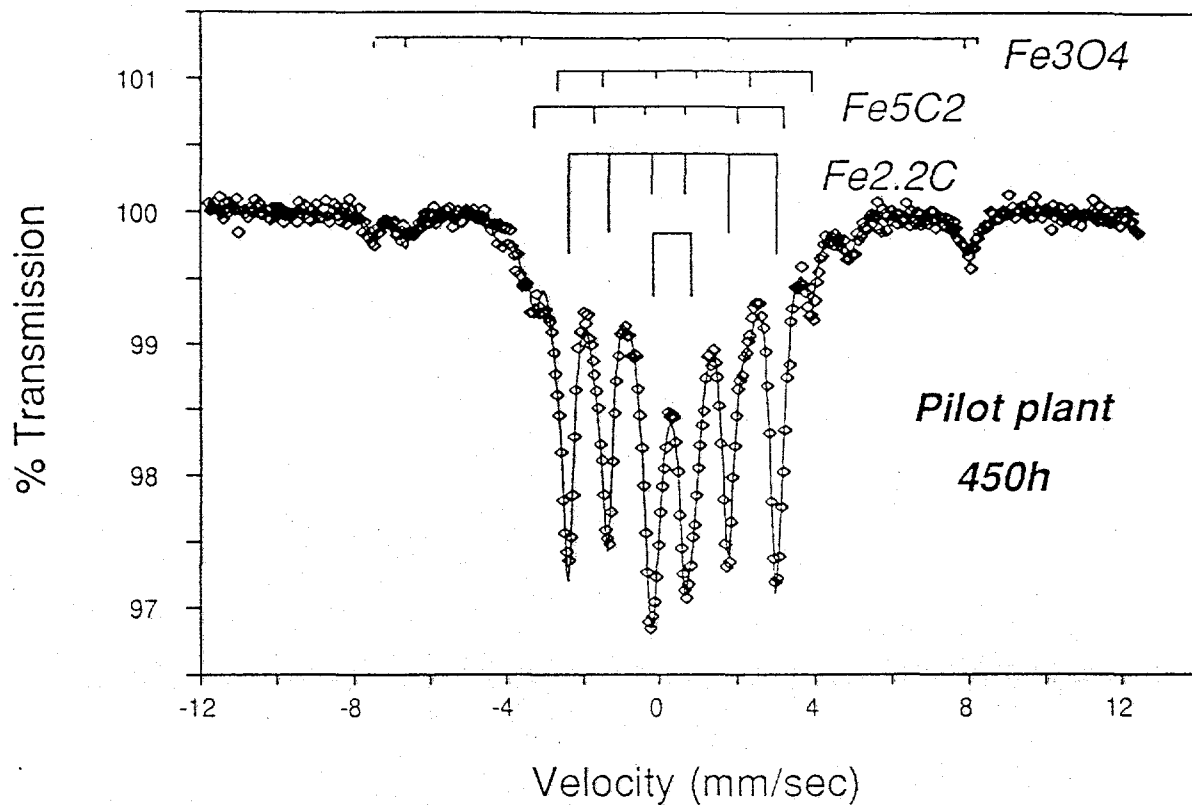
Summary and Conclusions

Over the past several years, we have used Mössbauer spectroscopy to investigate the phase distributions of a large number of iron-based F-T catalysts from a number of laboratories and from the La Porte pilot plant. This research has resulted in a better understanding of how different iron phases affect F-T synthesis and the WGS reaction. Briefly, magnetite appears to be the active phase for the WGS reaction and its activity increases with increasing B/A ratio or cation deficiency. F-T conversion, on the other hand, appears to increase with increasing carbide percentage. These results are summarized in more detail in references 3-13.

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Typical spectra of reacted F-T catalyst

