

DE-FC26-03NT41965

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

Technical Progress Report

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Reporting Period
October 1, 2004 to March 31, 2005

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ABSTRACT

In this reporting period, a fundamental filtration study was continued to investigate the separation of Fischer-Tropsch Synthesis (FTS) liquids from iron-based catalyst particles. The overall focus of the program is with slurry-phase FTS in slurry bubble column reactor systems. Hydrocarbon products must be separated from catalyst particles before being removed from the reactor system. An efficient wax product/catalyst separation system is a key factor for optimizing operating costs for iron-based slurry-phase FTS. Previous work has focused on catalyst particle attrition and the formation of ultra-fine iron carbide and/or carbon particles. With the current study, we are investigating how the filtration properties are affected by these chemical and physical changes of the catalyst slurry during activation/synthesis.

In this reporting period, a series of crossflow filtration experiments were initiated to study the effect of olefins and oxygenates on the filtration flux and membrane performance. Iron-based FTS reactor waxes contain a significant amount of oxygenates, depending on the catalyst formulation and operating conditions. Mono-olefins and aliphatic alcohols were doped into an activated iron catalyst slurry (with Polywax) to test their influence on filtration properties. The olefins were varied from 5 to 25wt% and oxygenates from 6 to 17 wt% to simulate a range of reactor slurries reported in the literature.

The addition of an alcohol (1-dodecanol) was found to decrease the permeation rate while the olefin added (1-hexadecene) had no effect on the permeation rate. A passive flux maintenance technique was tested that can temporarily increase the permeate rate for 24 hours.

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EXECUTIVE SUMMARY

In this reporting period, a fundamental filtration study to investigate the separation of Fischer-Tropsch Synthesis (FTS) liquids from iron-based catalyst particles was continued. 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 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 crossflow 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 high-alpha iron-based slurry-phase reaction processes. The change in filtration properties of iron catalyst slurries will be correlated with physical and chemical changes of the particles during Fischer-Tropsch conditions.

For first two years of this program, a state-of-the-art filtration test platform is being utilized to study effect of process parameters, slurry chemical/physical changes, and filter media on the permeate flux and quality (based on Fe content). Additionally, flux maintenance procedures are being developed to maintain the highest achievable permeation rate over the lifetime of the filter membranes. The unit is capable of testing slurry batches as large as 98 liters (26 gallons). This unit will allow several types of crossflow filter media to be investigated under simulated FTS conditions at flowrates from 4 to 20 lpm (liters/min). The crossflow filtration modules are zirconia-coated steel membranes having a nominal pore size of 0.1 μm . In year 3 of the program, a prototype filtration system will be retrofitted to an existing SBCR (slurry bubble column reactor) to test the efficacy of the filtration procedures developed using the filtration test platform.

For the current reporting period, a series of tests were initiated to study the effect of olefins and oxygenates on the filtration flux and filter membrane performance. Iron-based FTS reactor waxes contain a significant amount of oxygenates, depending on the catalyst formulation and operating conditions. Mono-olefins and aliphatic alcohols were doped into a catalyst slurry (with a Polywax blend and 5 wt% Fe at 200°C) to test their influence on filtration properties. The range of olefins (as 1-hexadecene) were varied from 0 to 29wt% and oxygenates from 0 to 17 wt% (initial charge as 1-dodecanol) to simulate a range of reactor slurries reported in the literature.

The addition of the alcohol (1-dodecanol) was found to decrease the permeation rate of a crossflow filter using an activated iron slurry. However, additional increases in the alcohol did not affect the permeation rates. Side reaction products of the 1-dodecanol apparently caused a color change in the permeate from bright white to light brown. The

addition of an olefin (1-hexadecene) had little to no effect on the permeate flux and quality.

A passive flux maintenance procedure was tested in which the trans-membrane pressure is suspended for an extended period. A single test for a 75 hour “off” period had shown that the flux can be increased by over 100%, but decays back to the original steady-state flux over 24 hours. A possible flux maintenance scheme could employ two filters; one filter in the “permeate mode” while a duplicate filter is being regenerated with slurry without trans-membrane pressure. Further studies are planned to investigate optimizing the regeneration periods.

XANES analysis was performed for an iron catalyst removed during the Fischer-Tropsch synthesis and sealed in its in-situ state by the wax product. Data collection was performed near the Fe K-edge at the synchrotron at Brookhaven National Laboratory, Beamline X-18b. The spectrum for the catalyst sample, which was promoted with 5%Rb, was analyzed against reference spectra including iron metal, two different iron oxide materials, and an iron carbide reference prepared at the CAER. Qualitative comparisons were conducted for both the normalized XANES spectra, as well as the derivative spectra, which provide much more detail regarding the inflections in the XANES line-shapes. Iron carbide was confirmed to be the most abundant constituent in the working catalyst. A linear combination XANES fitting of the reference spectra to that of the catalyst was carried out.

TASK 1. Fundamental Filtration Studies

Task 1.1 Shakedown (*subtask completed*)

Task 1.2. Solvent wax experiments (*subtask completed*)

Task 1.3/1.5. Filtration studies with doping of olefins and alcohols and Development of Filter media cleaning procedure.

INTRODUCTION

Filtration of olefin and oxygenate containing catalyst slurry.

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 FTS and WGS reactions. Complex mixtures of compounds are known to be formed during iron-based Fischer- Tropsch synthesis [1]. In addition to straight-chained paraffins, the formation of olefins and oxygenates can be substantial:

Paraffin formation- $(2n + 1) H_2 + n CO = C_nH_{2n+2} + n H_2O$

Alcohols- $2n H_2 + n CO = C_nH_{2n+2}O + (n-1) H_2O$

Olefins- $2n H_2 + n CO = C_nH_{2n} + n H_2O$

Olefin selectivity of iron catalysts is typically greater than 50% of the hydrocarbon products at low carbon numbers [1]. Of the olefins produced, more than 60% of are α -olefins. For iron, the olefin selectivity decreases asymptotically with increasing carbon number. For cobalt catalysts both the fraction of total olefins and alpha-olefins are smaller in comparison to that of Fe catalysts. From a chemical feedstock perspective,

alpha-olefins are desirable since they can be processed into branched alkanes for high-octane gasoline and other value-added chemicals.

The degree to which these olefin and alcohol products affect the filtration has not been documented in the literature. Certainly, the presence of olefins and alcohols in a catalyst slurry could influence the wax rheology to some degree. Consequently, one objective of this research program is to quantify effects of these side products on the separation of catalyst from wax.

Flux maintenance for crossflow filter media.

