

DE-FC26-03NT41965

Separation of Fischer-Tropsch Wax Products from Ultrafine  
Iron Catalyst Particles

Quarterly Report

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Reporting Period  
January 1 to March 31, 2004

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## ABSTRACT

In this reporting period, a fundamental filtration study was started to investigate the separation of Fischer-Tropsch Synthesis (FTS) liquids from iron-based catalyst particles. Slurry-phase FTS in slurry bubble column reactor systems is the preferred mode of production since the reaction is highly exothermic. Consequently, heavy wax products must be separated from catalyst particles before being removed from the reactor system. Achieving an efficient wax product separation from iron-based catalysts is one of the most challenging technical problems associated with slurry-phase FTS. The separation problem is further compounded by catalyst particle attrition and the formation of ultra-fine iron carbide and/or carbon particles.

Existing pilot-scale equipment was modified to include a filtration test apparatus. After undergoing an extensive plant shakedown period, filtration tests with cross-flow filter modules using simulant FTS wax slurry were conducted. The focus of these early tests was to find adequate mixtures of polyethylene wax to simulate FTS wax. Catalyst particle size analysis techniques were also developed. Initial analyses of the slurry and filter permeate particles will be used by the research team to design improved filter media and cleaning strategies.

## TABLE OF CONTENTS

	<u>Page</u>
Disclaimer .....	1
Abstract .....	3
Executive Summary .....	4
<b>Task 1. Fundamental Filtration Studies</b> .....	<b>6</b>
Task 1.1 & 1.2. Filtration Shakedown and Wax Solvent Study .....	6
Introduction .....	6
Experimental .....	9
Results and Discussion .....	12
Conclusions .....	16
References .....	17
Figures .....	19
Task 1.3. Filtration studies with doping of olefins and alcohols .....	32
Task 1.4. Ultra-fine Iron Filtration .....	32
Task 1.5. Development of Filter media cleaning procedure .....	32
Task 1.6. Chemical and physical characterization of slurry and filtrate.....	33
Introduction .....	33
Catalyst Preparation .....	34
Reaction Testing .....	35
Mossbauer Spectroscopy .....	36
EXAFS and XANES Analysis .....	37
References .....	37
Figures .....	38
<b>Task 2. Phase II Bubble Column Pilot Plant Studies</b> .....	<b>42</b>

## EXECUTIVE SUMMARY

In this reporting period, a fundamental filtration study was started to investigate the separation of Fischer-Tropsch Synthesis (FTS) liquids from iron-based catalyst particles. Catalyst consumption due to filtration losses is a major expense in the operation of slurry phase FTS reactors using iron-based catalysts. Attrition of such catalysts in slurry-phase reactors produces a significant amount of fines, making catalyst separation from the products difficult. During slurry-phase FTS with bubble column reactors, catalysts are generally separated from accumulated reactor wax by either internal filtration or an external settling system which circulates catalyst back to the reactor. Catalyst fines produced by attrition may cause filters to plug and are difficult to separate by settling. As a result, multiple filtration stages are needed in order for the waxes to be well-suited for down-stream processing.

The overall objective of this filtration study is to test the effectiveness of various cross-flow filtration procedures with a simulant FTS slurry. The wax products from a FTS reactor can vary widely depending on the type of process implemented. In this study, the focus is on a high-alpha iron-based slurry-phase reaction process. The change in filtration properties of iron catalyst slurries will be correlated with physical and chemical changes of the particles during Fischer-Tropsch conditions.

An existing pilot plant platform was modified into a cross-flow filtration test unit. The unit is capable of testing slurry batches as large as 98 liters (26 gallons). This unit will allow several types of cross-flow filter media to be researched under simulated FTS conditions at flowrates from 4 to 20 lpm. The prototype filtration modules are zirconia-coated steel membranes having a nominal pore size of  $0.1 \mu\text{m}$ . Work on the software for data acquisition and control was completed. New instrumentation such as flow meters and control valves were procured and installed.

During the shakedown phase of the program, a Polywax 3000 wax (without added catalyst) was used to check out the pumps, associated process instrumentation and the permeation/back-pulse system. This also provided a worst-case scenario for the clean-fluid permeation rate of the filter medium. Attempts to pass the Polywax 3000 through the  $0.1 \mu\text{m}$  membrane were not successful. Apparently, the filter medium was overwhelmed by the large molecular weight compounds of the heavy wax since no solids were present in the slurry.

Another filter  $0.1 \mu\text{m}$  module was tested with a 5 wt% catalyst slurry in a wax mixture of 86:14%  $\text{C}_{30}$  oil/Polywax 3000. While operating in a continuous filtration mode, the initial permeate flux was  $0.65 \text{ lpm/m}^2$  and steadily declined below  $0.3 \text{ lpm/m}^2$  over a 6-day test period. The lack of long-term flux stability was attributed to fouling from the higher molecular weight components from the Polywax 3000 and from the attrition of the catalyst particles resulting in higher concentration of fines (below  $1 \mu\text{m}$ ).

A subsequent 2-week duration test with a 5wt% catalyst in a Polywax 500 and back-pulsing displayed more stability and higher permeate flux rates ( $0.58 \text{ lpm/m}^2$  or  $20.6 \text{ GPD/ft}^2$ ). When the permeate back-pulsing was stopped, the permeate flux dropped 25% from  $0.58$  to  $0.43 \text{ lpm/m}^2$ . The permeate samples consistently had a bright white appearance and contained less than 1 ppm as Fe.

In order to quantify the degree of filter media fouling, a static permeation rig was constructed to test the permeability of the membranes before and after catalyst filtration tests. The curve of the membrane flux vs. trans-membrane pressure (TMP) will provide a snapshot of the tube's fouling condition. Results from the permeation rig have shown a significant degree of fouling due to the Polywax simulant slurries. However, heating the cross-flow filtration elements in air returns the tubes to their original state. Further tests will be conducted to investigate the mode of media fouling.

Work was started on refining analytical methods to characterize FTS catalyst slurries. While we are conducting EXAFS and XANES tests to define the Fe-phases which are present in working Fe-based FT catalysts after steady state conditions are attained in the reactor, this information cannot clearly elucidate the active surface phase. Therefore, we are utilizing indirect methods to further understand the active phase. Rubidium, but not potassium, is an alkali which can be studied by EXAFS instrumentation available to us, and certainly directly impacts the catalytic properties. Using EXAFS and XANES, we will first attempt to determine the chemical species and state of the Rb promoter. Also, understanding the active Fe phase in contact with Rb may shed further light on the Fe-based species involved as the catalytically active site. EXAFS may provide this information. The information provided in this report shows the preliminary results of reactor testing of Rb-promoted catalysts, as well as preliminary chemical characterization of the state of Fe in the catalysts, as measured by Mossbauer spectroscopy.

## **TASK 1. Fundamental Filtration Studies**

### Task 1.1 Shakedown and Task 1.2. Solvent wax experiments

#### INTRODUCTION

Traditionally, iron catalysts have been used for F-T synthesis when the syngas is coal-derived, because they have the ability to simultaneously carry out the WGS reaction. Thus, less hydrogen is required and oxygen exits the reactor in the form of CO<sub>2</sub>. Cobalt, suffers from a low WGS activity, making it unsuitable for general use with low H<sub>2</sub>/CO ratio syngas feeds. Iron catalysts such as those used by Sasol are typically prepared by precipitation while cobalt catalysts are generally supported on high surface area oxides such as alumina, silica and titania. Both types of catalysts, and probably cobalt more so than iron, are very sensitive to sulfur poisoning. However, filtration issues in cobalt-based FTS reactors are less problematic since catalyst supports are more attrition resistant than that of iron-based systems.

Because the Fischer-Tropsch synthesis (FTS) reaction is so exothermic, one of the major problems in control of the reaction is heat removal. Recent work has concentrated on the use of slurry phase reactors which are able to solve the problem of heat removal from this very exothermic reaction, as well as use low H<sub>2</sub>/CO ratio syngas, provide high catalyst and reactor productivity, permit catalyst regeneration, and have relatively simple designs and low initial costs.

Catalyst attrition is a major problem in the operation of slurry phase FT reactors using iron-based catalysts (1,2). Attrition of such catalysts in slurry reactors produces significant amount of fines, making catalyst separation from the products difficult, as the

catalyst particles do not settle well. During slurry phase FTS with bubble column reactors, catalysts are generally separated from accumulated reactor wax by either internal filtration or an external settling system which circulates catalyst back to the reactor. Catalyst fines produced by attrition may cause filters to plug and are difficult to separate by settling. Ultimately, the long residence time of a catalyst particle in an industrial reactor is sufficient to break down catalyst particles. Therefore, a robust filtration system is needed for FTS to be a viable technology.

Generation of fines from a SBCR can occur in 3 stages: 1. The release of nascent fine particles from the surfaces of the bulk catalyst particle that were formed during catalyst preparation; 2. Initial products of attrition from physical breakage of the catalyst particles; and 3. On a longer time-scale, the formation of iron carbide crystallites. Each of these stages present unique filtration problems during the production of FTS wax.

Some limited fundamental studies have shown that attrition resistance of iron-based catalysts depends on the type of activation the catalyst receives. However, these studies have not attempted to correlate the change in filtration properties of catalyst slurries with physical and chemical changes of the particles under conventional FTS conditions. Iron-based Fischer-Tropsch (FT) catalysts undergo a series of phase transformations during activation and use.