Figure 1

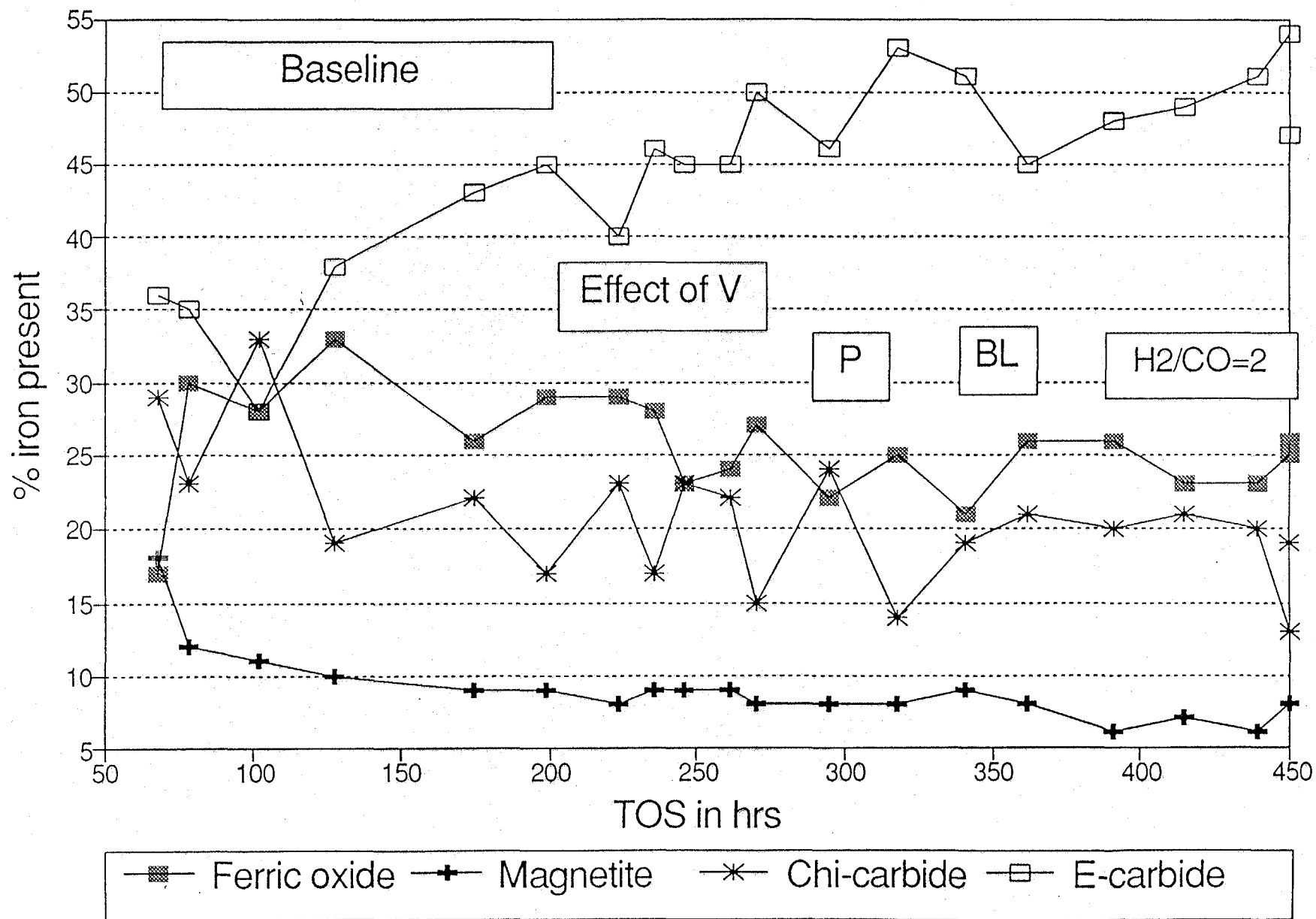


Fig. 2 Variation of iron phases in the catalysts with TOS

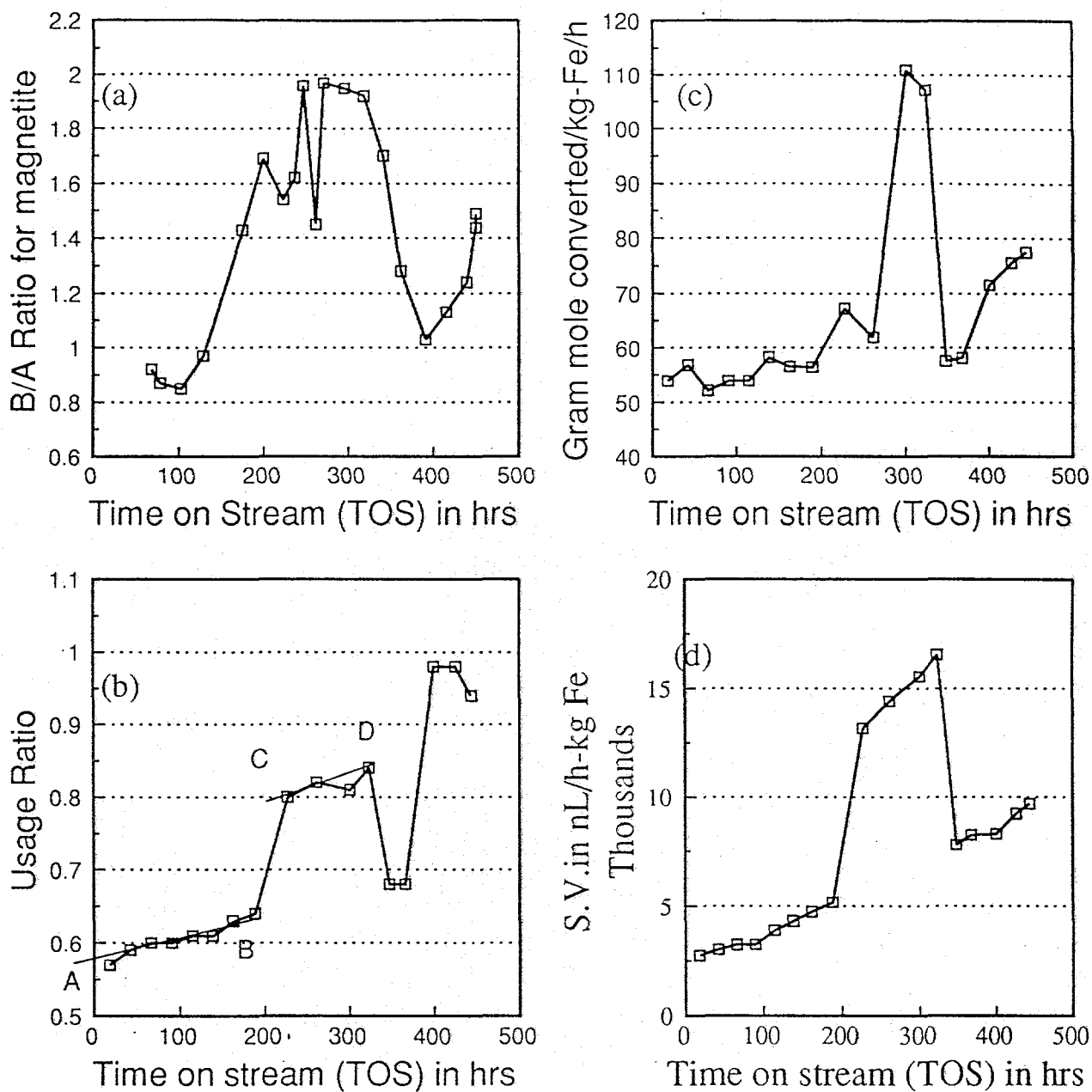


Fig.3 Variation of (a) B/A ratio, (b) usage ratio, (c) CO conversion rate, and (d) space velocity as a function of time on stream.