Crossflow filtration systems utilize high liquid axial velocities to generate shear at the liquid-membrane interface. Shear is necessary to maintain acceptable permeate fluxes, especially with concentrated catalyst slurries. The degree of catalyst deposition on the filter membrane is a function of the shear stress at the surface and particle convection with the permeate flow [2]. Membrane surface fouling also depends on many application-specific variables such as: particle size in the retentate, viscosity of the permeate, axial velocity, and the trans-membrane pressure. All of these variables can influence the degree of deposition of particles within the filter membrane and thus decrease the effective pore size of the membrane.

Several operating techniques have been used in industrial ultrafiltration applications to improve permeation flux performance [2-5]. These include: backflushing or backpulsing with clear permeate; backflushing an inert gas through the membrane; and the use of mechanical devices to increase turbulence near the membrane. Each of these techniques essentially disrupts the boundary layer of concentrated particles at the membrane surface.

A more passive technique suggested by Pall Corporation product engineers is to disrupt the permeation flow while allowing the retentate to circulate axially through the crossflow tube. This would in theory allow inertial lift of the particles on the membrane surface in the absence of the permeate convective force component. Unlike backpulsing, this passive approach would not expend cleaned permeate product or require high-pressure inert gas handling. The approach of switching a filter tube off momentarily would be simple and thus likely more economical to implement.

EXPERIMENTAL

Filtration Test Platform. An existing pilot plant platform was modified into a crossflow filtration test unit (Figures 1 and 2). This unit, depicted schematically in Figure 1, will allow several types of crossflow 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. The filters’ stainless steel membranes have a nominal pore size of 0.1 μm . 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 using an 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 Liberty Process Equipment (progressive cavity) pump is used to circulate the mixture through the crossflow 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 (C₃₀ to C₁₀₀) will allow a range of effective slurry viscosities to be studied. 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.

Filter Back-flush System. As shown in Figure 2, 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 3. A 4-liter vessel filled with clean/filtered C_{30} oil is heated to a temperature between 180 to 220 $^{\circ}\text{C}$. The C_{30} 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_{30} oil is measured. The curve of the membrane flux vs. TMP will provide a snapshot of the tube’s fouling condition.

Olefin and Alcohol Sample Analysis. Approximately 0.25 g of wax and 7 ml of o-xylene(HPLC grade) are placed in a 16 x 125 mm culture tube and then put in a Thermoclyne dry heating bath. The sample is heated until the wax is dissolved and then transferred to a sample vial for analysis by gas chromatography. The sample is analyzed on an HP 5890 Series II Plus gc equipped with an FID detector. The column used is a 25 meter SGE aluminum clad HT5, 0.53 mm id and 0.15 μm film thickness. Identification of the compounds of interest was accomplished by running standards and by spiking the

sample with the standard compounds of interest and comparing the appropriate retention times.

RESULTS AND DISCUSSION

Alcohol Filtration Tests with Polywax 500/655 Activated Catalyst Slurry.

As previously reported [6], a blend of Polywax 500 and 655 (81.3wt% and 18.7%, respectively) with a CO-reduced iron catalyst was used for the evaluation of filtration with and without an alcohol compound. All of the filtration tests were conducted with a trans-membrane pressure (TMP) of 1.4 bar, 200 °C and an iron slurry concentration of 5 wt%. The axial velocity of the slurry within the filter was maintained at 13 m/s. Dodecanol (specifically 1-dodecanol, $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$) was chosen as the alcohol additive since its low vapor pressure would insure a sufficient residence time in the slurry phase.

Given that alcohols are known to be reactive in the presence of an iron catalyst [7,8], an excessive quantity of 1-dodecanol was added once the filtration flux reached equilibrium. The initial dosages of dodecanol were 6, 11, and 17wt%. In order to maintain a constant iron catalyst concentration of 5 wt%, a mass of filtered permeate was extracted from the slurry that was comparable to the mass of the 1-dodecanol to be added.

The permeation flux versus time-on-stream for the alcohol addition run is shown in Figure 4. Before adding the 6 wt% 1-dodecanol dosage, the permeate flux was allowed to reach an equilibrium during the filter membrane/slurry induction period. During this period the flux dropped from 0.65 to 0.40 lpm/m². Once the first dose of 1-dodecanol was added, the flux increased to 0.46 lpm/m² and subsequently dropped to less than 0.2 lpm/m² over a 2-day period. As shown in Figure 5, the permeate color changed

from a bright white color to a brownish color after the dodecanol was added. This change in the permeate can be attributed to the increase of iron (from 50 to 250 ppm) and possibly the existence of reaction products of the dodecanol to secondary oxygenates such as ketones, aldehydes, and/or acids. However, it is not known if these reaction products caused the initial decrease of the permeation flux.

Subsequent additions of the dodecanol (11 and 17%) had only a minor effect on the permeation flux. In Figure 6, the equilibrium permeation flux is plotted versus the initial concentration of the dodecanol. Once the initial 6 wt% dose of dodecanol was added, the steady-state flux was maintained at 0.2 lpm/m^2 . Likewise, the permeate quality, in terms of iron concentration, did not vary substantially with increasing alcohol concentration as shown in Figure 7.

In Table 1, the analytical results of the alcohol concentration of the permeate are listed for the duration of the filtration study. The column labeled “wt% Dodecanol (added)” is the target concentration of the alcohol based on mass percent. The adjacent column labeled “wt% Dodecanol (measured)” represents the measured concentration of the alcohol in the permeate after a steady-state filtration flux was obtained. The analytical results were obtained using a GC. In addition to the dodecanol peak, two other unknowns were present in all but the initial samples before the alcohol was added (labeled “%Unknown-1” and “%Unknown-2”, respectively). Further analytical work is underway to identify these unknown compounds and to characterize what effect they may have on the filtration flux.

Table 1. Concentration of 1-deodecanol and unknown reaction products.

Time on Stream (hrs)	Wt% Dodecanol (added)	Wt% Dodecanol (measured)	% Unknown-1	%Unknown-2
72	0	0	0	0
144	6	0	0.59	0
167	11	0.54	0.8	1.81
200	17	0.74	1.23	7.33

Olefin-doping Wax Permeation Study.

The base slurry specifications and operating conditions for the olefin doping study were identical to that of the previously mentioned alcohol doping tests. The method for doping the olefins in the catalyst was similar in that a constant 5 wt% concentration of iron was maintained throughout the test run. 1-Hexadecene (C₁₆H₃₂) was selected as the doping agent since the vapor pressure of lower molecular weight olefins would cause material balance uncertainties. The target concentration levels of the olefin were 0, 14, 26, and 29 wt%. This range of concentrations is typical for various iron-based FT processes [1].