Catalyst activation with carbon monoxide or syngas typically results in the conversion of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  and ultimately to one or more carbides during reaction synthesis (1). Fine particles extracted from a FTS slurry are shown in Figures 1 and 2. The slurry samples were dissolved in ortho-xylene and subsequently evaporated over a lacy carbon substrate. As shown in Figure 1, the iron crystallite agglomerates can be as



large as 0.2 to 1.0  $\mu\text{m}$ . However, iron particles on the order of 10-20 nm are also predominant as shown in Figure 2. The mobility of these smaller nm-scale particles is unknown. During the filtration process, clusters of these particles may agglomerate and make for more efficient separation. It is also likely that a portion of these smaller crystallites migrate into the filter media and cause irreversible fouling.

Numerous separation processes have been proposed in the literature based on a variety of filtration media along with washing/cleaning techniques (3-7). Most of these filtration methods are for primary filtration (removing wax products with reduced catalyst concentration, below 2000 ppm). Secondary filtration should reduce the catalyst concentration below about 10-15 ppm such that the wax can be compatible with downstream processes such as cracking.

## EXPERIMENTAL

*Filtration Test Platform.* An existing pilot plant platform was modified into a cross-flow filtration test unit. This unit, depicted schematically in Figure 3, will allow several types of cross-flow filter media to be researched under simulated FTS conditions. Three prototype filtration modules were received from Pall, Inc. The modules have an inlet (filtrate) and outlet (retentate) ports with ½” tubing ends, and a permeate port, located near the midpoint of the unit, as shown in Figure 4. The filters’ stainless steel membranes have a nominal pore size of 0.1  $\mu\text{m}$ . The surface of the filter media substrate is coated with a proprietary sub-micron layer of zirconia.

The filtration piping and instrumentation is heated via several circuits of copper heat-trace tubing. A Therminol 66 heat transfer fluid is circulated through the heat-trace tubing by electrically-heated hot oil system. The temperature controller was calibrated to operate over a temperature range of 180 to 250 °C.

Data gathering and process control functions are accomplished by a National Instruments real-time computer system. A 98 liter (26 gallon) slurry mixing tank is heated by hot-oil circulation jacket. Slurry mixtures of catalyst and wax are loaded batch-wise into the system. A Moyno (progressive cavity) pump is used to circulate the mixture through the cross-flow filter element. A manually-actuated valve, located downstream of the filter element, maintains a slurry flow rate set-point of 2 to 40 lpm.

Unfiltered slurry (or retentate) passing through the filter tube is recycled to the mixing tank. The differential pressure across the filter medium or trans-membrane pressure (TMP) is automatically controlled by a let-down valve. The permeate can be

recycled to the slurry tank for continuous filtration simulation (in order to maintain a constant solids concentration in the system) or can be collected and removed from the system to test semi-batch filtration schemes. The permeation rate is periodically measured by diverting the stream into a collection flask over a convenient time interval. Samples can be collected before the filter for characterization. In tests where the catalyst is activated, a gas pad of CO or syngas can be applied to the system otherwise the system vapor space is purged with inert gas such as argon or nitrogen. Slurry temperature, simulating the FTS activation conditions, can be controlled up to 240 °C. Modular filtration media can be tested under various filtration rates, differential pressures and operating modes. The system is designed so that the filter unit can be bypassed in order to change filters while the slurry continues recirculation.

A variety of precipitated catalyst slurries mixed with various molecular weight waxes (C<sub>30</sub> to C<sub>100</sub>) will allow a range of effective slurry viscosities to be studied (8). Olefins and alcohols will be doped into the catalyst slurry to test their influence on filtration properties. In addition, we are proposing that a series of filtration experiments with ultra-fine iron particles (less than 3 μm) for evaluating the “worst-case” scenario of wax/catalyst separation. Small sections of the filter media tested will be microscopically examined to determine the extent of ultra-fine particle penetration.

*Filter Back-flush System.* As shown in Figure 5, the back flush system consists of a piston pump that is triggered by a computer controlled timer. The back-flush fluid consists of cleaned permeate stored in a 40 ml tube bomb located near the suction side of

the piston pump. This system will be used throughout the study to develop an optimum cleaning program that can sustain a permeate flux rate over a many days.

*Static Permeation Apparatus.* In order to quantify the degree of filter media fouling, we constructed a static permeation rig to test the permeability of the membranes before and after catalyst filtration tests. A schematic of the apparatus is shown in Figure 6. A 4-liter vessel filled with clean/filtered C<sub>30</sub> oil is heated to a temperature between 180 to 220 °C. The C<sub>30</sub> oil is commercial polyalphaolefin known as Durasyn 164, produced by Amoco. A differential pressure or an effective TMP can be varied across the filter membrane via helium gas through a pressure regulator. The resulting permeation rate of the C<sub>30</sub> oil is measured. The curve of the membrane flux vs. TMP will provide a snapshot of the tube's fouling condition.

## RESULTS AND DISCUSSION

The objective of the initial filtration trials was to test the effectiveness of various cross-flow filtration procedures with a simulant FTS slurry. The wax products from a FTS reactor can vary widely depending on the type of process implemented. In this study, the focus is on a high-alpha iron-based slurry-phase reaction process.

A typical carbon distribution for a high-alpha iron catalyst/wax slurry and a wax simulant (Polywax 500) are shown in Figure 7. For the FTS wax, hydrocarbons molecules range from carbon numbers 12 to +70. The majority of the hydrocarbons produced are straight-chain and paraffinic. For iron-based catalysts, olefins make up 10-30% or more of the compounds in carbon numbers less than about 30. A considerable smaller portion of the FTS wax may contain oxygenates such as alcohols. In a later phase of this program, the effects of these compounds on filtration efficiency will be investigated. Initially we have concentrated on the filtration of straight-chain paraffin compounds.

The Polywax 500 is a commercial polyethylene polymer (manufactured by Baker-Petrolite) with a narrow carbon number distribution with an nominal average molecular weight of 500. As shown in Figure 7, the Polywax 500 product does not contain carbon compounds above about 43. Therefore, the melting point is about 85°C as compared to 90-110°C for that of a typical FTS wax. In our previous DoE study, we routinely used a Polywax 3000 (with a melting of >120 °C) product as a start-up solvent for our 1-liter CSTRs. The Polywax 3000 contains virtually no compounds with less than 70 carbons; therefore, it was useful for studying FTS chemistry since there was minimal analytical

interference for quantifying the rate of FTS products formation. Furthermore, the start-up solvent remains in the reactor even at high gas flow because of its low vapor pressure.

Shake-down Tests. During the shake-down phase of the filtration test platform, a batch of Polywax 3000 was melted without catalyst and heated to 200 °C. This test slurry was useful for checking potential “cold” areas within the unit and its associated instrumentation lines since Polywax 3000 would solidify at a lower temperature. It also provided a worst-case scenario for the clean-fluid permeation rate of the filter medium. Unfortunately, the filter medium was not able to pass permeate with the Polywax 3000. The membrane became fouled over a period of minutes. Without success, an effort was made to purge the filter medium of the heavy wax with 210 °C light (C<sub>30</sub>) oil and then ortho-xylene. Apparently, the filter medium was overwhelmed by the large molecular weight compounds since no solids were present in the slurry.

Wax Simulant Tests. Another filter module was tested with a mixture of 86:14% C<sub>30</sub> oil/Polywax 3000 oil without catalyst. Before catalyst was added, the unit was able to produce a steady permeate rate with a flux of 1 lpm/m<sup>2</sup> at a TMP of 1.38 bar. Unactivated iron catalyst was added to the wax mixture to produce a 5 wt% catalyst/wax slurry. Consequently, the permeate flux dropped to 0.65 lpm/m<sup>2</sup>. The test was continued for 6 days in a continuous filtration mode (i.e., the permeate was remixed with the retentate in the 98 liter (26 gallon) recycle tank). The permeate flux measured in this test is plotted versus time on-stream in Figure 8. During the first day, the permeation flux dropped below 0.5 lpm/m<sup>2</sup>. In the subsequent 5 days, the rate of flux decline decreased

but did not stabilize. The test was ended after the flux dropped below  $0.3 \text{ lpm/m}^2$ . The lack of flux stability could be due to two factors: 1. the fouling from the higher molecular weight component contributed from the Polywax 3000; and 2. from the attrition of the catalyst particles resulting in higher concentration of fines (below  $1 \mu\text{m}$ ).

Filtration Tests with Polywax 500/Catalyst Slurry. After problems with the Polywax 3000 and C<sub>30</sub> oil catalyst slurry, baseline filtration tests using Polywax 500 (with an average C<sub>25-30</sub>) and 5 wt% iron oxide catalyst were conducted with and without permeate back-pulsing. The initial flux, at 205 °C, was nearly  $0.85 \text{ lpm/m}^2$  ( $30 \text{ GPD/ft}^2$ ) at a TMP of 1.38 bar (20 psid). The test conditions were held constant throughout a week-long period (with back-pulsing) while the permeation rate was monitored on a daily basis. The permeation rate reached a steady-state flux rate of  $0.58 \text{ lpm/m}^2$  ( $20.6 \text{ GPD/ft}^2$ ) after 6 days with a periodic back-pulsing program. After 9 days TOS, the back-pulse program was stopped. Consequently, the permeate flux dropped 25% from  $0.58$  to  $0.43 \text{ lpm/m}^2$ . The test was continued another 7 days (a total of 16 days TOS) without back-pulsing.