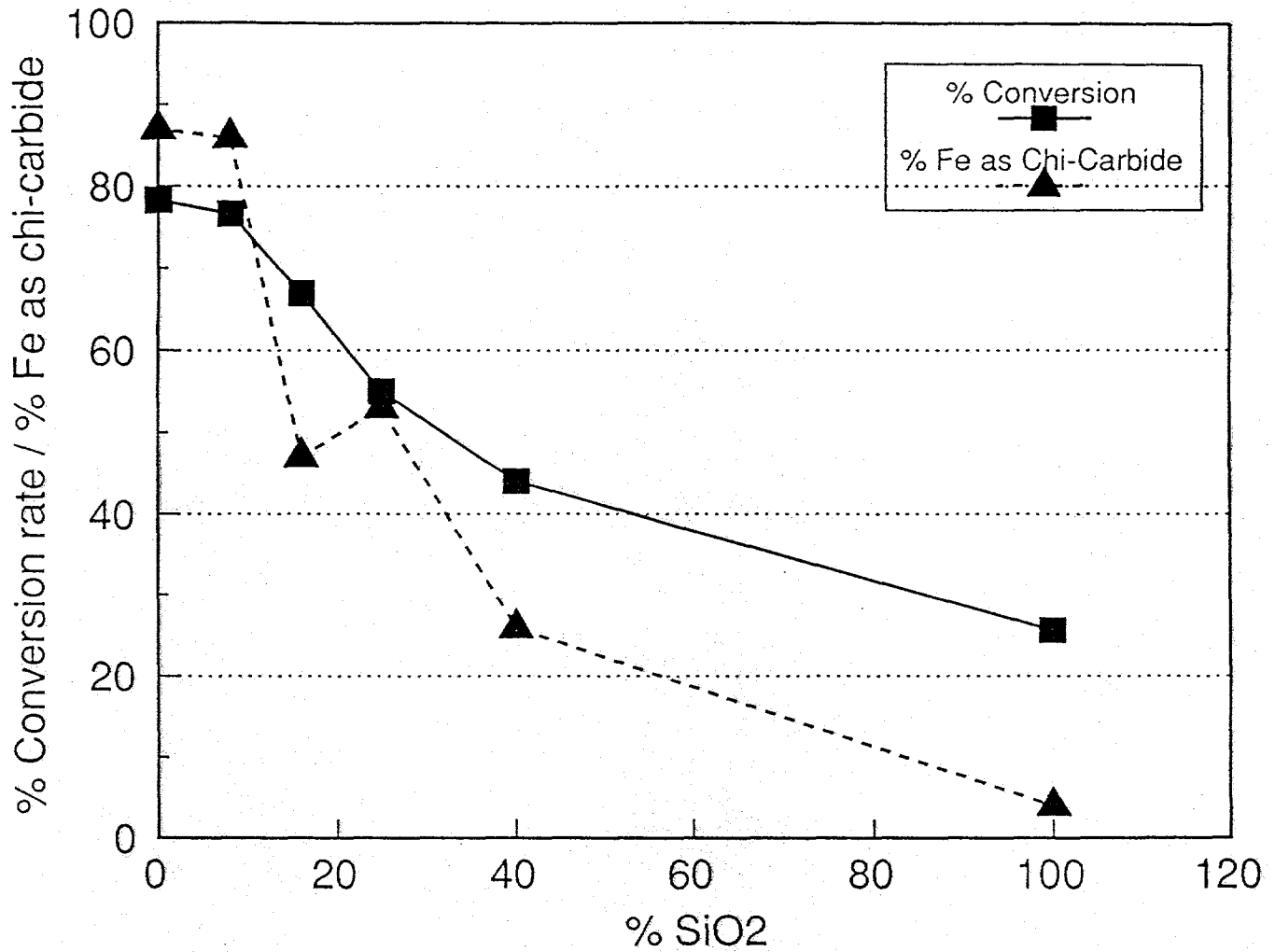


Figure 4. Variation of (a) χ -carbide formed during reaction (10-50 hours) and (b) $(CO + H_2)$ conversion with silica content.

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July 26, 1999

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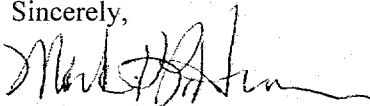
RE: Contract No. DE-AC22-94PC93066 --- Final Performance Report

Dear Mr. Dawson:

Enclosed please find the original and one (1) copy of the Final Performance Report for the above-referenced contract.

According to Professor Huffman he has sent all the Quarterly Reports he can locate. Hopefully this will complete the close out process for this project and DOE will reimburse the outstanding final amount for \$2,112.94. If I may provide additional assistance, please contact pittman@pop.uky.edu or call the following telephone number (606) 257-4826.

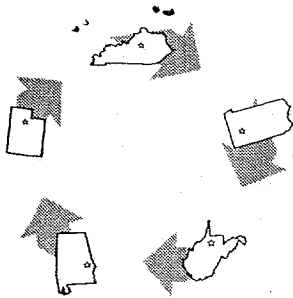
Sincerely,


Mark H. Pittman
Research Administrator

cc: Gerald Huffman/427738

Letters/Closeout/HuffmanFETC427738FinalReport01.doc

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July 21, 1999

Mr. Kelly Dawson
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Dear Mr. Dawson:

Enclosed is our final report for DOE Contract No. DE-AC22-94PC93066, "Mössbauer Spectroscopy Studies of Iron Catalysts Used in Slurry Phase Fischer-Tropsch Synthesis."

Sincerely,

Gerald P. Huffman
Director, CFFLS / University of Kentucky