As shown in Figure 8, the baseline flux, without 1-hexadecene added, stabilized to 0.30 lpm/m² at 200°C with a 1.4 bar trans-membrane pressure. As with previous filtration runs using an activated iron catalyst slurry, the duration of the induction period for the catalyst particles and membrane was approximately 48 hours TOS. Initially, the permeate appearance was a bright white. With the first dosage of the olefin (14wt% as 1-hexadecene), the permeate flux remained essentially unchanged and stable after 48 hours TOS at 0.31 lpm/m². A slight permeate color change was observed with increasing TOS as shown in Figure 9. The iron content increased from 25 to 272 ppm with the addition

of the olefin as shown in Figure 10. However, this can be attributed to the formation of finer catalyst particulate caused by attrition as was observed in the alcohol doping study.

Likewise, no appreciable change in the permeate flux was observed at the 26 wt% or the 29 wt% olefin level (see Figure 11).

Table 2. Comparison of measured versus calculated 1-hexadecene permeate concentration .

Time on Stream (hrs)	Wt% Hexadecene (added)	Wt % Hexadecene (Measured)
0	0	0.34
50	14	14.14
76	26	25.66
170	29	29.44
190	29	40.34

Testing of a passive filter media cleaning procedure.

An opportune chance to test the passive flux maintenance procedure came during a long holiday weekend. After 100 hours TOS (see Figure 8), the permeate valve was closed and thus the trans-membrane pressure fell to zero. The pilot plant remained in a stand-by mode and unmanned for approximately 75 hours. During this period, the catalyst slurry was circulated through the crossflow filter, without permeate flow radially through the filter membrane (i.e., test conditions were constant with the exception of the absence of a trans-membrane pressure). Once the 1.4 bar trans-membrane pressure was reinstated, the flux momentarily increased by 116% (from 0.3 to 0.65 lpm/m²); however, over the next 24 hours the flux returned to the baseline flux before interruption of the permeate flow.

Even though the flux returned to the steady-state value before the permeate valve was closed, there was a 24-hour period of increased flux. Further tests are needed to determine the optimum period of filter down-time. A possible flux maintenance scheme

could employ two filters; one filter in the “permeate mode” while a duplicate filter is being regenerated with slurry without trans-membrane pressure. These units could be cycled at some optimum time period such that a higher permeate flux could be maintained than that of a single filter.

CONCLUSIONS

The addition of an alcohol (1-dodecanol) was found to decrease the permeation rate of a crossflow filter using an activated iron slurry. However, additional increases in the 1-dodecanol did not affect the permeation rates. Additionally, the color of the cleaned wax was significantly darker with the addition of the alcohol as compared to that of a paraffin-only catalyst wax. Much of this color difference may be due to side reaction products of the 1-dodecanol. The addition of an olefin (1-hexadecene) had little to no effect on the permeate flux and quality.

A passive flux maintenance procedure was tested in which the trans-membrane pressure is suspended for an extended period. The flux can be increased by over 100% , but decays back to the original steady-state flux over 24 hours.

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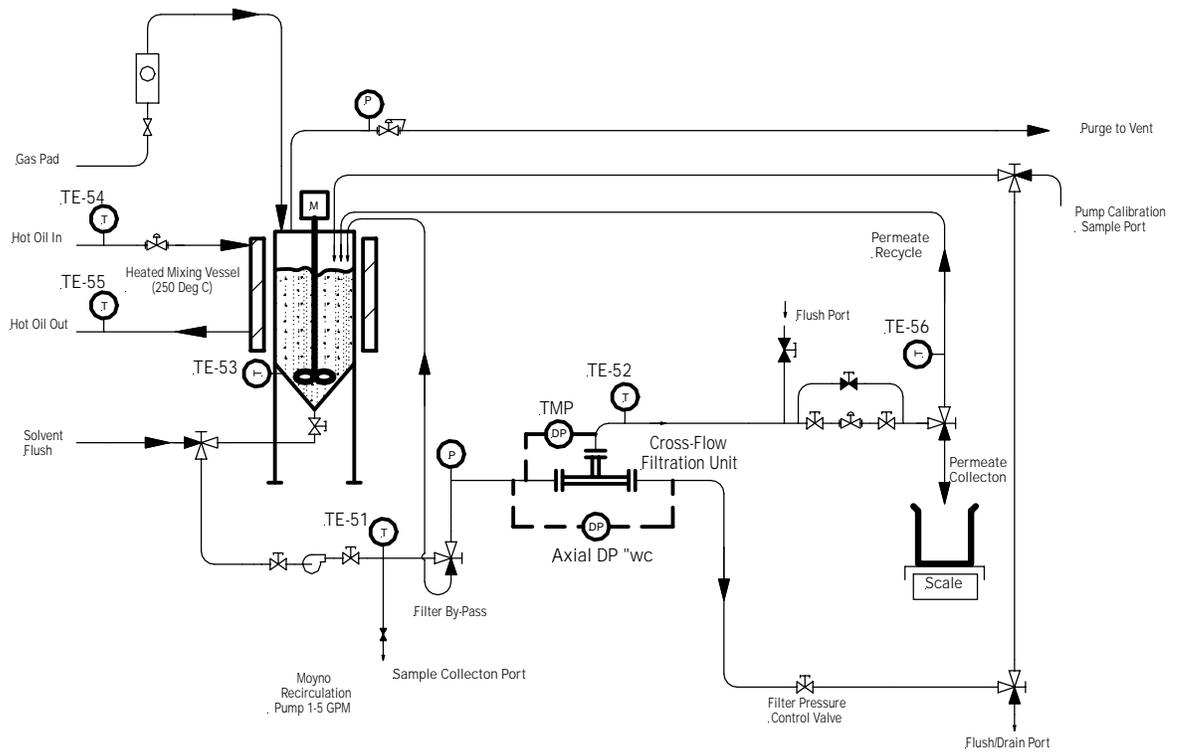


Figure 1. Schematic of the filtration test platform.