The quality of the permeate was quantified by iron analyses over the duration of the Polywax 500/catalyst run. Typical permeate and slurry samples are shown in Figure 10. The permeate samples consistently had a bright white appearance and contained less than 1 ppm as Fe. The dark red appearance of the slurry was consistent with that of an unreduced iron oxide catalyst.

Slurry Particle Size Analyses. We attempted to extract periodic samples of the slurry with warm ortho-xylene in a  $0.8 \mu\text{m}$  fiber thimble filters in a soxhlet extraction

apparatus. Slurry samples taken during this test were extracted in o-xylene and subsequently submitted for particle size analyses. Problems were encountered in recovering catalyst samples in the extraction thimbles, especially for the longer duration test runs. Over 30-50% of the catalyst particles passed through the extraction thimble indicating substantial attrition of the particles.

Qualitatively, the change in particle size may be observed over time by the particle settling of large slurry samples. After each test campaign, the slurry was emptied from the test system into metal buckets to cool and solidify over a 3-4 hour period. Solidified slurry (inverted bucket samples) from two tests of 12 and 26 days in duration are shown in the Figure 11 and 12, respectively. In the 12-day run, substantial catalyst settling had occurred, leaving a distinct dark band of catalyst at the bottom and a light brown layer of wax on top. Oppositely, the 26-day run sample showed no signs of gravity settling with a consist dark brown appearance from top to bottom. From this observation, the slurry properties change significantly over the time-scale of the filtration tests.

Since the catalyst was unactivated in all cases and recirculated in an inert nitrogen atmosphere, it is likely that most of the particle attrition is from mechanical abrasion. The starting median particle size of the iron catalyst was  $43 \mu\text{m}$ , yet a substantial portion of the slurry samples taken after 1 day of recirculating through the filtration system passed through a  $0.8 \mu\text{m}$  filter thimble during the soxhlet extraction. Another possible attrition mechanism is the thermal shock of the catalyst particles during mixing with the  $200^\circ\text{C}$  Polywax 500.



## CONCLUSIONS

Higher molecular weight components and catalyst fines from FTS contribute to membrane fouling. Initial test results using a commercial high-molecular weight product (Polywax 3000) through a  $0.1 \mu\text{m}$  membrane proved that the wax alone could foul the filtration medium. It seems that the filter medium pores can be overwhelmed by the large molecular weight compounds of the heavy wax.

Filtration tests with a mixture of 5 wt% iron catalyst in a solvent of  $\text{C}_{30}$  oil and Polywax 3000 were conducted at  $200^\circ\text{C}$ . The initial permeate flux was  $0.65 \text{ lpm/m}^2$  and steadily declined below  $0.3 \text{ lpm/m}^2$  over a 6-day test. The lack of long-term flux stability was also attributed to the fouling from the higher molecular weight components from the Polywax 3000. Qualitative particle settling tests indicate that catalyst attrition is changing the slurry properties over the time-scale of the filtration tests.

A slurry mixture of 5wt% catalyst in a Polywax 500 and back-pulsing displayed more stability and higher permeate flux rates ( $0.58 \text{ lpm/m}^2$  or  $20.6 \text{ GPD/ft}^2$ ). When the permeate back-pulsing was stopped, the permeate flux dropped 25% from  $0.58$  to  $0.43 \text{ lpm/m}^2$ . The permeate samples consistently had a bright white appearance and contained less than 1 ppm as Fe.

Results from the permeation rig have shown a significant degree of fouling due to the Polywax simulant slurries. However, heating the cross-flow filtration elements in air returns the tubes to their original state. Further tests will be conducted to investigate the mode of media fouling.

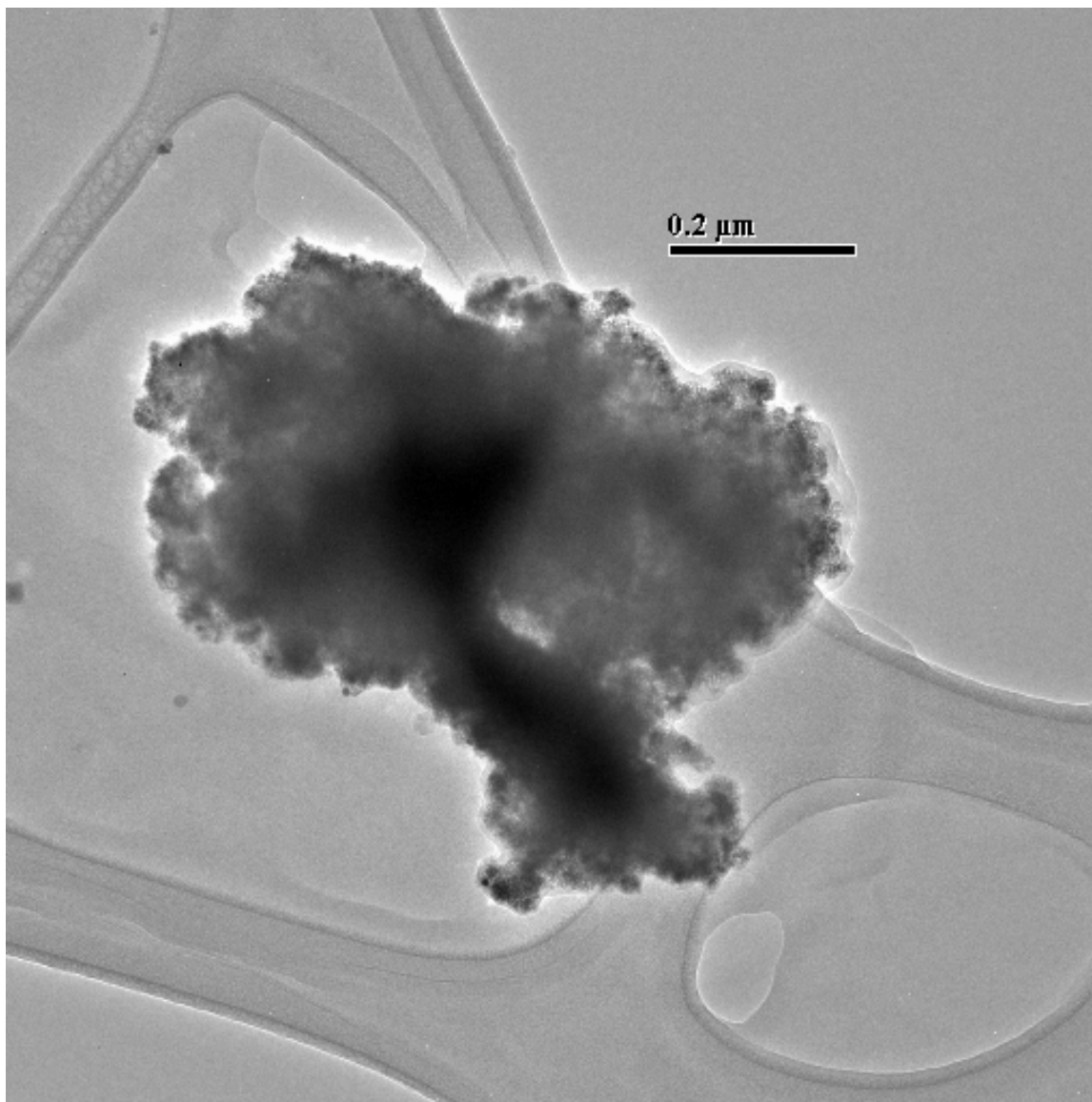
Further research is needed to: 1. Quantify velocity/shear effects; 2. Optimize back-pulsing and other flux maintenance procedures; 3. Quantify slurry particle size attrition; and 4. Develop a more realistic slurry simulant with various molecular weight Polywax compounds and ultrafine iron catalyst particles.