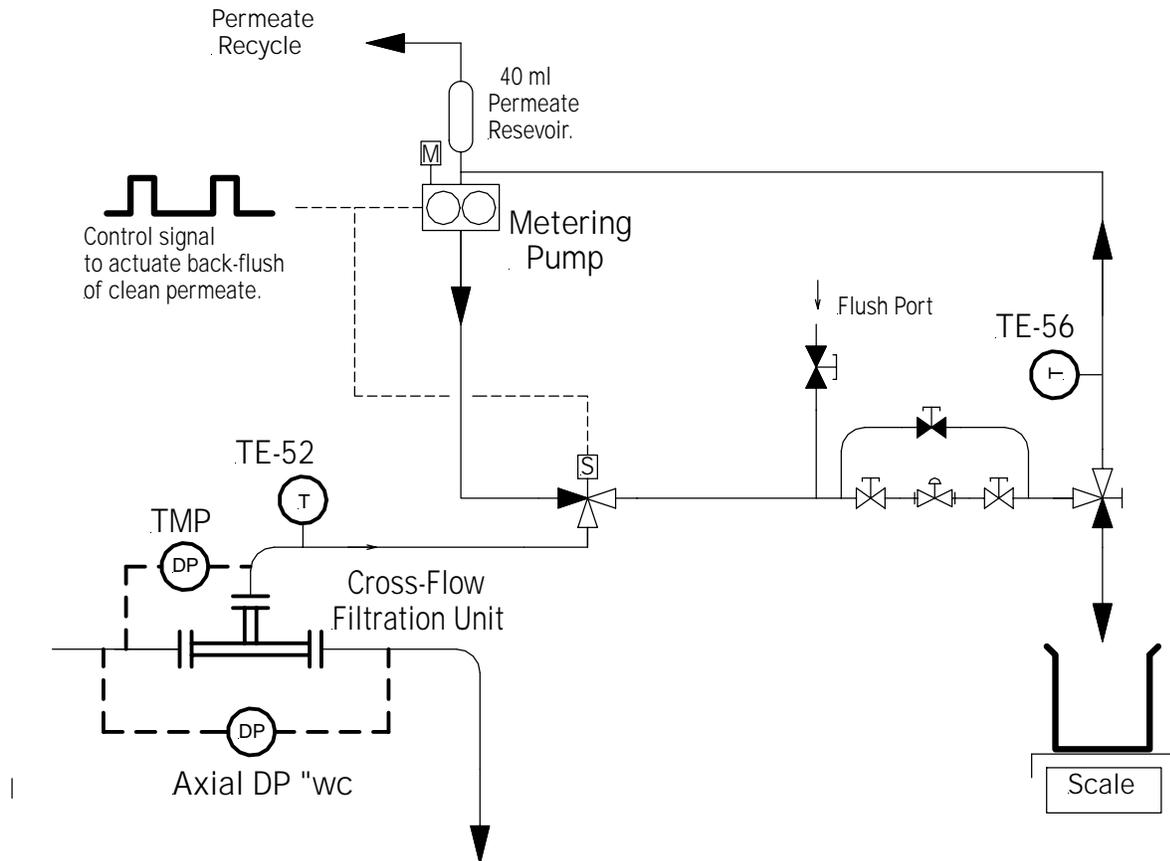


Figure 2. Schematic of the Permeate Back-Pulse System.

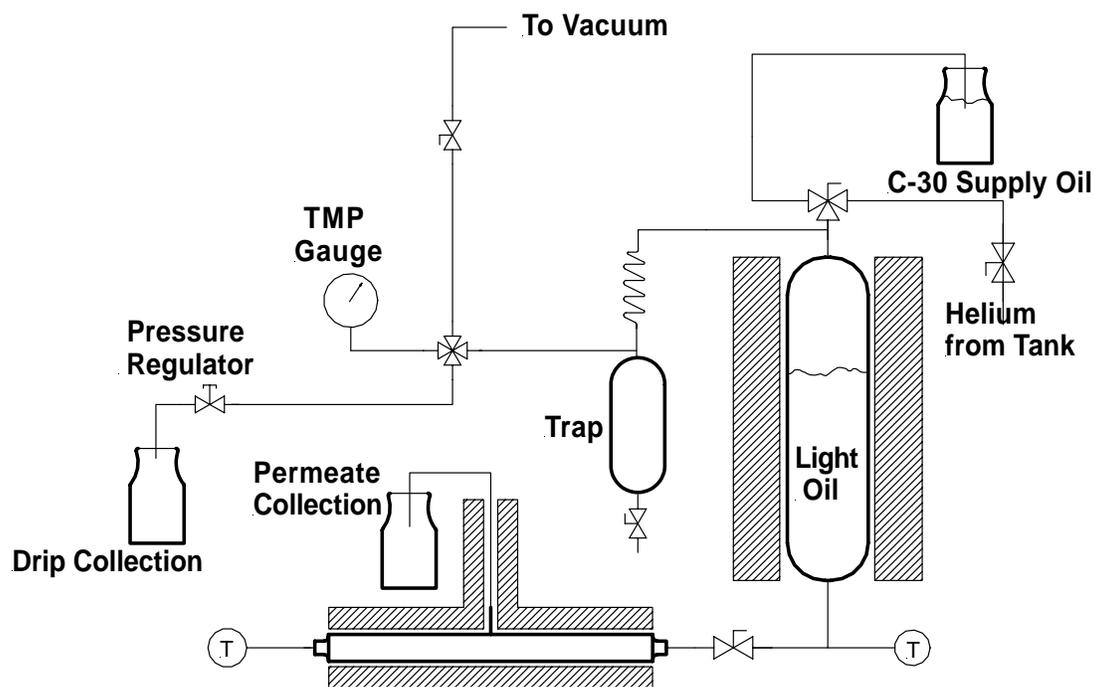


Figure 3. Schematic of the Static Permeation Test Apparatus.

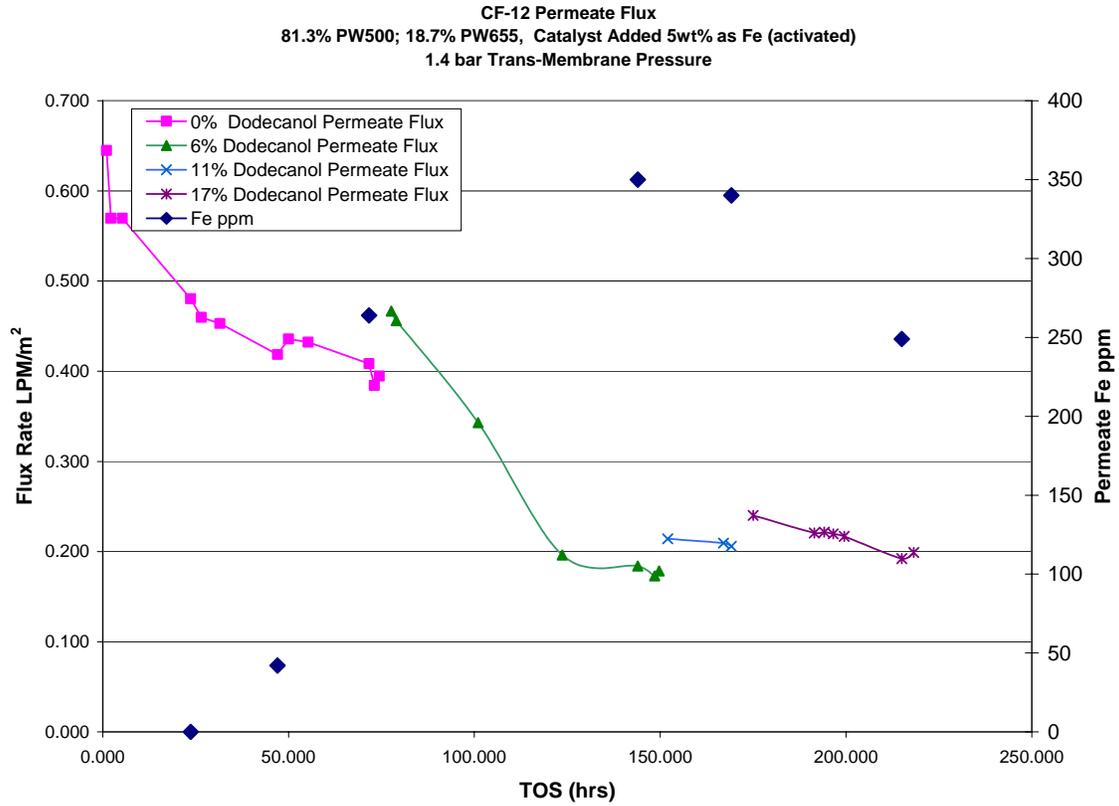


Figure 4. Permeate flux vs. time-on-stream with alcohol (1-dodecanol) additive.

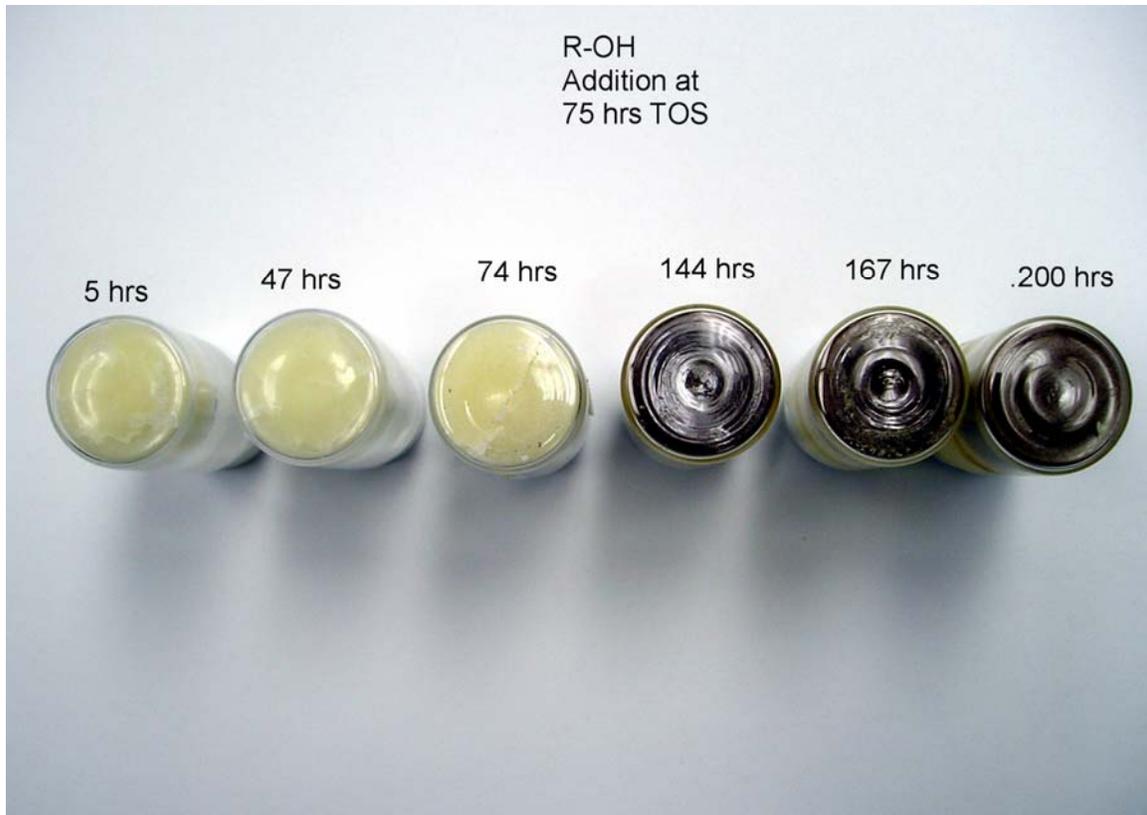


Figure 5. Picture of permeate samples with alcohol additive, various TOS.

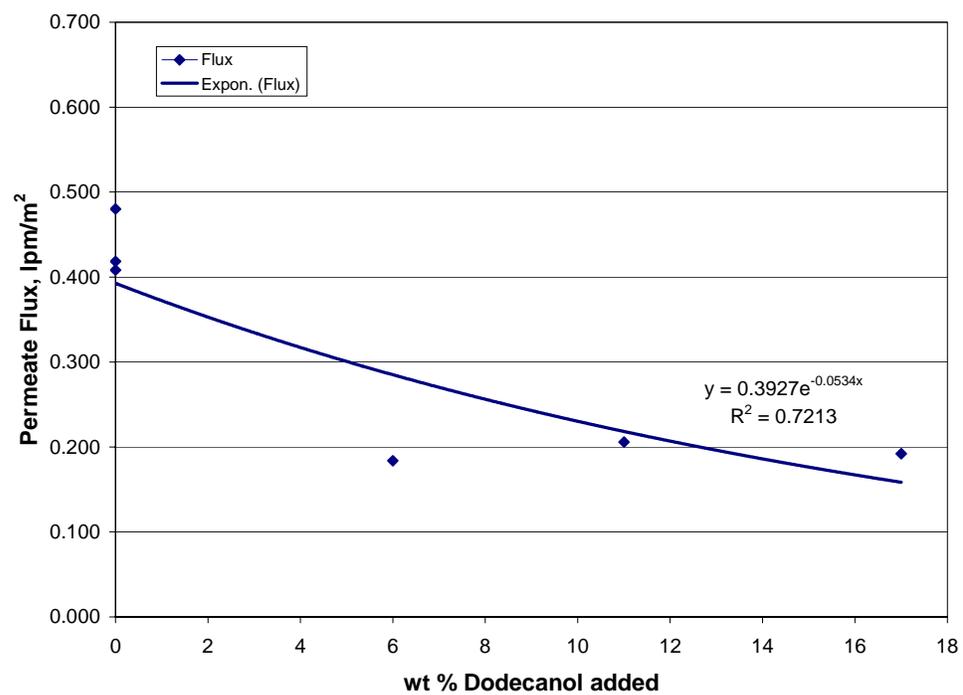


Figure 6. Permeate flux vs. starting 1-dodecanol concentration.