## REFERENCES

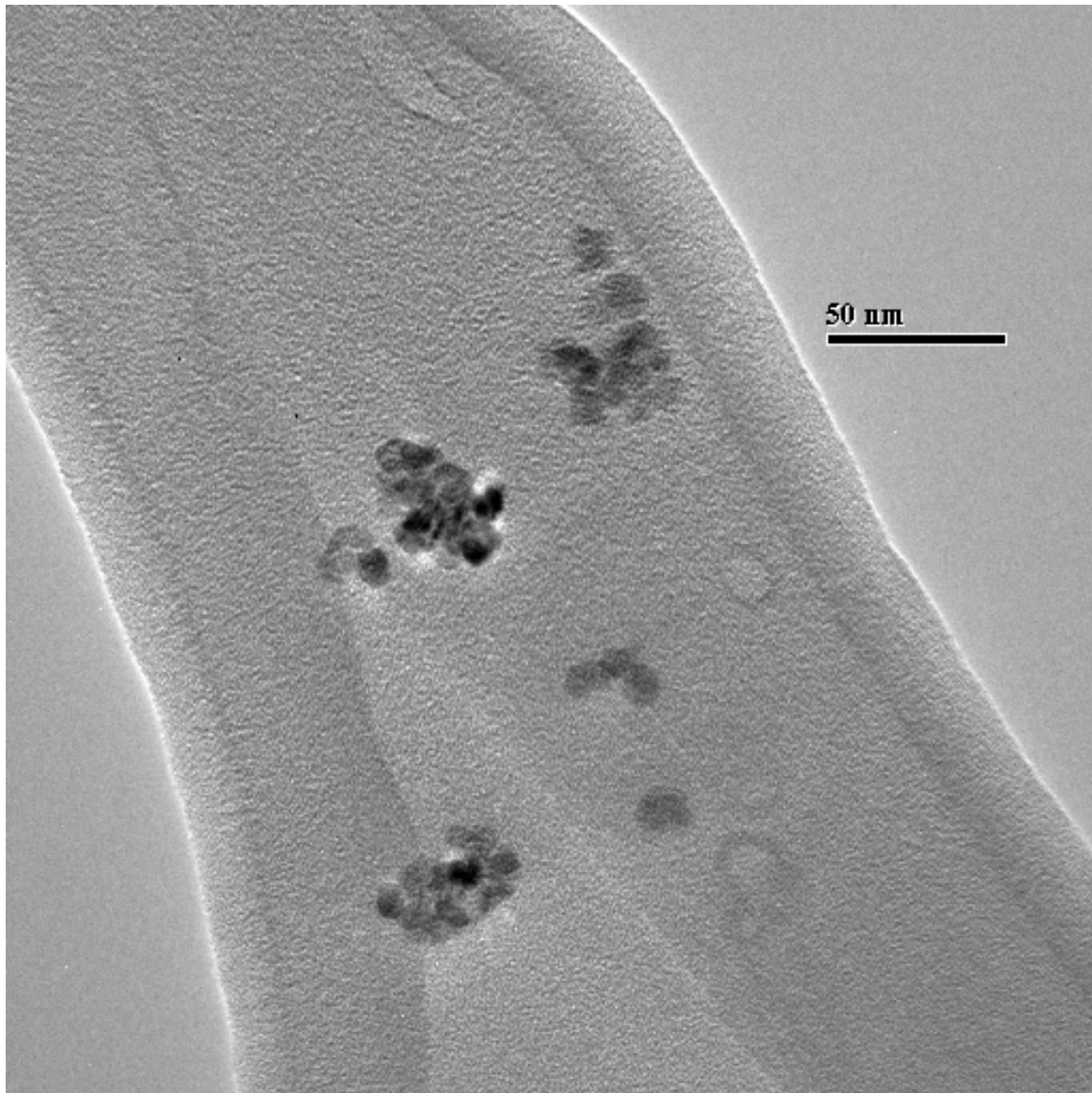
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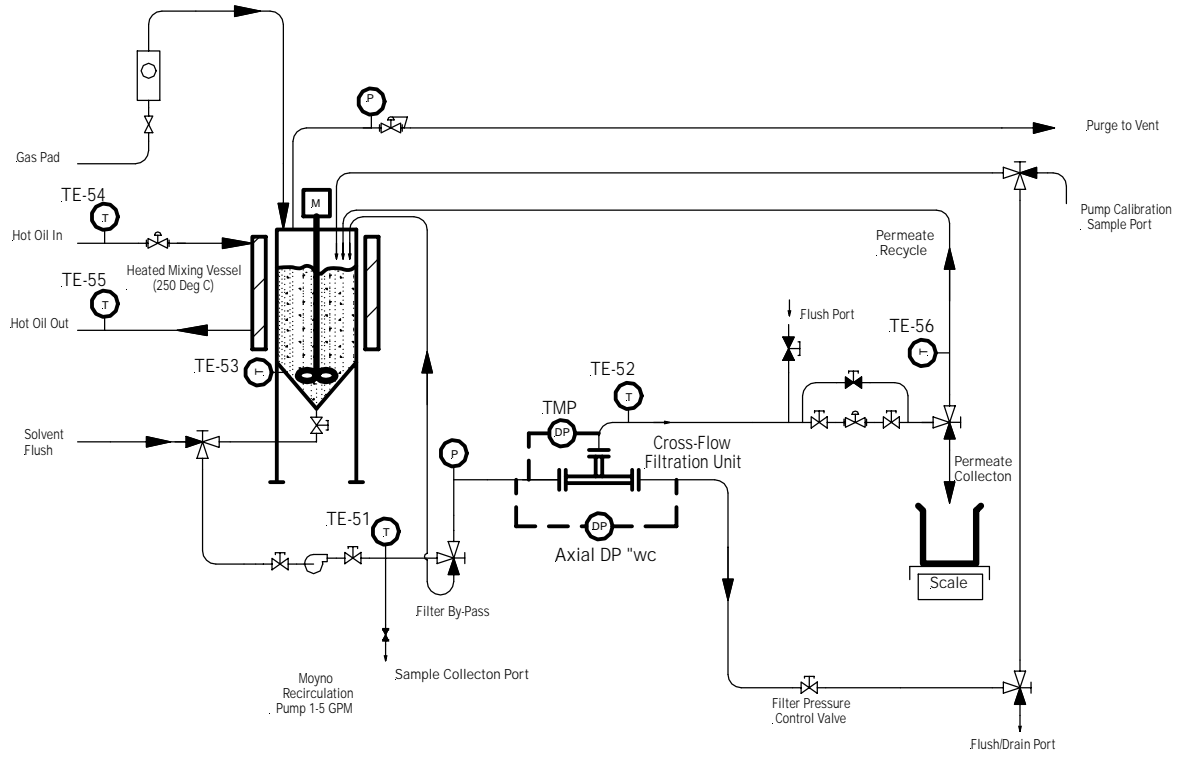
FIGURES for Task 1.1 & 1.2



**Figure 1. TEM Micrograph of an Iron Catalyst Particle in a Wax Slurry.**



**Figure 2. TEM Micrograph of Iron Catalyst Crystallites.**



**Figure 3. Schematic of the filtration test platform.**

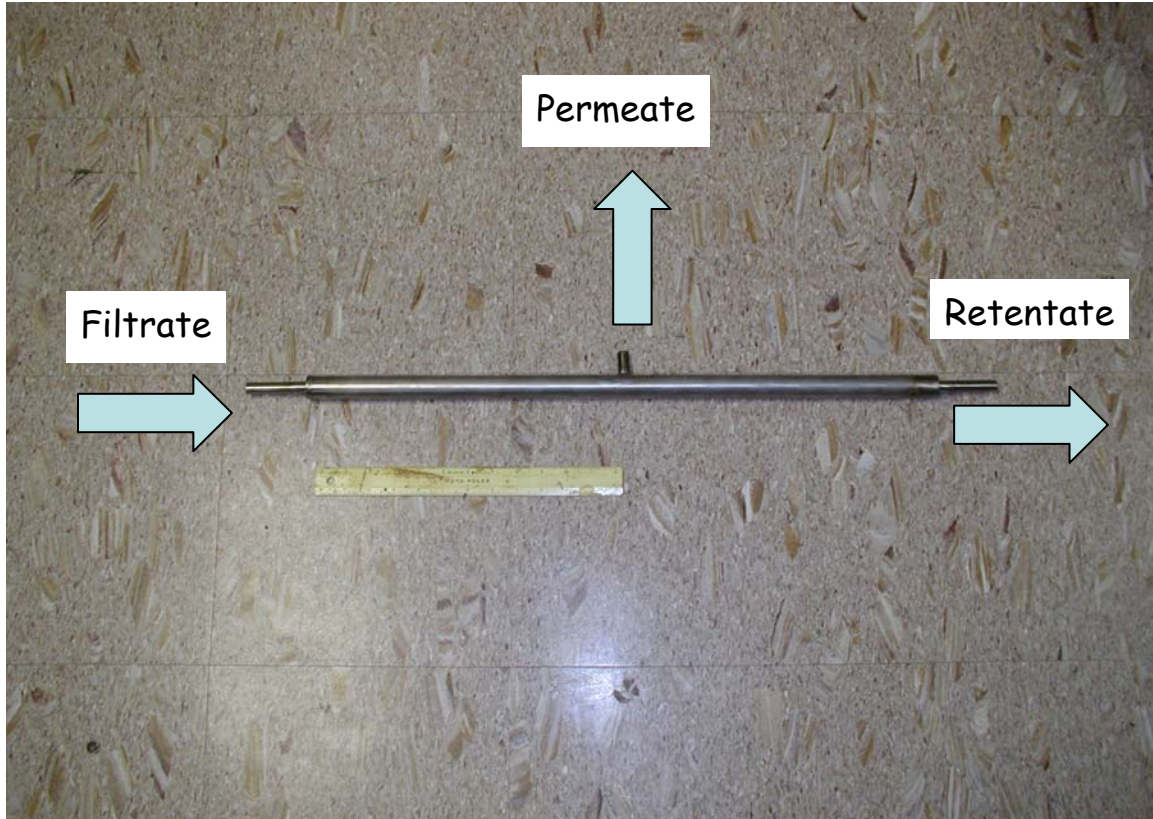
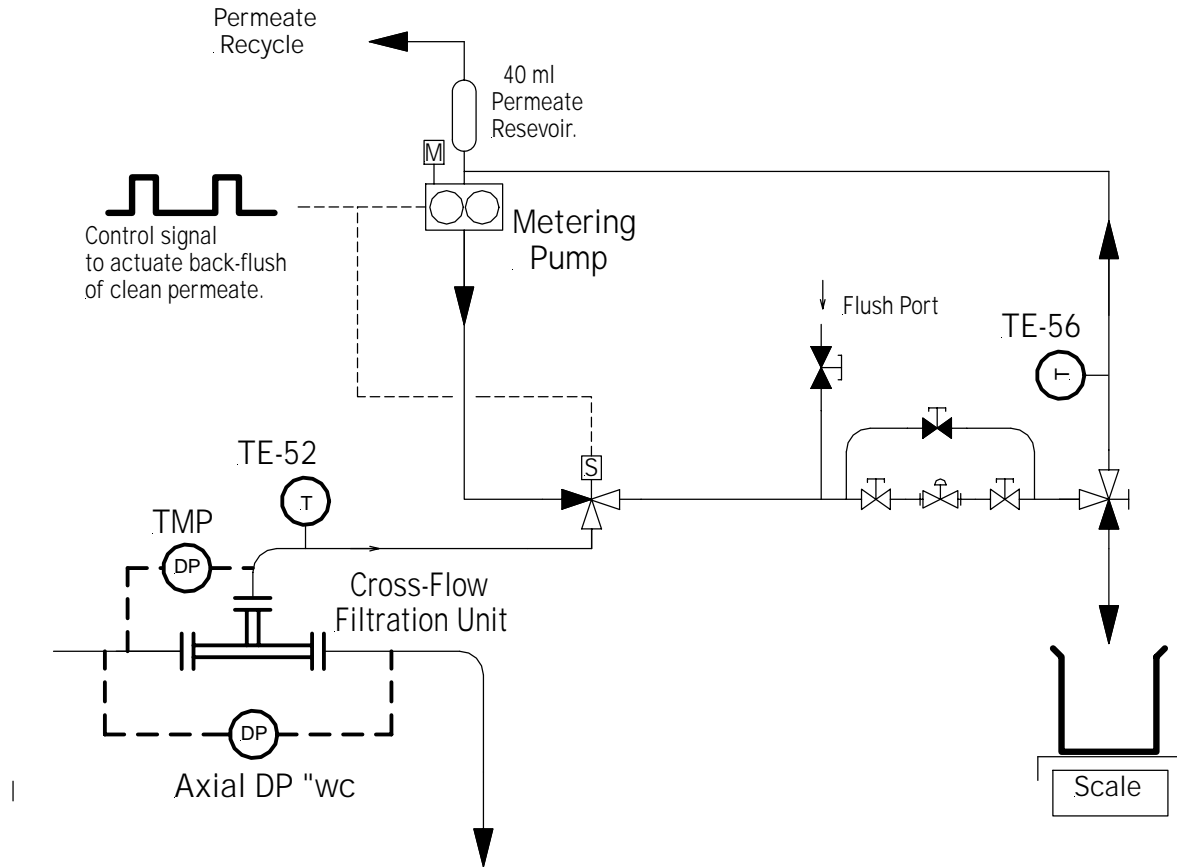


Figure 4. Photograph of a cross-flow filtration test module.



**Figure 5. Schematic of the Permeate Back-Pulse System.**



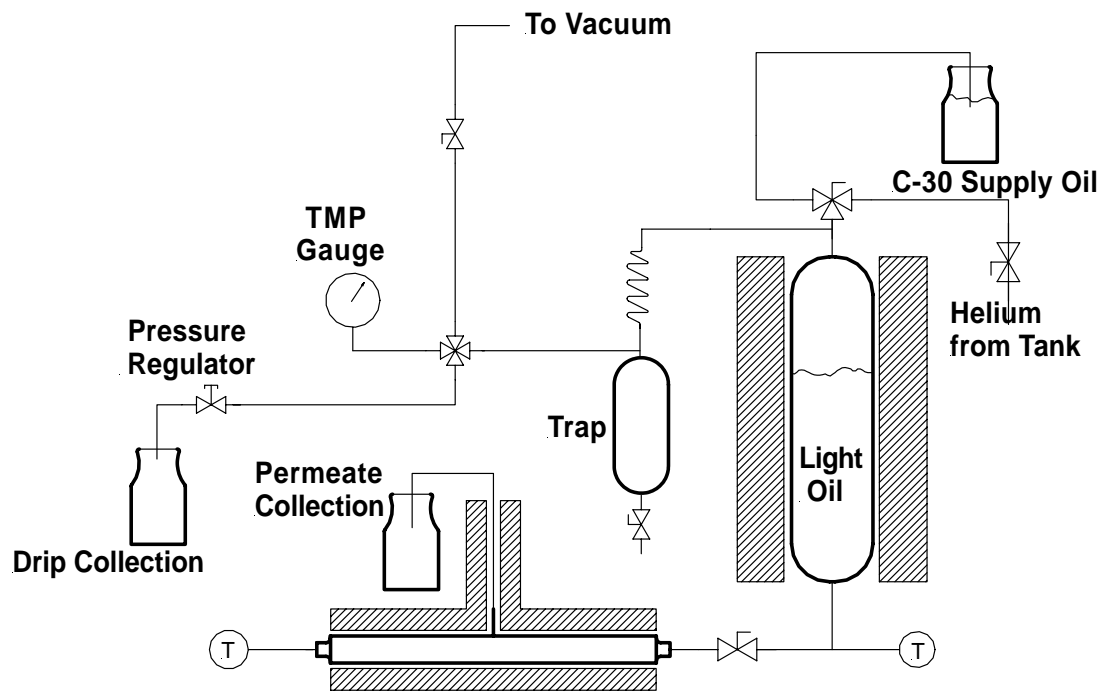


Figure 6. Schematic of the Static Permeation Test Apparatus.