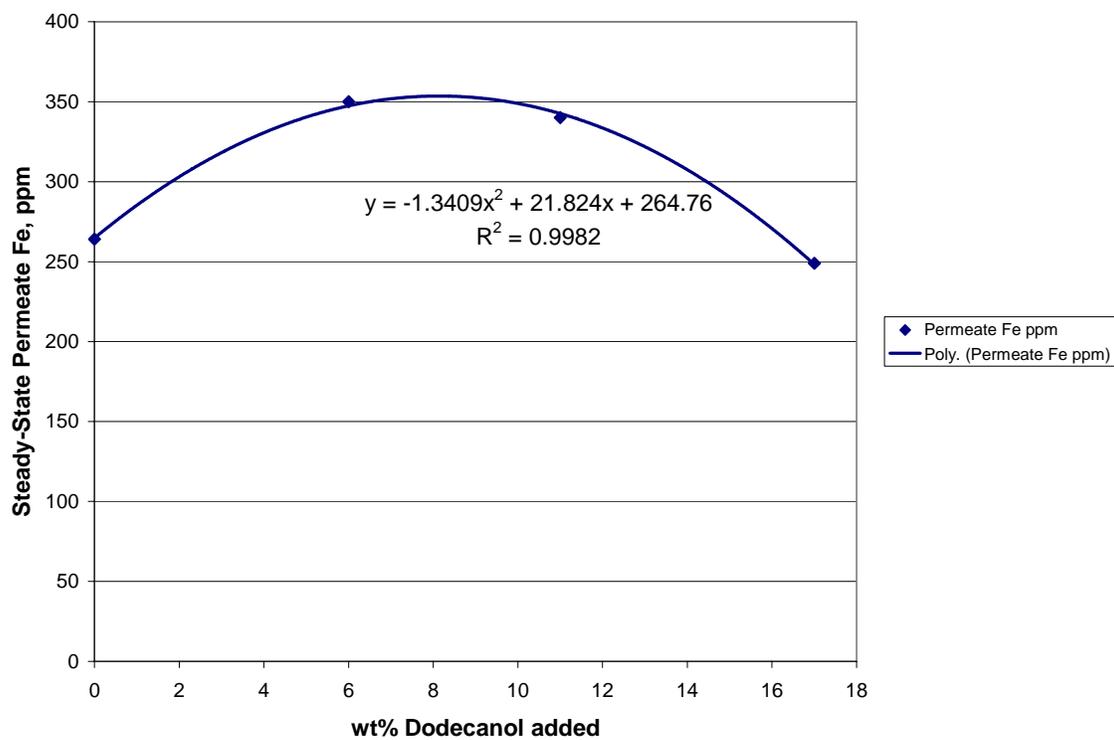


Figure 7. Permeate iron concentration (at steady-state) vs. concentration of 1-dodecanol.

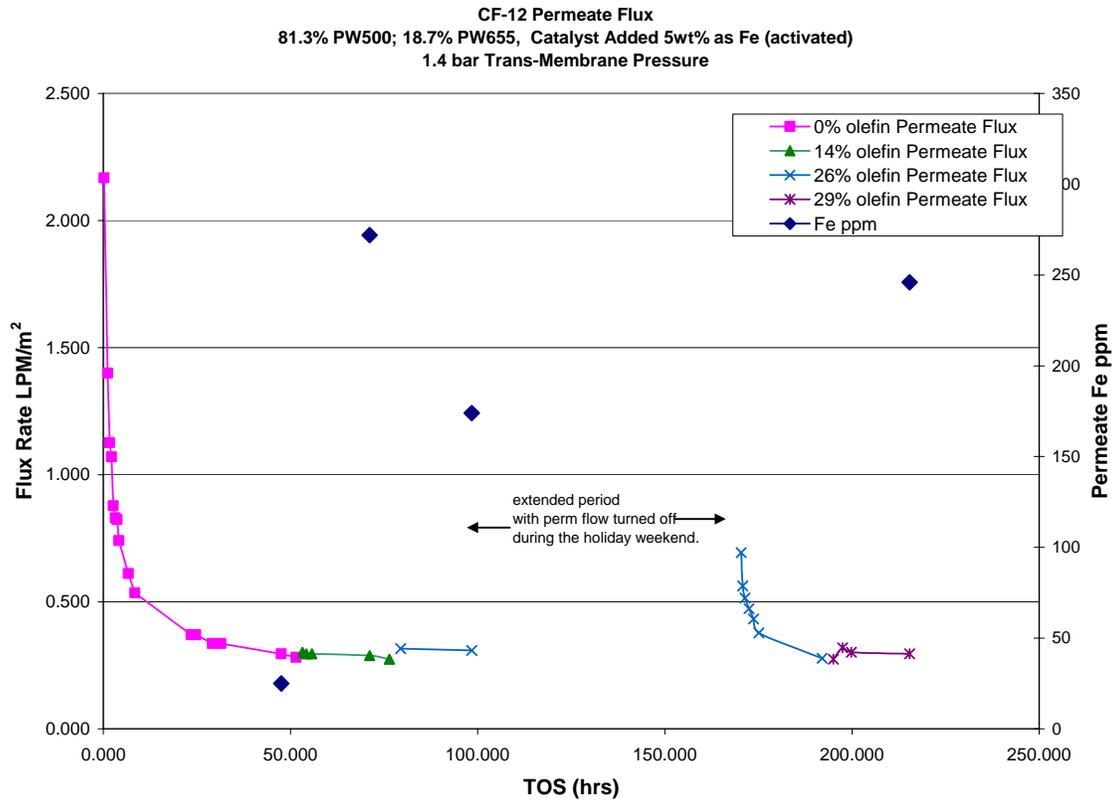


Figure 8. Permeate flux vs. time-on-stream with olefin (1-hexadecene) additive.