## Wax Product Distribution

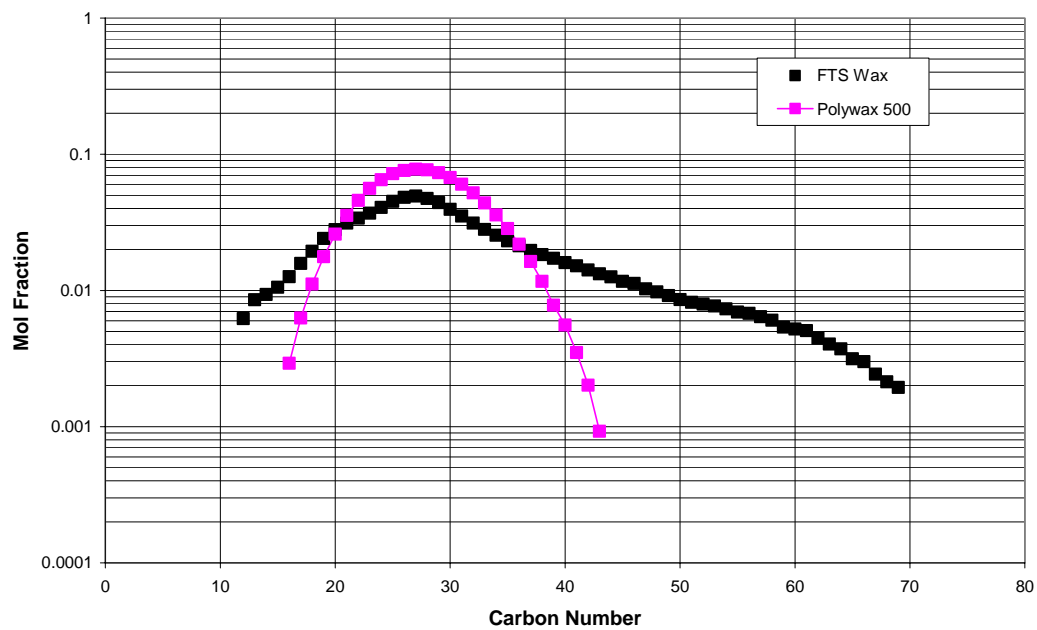
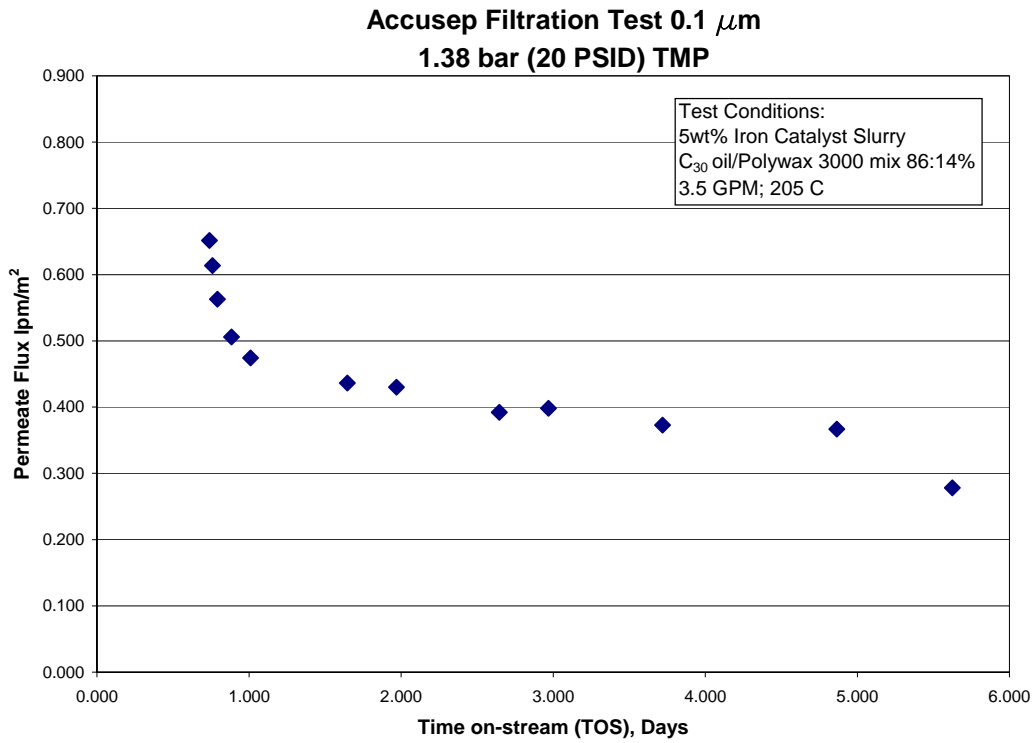
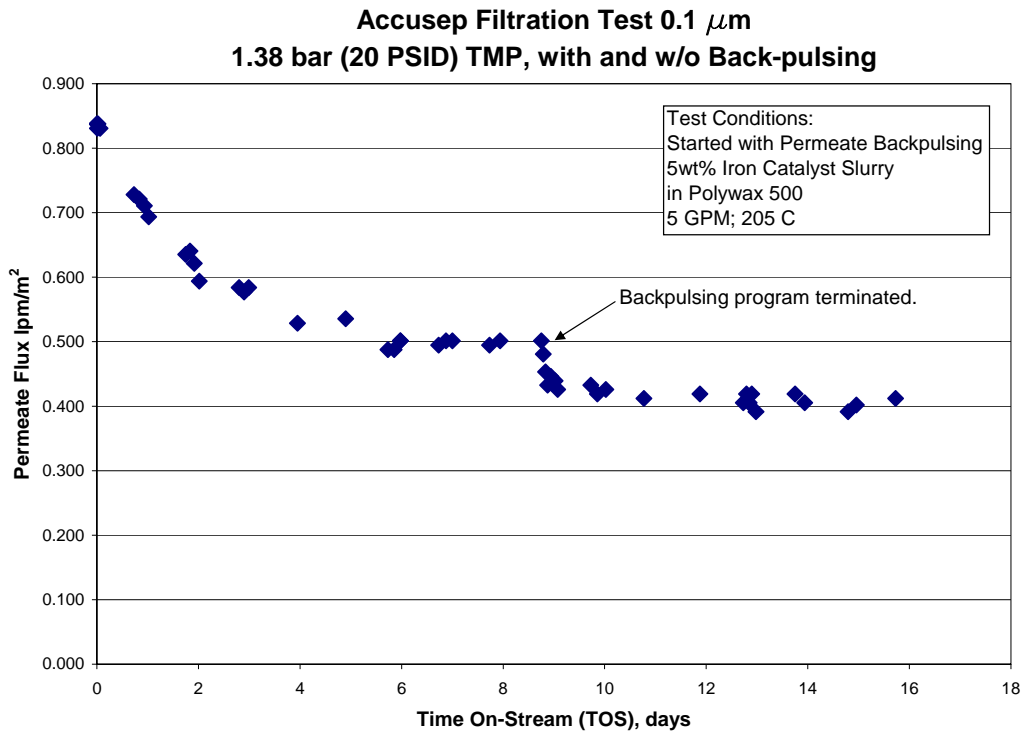


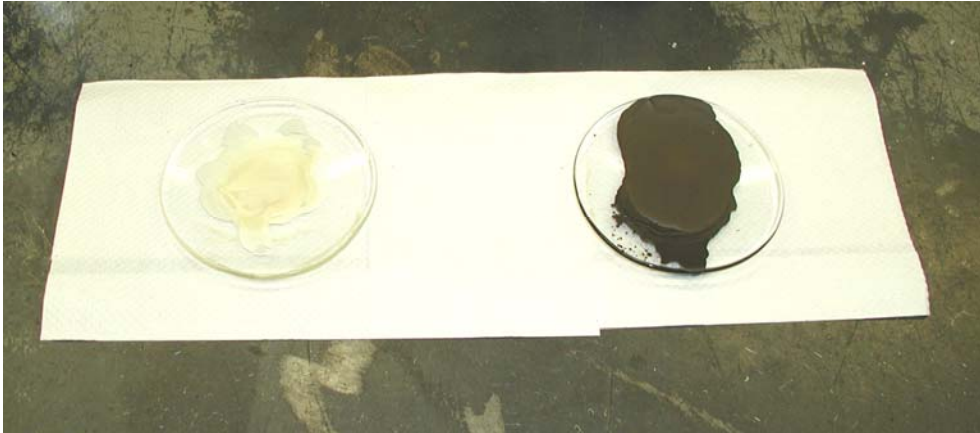
Figure 7. Carbon number distribution comparison of the Polywax 500 simulant with a High  $\alpha$  FTS wax.



**Figure 8. Initial filtration test using a mixture of Polywax 3000 and C<sub>30</sub> oil.**



**Figure 9. Filtration test with Polywax 500 simulant , with and w/o backpulsing.**



**Figure 10. Photograph comparison of the permeate (L) and unfiltered slurry (R) using a Polywax 500 simulant.**

## Slurry online 12 days

(from Polywax 500/Iron Slurry tests)



Figure 11. Photograph of "frozen" catalyst/wax mixture after 12 days of circulation.

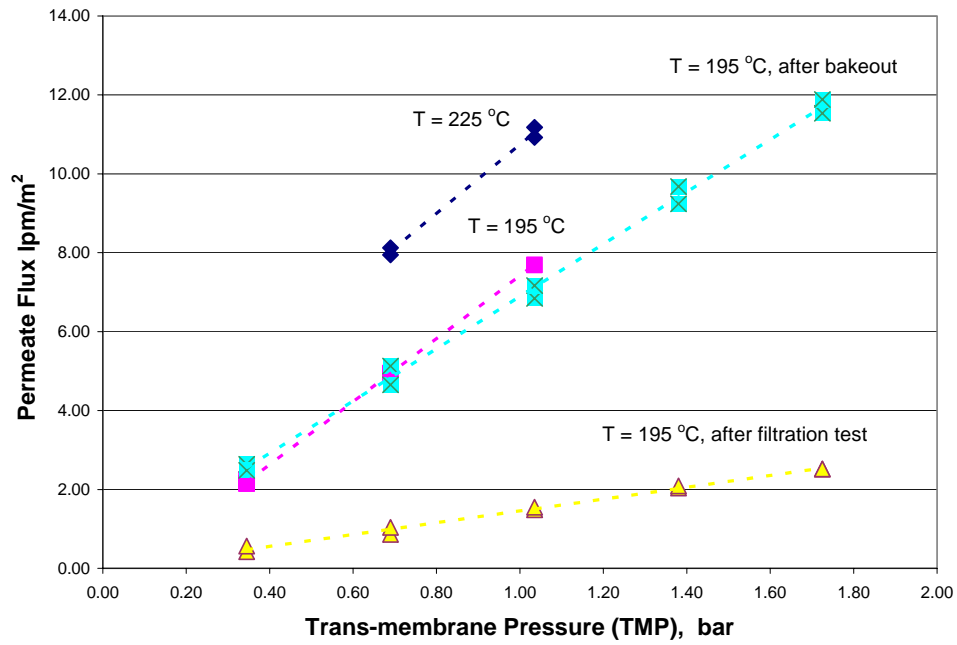
## Slurry online 26 days

(from Polywax 500/iron Slurry tests)



**Figure 12. Photograph of "frozen" catalyst/wax slurry after 26 days of circulation.**

**Pall Accusep Tube  
Static Permeability with C<sub>30</sub> Oil**



**Figure 13. C<sub>30</sub> oil Flux vs. TMP using the static permeation test apparatus.**



Task 1.3. Filtration studies with doping of olefins and alcohols (CAER)

*No work scheduled for this task during the current reporting period.*

Task 1.4. Ultra-fine Iron Filtration (CAER)

*No work scheduled for this task during the current reporting period.*

Task 1.5. Development of Filter media cleaning procedure (CAER)

*No work scheduled for this task during the current reporting period.*

## Task 1.6. Chemical and physical characterization of slurry and filtrate

### INTRODUCTION

The impact of Group 1 alkali promoters (i.e., Li, Na, K, Rb, and Cs) on the Fischer-Tropsch synthesis and water-gas shift rates and product selectivity were previously studied using a CSTR. Rubidium is a promoter with an  $L_{III}$  electronic transition that can be studied by EXAFS and XANES synchrotron techniques and will therefore, be the focus of the current study. In our previous investigation (1) Rb was found to:

- Decrease the overall CO conversion
- Increase the deactivation rate
- Decrease the WGS rate as a function of  $1/SV$
- Improve the product selectivity by decreasing the C2-C4 selectivity and increasing the higher molecular weight fraction (C5+)
- Decrease the methane selectivity
- Increase the C2 olefin/paraffin selectivity

Utilizing EXAFS and XANES, the goal of the current investigation was to determine the chemical compound that represents the alkali promoter in the working catalyst. Also, the catalytically active surface in the iron catalyst is still a matter of debate. As it is clear that Rb impacts the relative catalytic activity, the use of EXAFS might help to determine the Fe phase in contact with Rb, and thereby provide insight into the working catalytically active site responsible for Fischer-Tropsch synthesis activity.