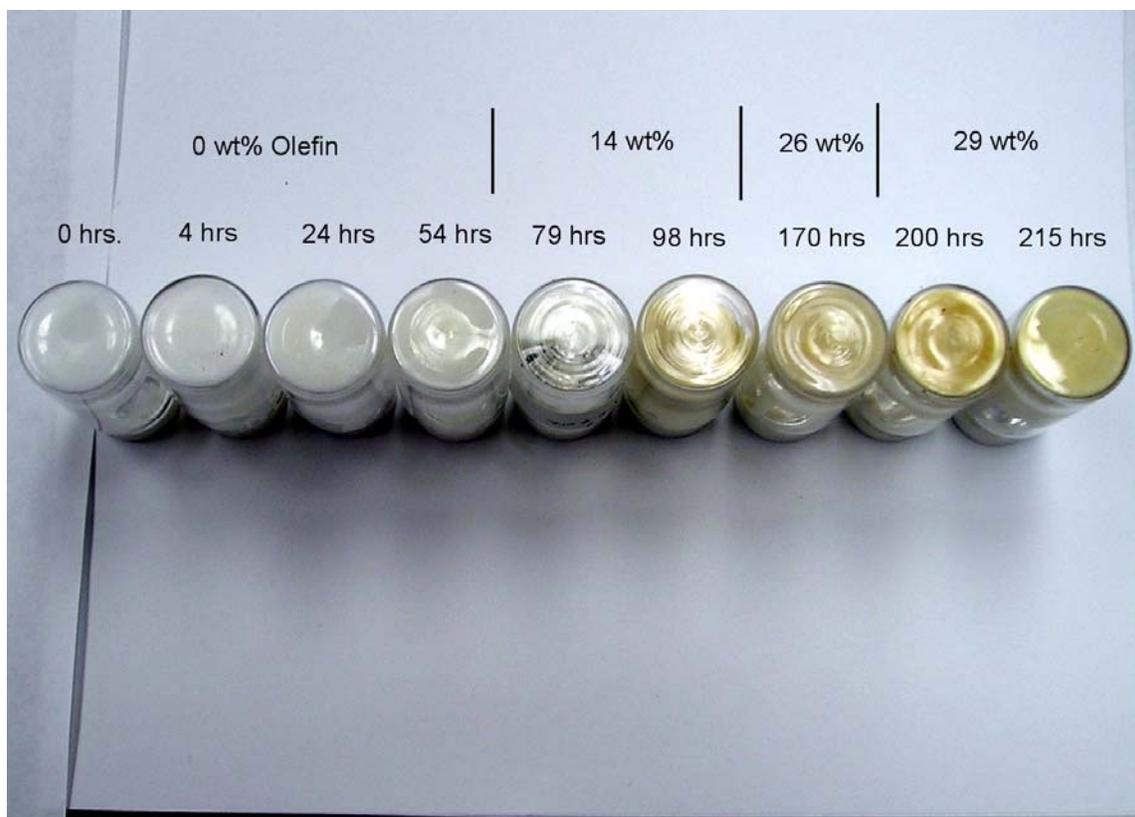


Figure 9. Picture of permeate samples with olefin additive at various time-on-stream intervals.

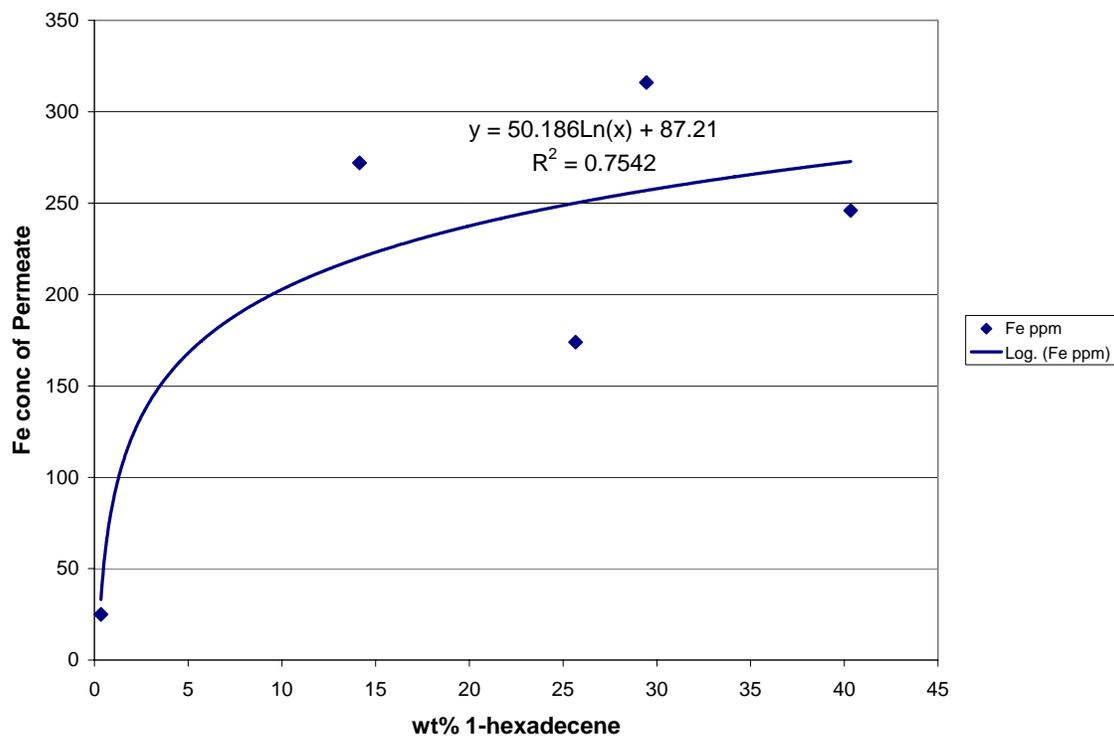


Figure 10. Permeate iron concentration vs. olefin (1-hexadecene) concentration.