The preliminary results reported show the reaction test data carried out in the CSTR and the results of Mossbauer analysis from the catalysts retrieved for XAFS analysis. The EXAFS/XANES results will be reported in the next quarterly report.

## CATALYST PREPARATION

*Preparation of alkali metal promoted catalysts.* A well-studied iron catalyst was split into two separate batches and promoted with Rb at two levels: 1.44/100 and 5.0/100 Rb to Fe atomic ratio. The two loadings were used, because it was difficult to assess whether or not the Rb signal would be observed by X-ray absorption spectroscopies in the lower loaded catalyst (see Figures 1 and 2). The original precipitated iron catalyst was prepared with tetraethyl orthosilicate, iron nitrate, potassium carbonate and copper nitrate. Ferric nitrate solution was first prepared by dissolving  $\text{Fe}(\text{NO}_3)_3$  in distilled and deionized water, and the amount of orthosilicate needed to make Si:Fe of 4.6 was added. The mixture was stirred vigorously until the tetraethyl orthosilicate was hydrolyzed. Tetraethyl orthosilicate and iron nitrate mixture was then added to a CSTR precipitator vessel together with ammonium hydroxide. By maintaining the slurry pH at 9 and an average residence time of 6 minutes, a base catalyst material with an iron to silicon molar ratio of 100:4.6 was obtained. The slurry was then filtered with a vacuum drum filter and washed twice with deionized water. The final filtration cake was dried in an oven with flowing air at 110°C for 24 hours. The catalyst was crushed and calcined in a 350°C oven under an air flow for 4 hours.

In this study, the iron catalyst was impregnated with an aqueous rubidium nitrate

solution. Rubidium was added to obtain a promoter to iron atomic ratio of either 1.44/100 or 5.00/100. The catalyst was dried at 110°C overnight with good mixing following the impregnation.

*In-situ catalyst activation.* Iron catalysts must be activated with either H<sub>2</sub>, CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron-based catalysts. It was reported that catalysts activated with CO yielded higher long-chain hydrocarbons than syngas and H<sub>2</sub> activated catalysts. In addition, activation conditions may also influence the performance of the iron catalyst. In this study, the promoted iron catalysts were pretreated with CO at 270°C, 1.2 MPa for 24 hours.

## REACTION TESTING

In two separate tests, the reactor was loaded with 40.0 g of Rb-promoted catalyst. The initial conditions for the reactor were 175 psig, 270 °C, with the traps at 200, 100, 0 °C. The feed gas was initially set to 72.0 slph with a composition of 40% H<sub>2</sub> and 60% CO for a H<sub>2</sub>:CO ratio of 0.67 and WHSV of 3. 180.0 g of the startup oil C-30 was used. Synthesis was started on 2/13/2004. The catalyst was pretreated with CO at 270 ° C for 24 hours. The catalyst composition was 60.0 % Fe. After the CO conversion stabilized, the catalyst was run for approximately 180 hours, at which point the run was stopped, and the catalyst retrieved, solidified in the waxy matrix to allow for spectroscopic

characterization in the in-situ state. Detailed selectivity reports will be provided in the next quarterly report.

## MOSSBAUER SPECTROSCOPY

Mossbauer spectroscopy was carried out at 20K on the two used catalyst samples (i.e., after steady state synthesis was reached in the CSTR), as well as an iron carbide reference material prepared at the CAER. The iron carbide reference material was also verified by XRD (not shown). Results of the Mossbauer fitting analysis are reported in Figures 3-5. The experimental data is represented by the dots. The solid curves (dark red, dark green, green, blue and red) represent sub-spectra calculated from the fitting routine. The solid black-curve represents the sum of all calculated sub-spectra.

- The dark red-sub-spectra are from Fe in Fe-oxide phase of nano-size. The phase is not in the equilibrium state and it is most likely to be  $\text{Fe}_{3-\square}\text{O}_{4-\square}$  with varying degree of vacancy,  $\square$ .
- The dark green and green-sub spectra are from Fe in  $\epsilon\text{-Fe}_{2+x}\text{C}$ .
- The dark green and two blue-sub-spectra are from Fe in the Hagg carbide ( $\text{Fe}_5\text{C}_2$ ).

**The dark green sub-spectrum is common to both  $\epsilon\text{-Fe}_{2+x}\text{C}$  and  $\text{Fe}_5\text{C}_2$ .**

- The red spectrum is from Fe in paramagnetic/superparamagnetic state.

The results of the fittings are reported in Table 1. The results indicate two important confirmations. First, the iron carbide reference material should serve as a good

standard for carrying out EXAFS studies. Secondly, the Fe-based catalysts have formed iron carbidic phases during catalyst activation.

Table 1 Results of the Mossbauer fitting analysis - Percentage of Fe in the different Phases in Samples (without correction because of different recoil free fraction)

Sample	$\epsilon\text{-Fe}_{2+x}\text{C}$	Hagg Carbide ( $\text{Fe}_5\text{C}_2$ )	$\text{Fe}_{3-\square}\text{O}_{4-\square}$	paramagnetic/ superparamagnetic
Catalyst 1.44/100 Rb/Fe	53	33	9	5
Catalyst 5.0/100 Rb/Fe	46	34	20	0
Iron carbide reference	0	46	54	0

\* Uncertainty is  $\pm 3$

## EXAFS AND XANES ANALYSIS

In March, 2004, CAER researchers visited the synchrotron at Brookhaven National Laboratory, Beamline X-18b, and carried out EXAFS/XANES studies at the K-edge of Fe on both Fe-based catalysts, as well as reference materials, including an Fe metallic foil,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and the Fe-carbide reference. The two Rb promoted catalysts were also examined at the  $L_{III}$  edge of Rb. Analyses are ongoing and will be provided in the following quarterly report.

## REFERENCES

1. W. Ngantsoue-Hoc, Y. Zhang, R.J. O'Brien, M. Luo, and B.H. Davis, Appl. Catal. 236 (2002) 77

## FIGURES for Task 1.6

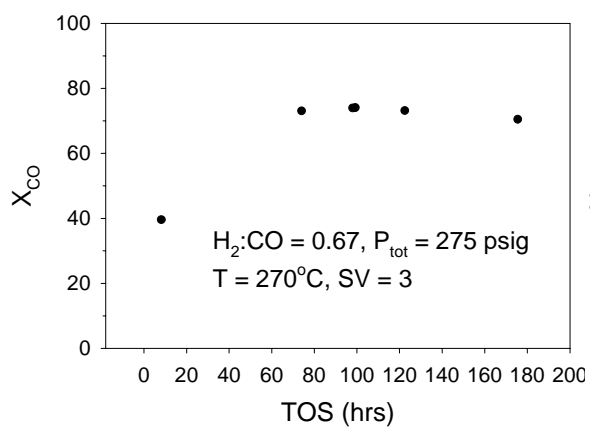


Figure 1. Catalyst promoted with  
1.44/100 Rb:Fe.

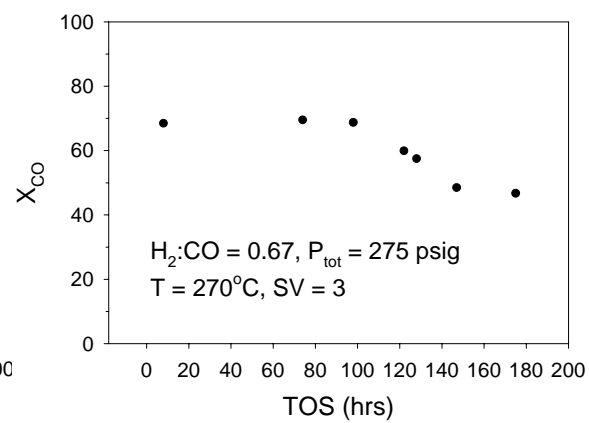


Figure 2. Catalyst promoted  
with 5.0/100 Rb:Fe.

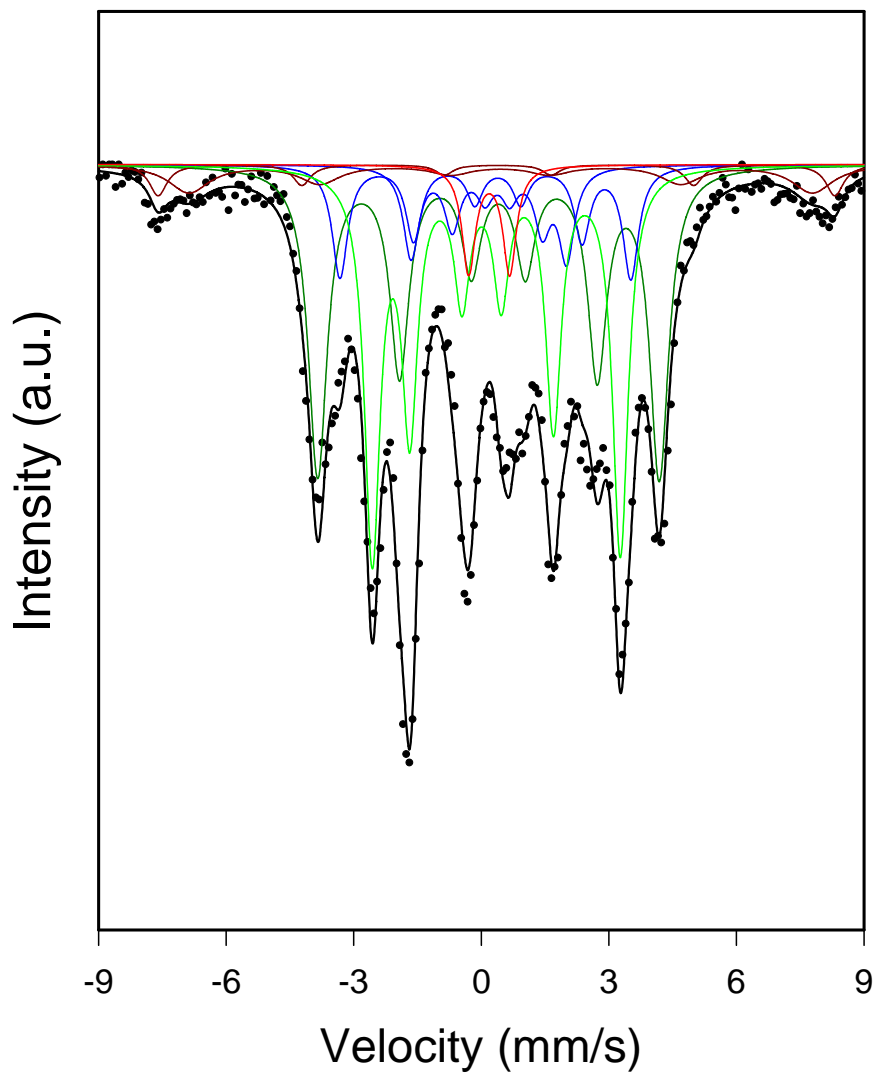


Figure 3. Intensity versus Doppler velocity for the catalyst with 1.44/100 Rb/Fe atomic ratio.



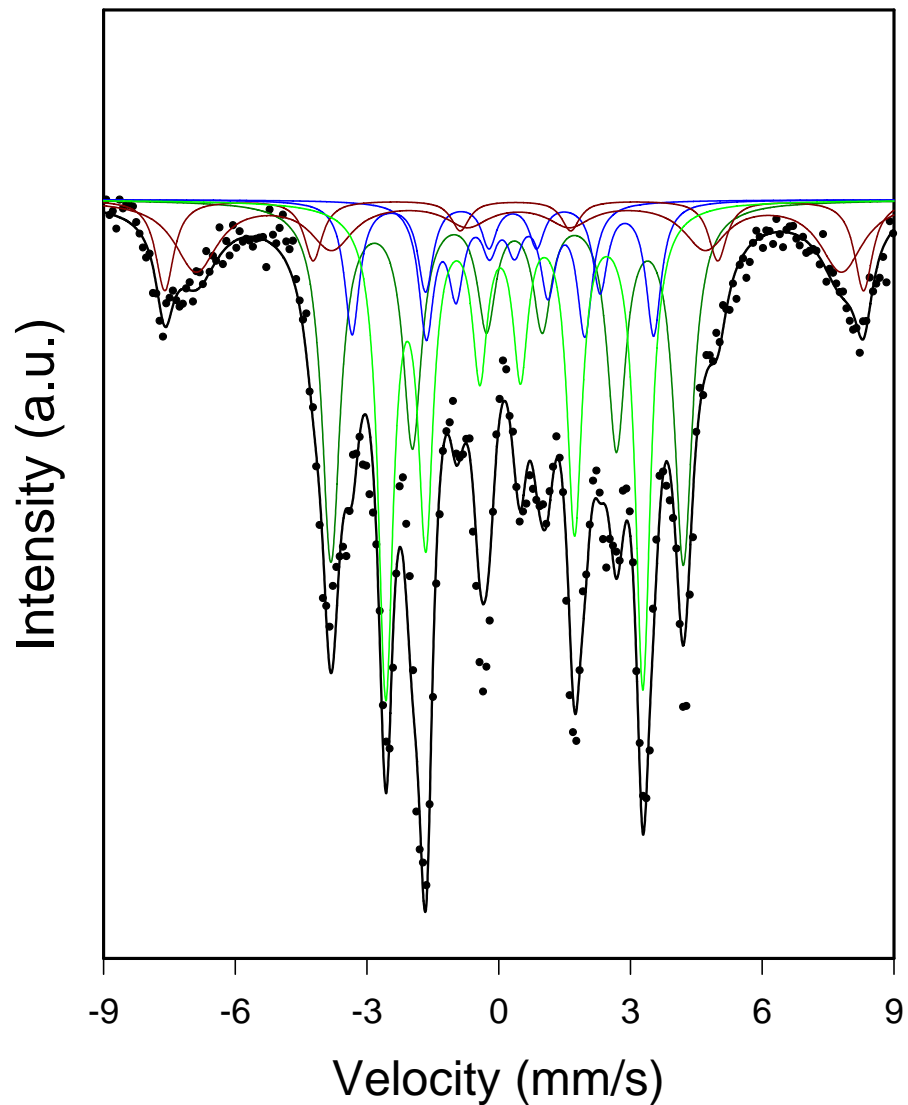


Figure 4. : Intensity versus Doppler velocity for the catalyst with 5.0/100 Rb/Fe atomic ratio.

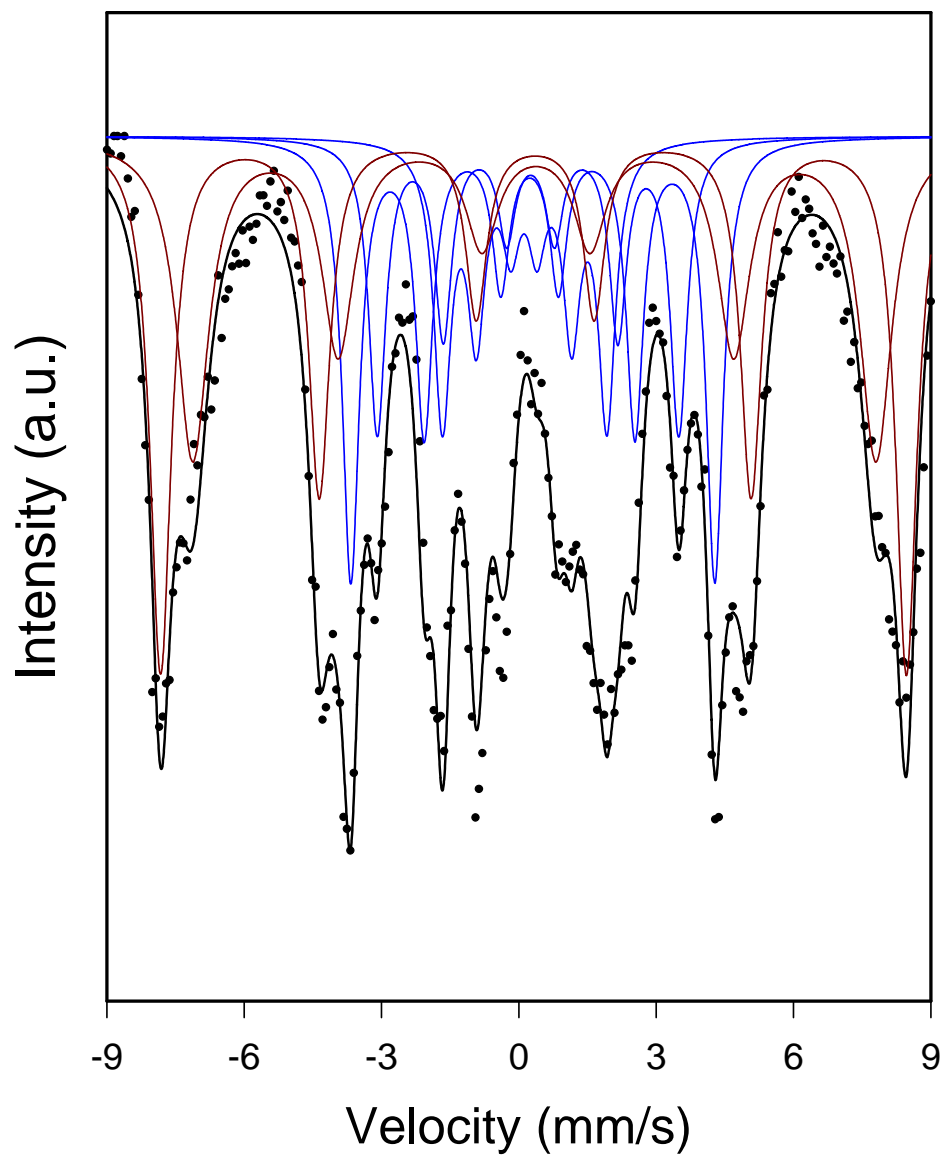


Figure 5. : Intensity versus Doppler velocity for the iron carbide reference material.

Task 2. Phase II Bubble Column Pilot Plant Studies

*No work scheduled for this task during the current reporting period.*