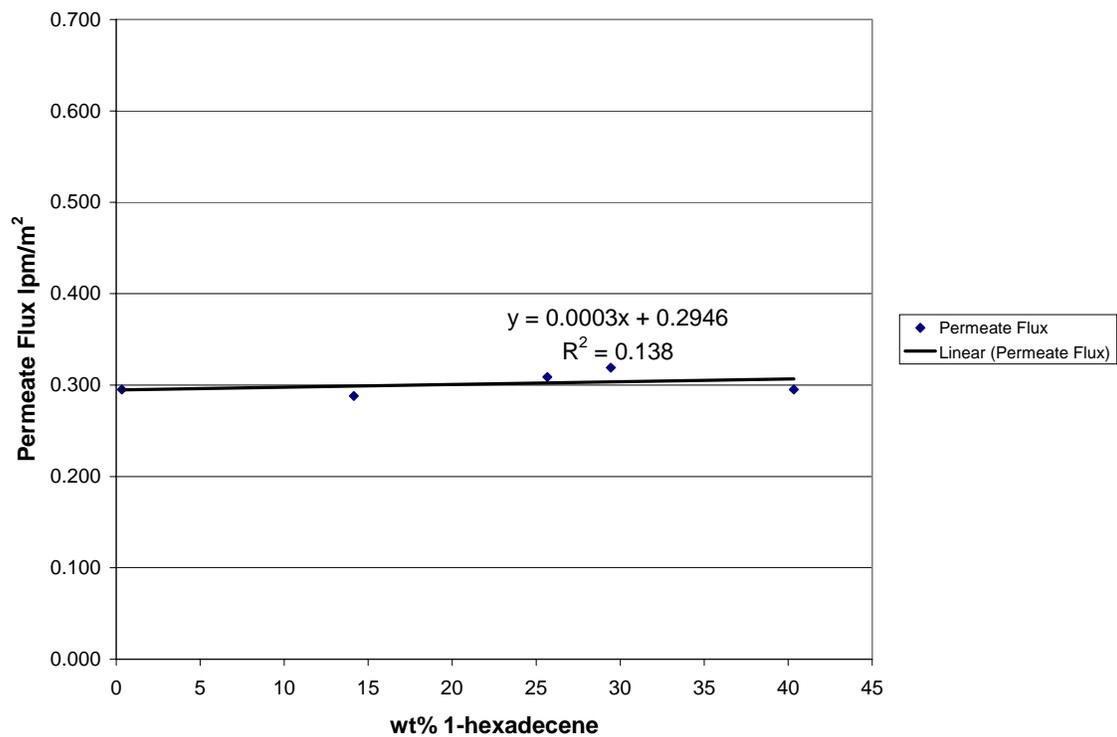


Figure 11. Permeate flux vs. olefin (1-hexadecene) concentration.

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)

See Task 1.3.

Task 1.6. Chemical and physical characterization of slurry and filtrate

INTRODUCTION

The chemical and physical changes of the catalyst associated with the process of attrition was studied through the use of a number of characterization methods. One hypothesis that has received considerable attention is that Fe is lost from the surface of the catalyst as iron carbide fines (potentially from the working active surface phase), which can subsequently block the filters, and result in a deleterious increase in the filter pressure drop, as well as a decreased filtering capacity. This type of attrition is known as “chemical attrition” (1-3). We have chosen rigorous characterization as a means to attempt a validation of this type of attrition mechanism (4). During this period, XANES spectroscopy carried out at the synchrotron at Brookhaven National Laboratory, Beamline X-18b, was utilized to characterize the chemical state of the Fe species present in a working Rb-promoted Fe-based catalyst. This work was carried out to supplement the earlier EXAFS and Mossbauer characterization results of real working Fe-based FT catalysts.

The work was conducted in part to refine the analytical methods which will be used in the near future to characterize used catalyst slurries. These XANES studies were carried out at the K-edge of Fe on both Fe-based catalysts, as well as reference materials, including an Fe metallic foil, Fe₂O₃, Fe₃O₄, and an Fe-carbide reference material prepared at the CAER.

EXPERIMENTAL

XANES. X-ray absorption near edge spectroscopy measurements on references and catalyst samples were conducted at the National Synchrotron Light Source (NSLS) at

Brookhaven National Laboratory (BNL), using beamline X18b equipped with a Si(111) channel cut monochromator. A crystal detuning procedure was employed to prevent glitches arising from harmonics. The second crystal of the channel cut monochromates is weakly linked to the crystal and slightly spring loaded. The other side is a picomotor, a very fine high pitch screw that turns by piezo, which allows for slight detuning of the crystal. The X-ray ring at the NSLS has a flux of $1E10$ photons per second at 100 mA and 2.5 GeV, and the energy range capability at X18b is 5.8-40 keV. As previously reported, the catalysts were previously run in the CSTR until steady state conversion was achieved. Catalyst was suspended in the waxy FT matrix for analysis. XANES data were recorded near Fe K-edge after cooling under He flow to liquid N₂ temperatures.

Data reduction of the XANES spectra was carried out with WinXAS (5). Standard data reduction was carried out by pre-edge background removal and normalization by division of the height of the absorption edge. Linear combination fitting of the experimental catalysts with the references was carried out using WinXAS over the range energy range of 7.1 to 7.16 keV.

RESULTS AND DISCUSSION

The catalyst studied in this reporting period was removed from a CSTR reactor under inert gas conditions and solidified in the FT wax matrix to preserve it for study by EXAFS and XANES. In this quarterly report, the XANES results are provided. Normalized absorptivity versus energy plots in the near edge region, along with the corresponding derivative spectra, for the iron K-edge data are reported in Figures 12 and 13, respectively.

Qualitatively, in examining the normalized XANES spectra, the spectrum corresponding to the activated 5%Rb catalyst matches most closely with that of the Fe_3C reference material. Fitting of the spectra, by taking a linear combination of the reference material (6), showed that the best fit was obtained when Fe_3C , Fe-oxide, and Fe foil were included in the fitting. The best fit obtained was 47.2% Fe_3C , 36.0% Fe^0 , and 16.9% Fe-oxide. Interestingly, there is quite good agreement with this XANES results and those of the Mossbauer results previously reported, where the lower content Fe carbide was found to be in abundance at 47%, the higher content Fe “Hagg” carbide was 33%, and the Fe-oxide was close to 20%. The results also are in agreement with the previous EXAFS data, which clearly detected iron carbide by comparison of the Fourier Transform magnitude peak positions (i.e., atomic distance from the absorber) (4).

An even better qualitative comparison can be made by considering the derivative spectra obtained from the normalized absorptivity XANES spectra (Figure 13). This is because the derivative spectra can pick up key inflections in the onset of absorption that are difficult to detect by analysis of the normalized absorptivity spectra. It is evident that qualitatively, the activated 5%Rb promoted iron catalyst matches most closely with that of the Fe_3C reference. Not only do the peak positions match very closely with that of the Fe_3C (see dotted lines), but their intensities are also relatively similar, with excellent agreement observed especially in the shape, intensity, and position of the onset peak (7.112 keV). A slight peak at 7.123 keV for the Fe_3C reference suggests a slight degree of oxidation, most likely confined to a passivation layer in the surface shell, as this peak matched very closely a peak observed in the Fe oxide reference materials (see dotted line).

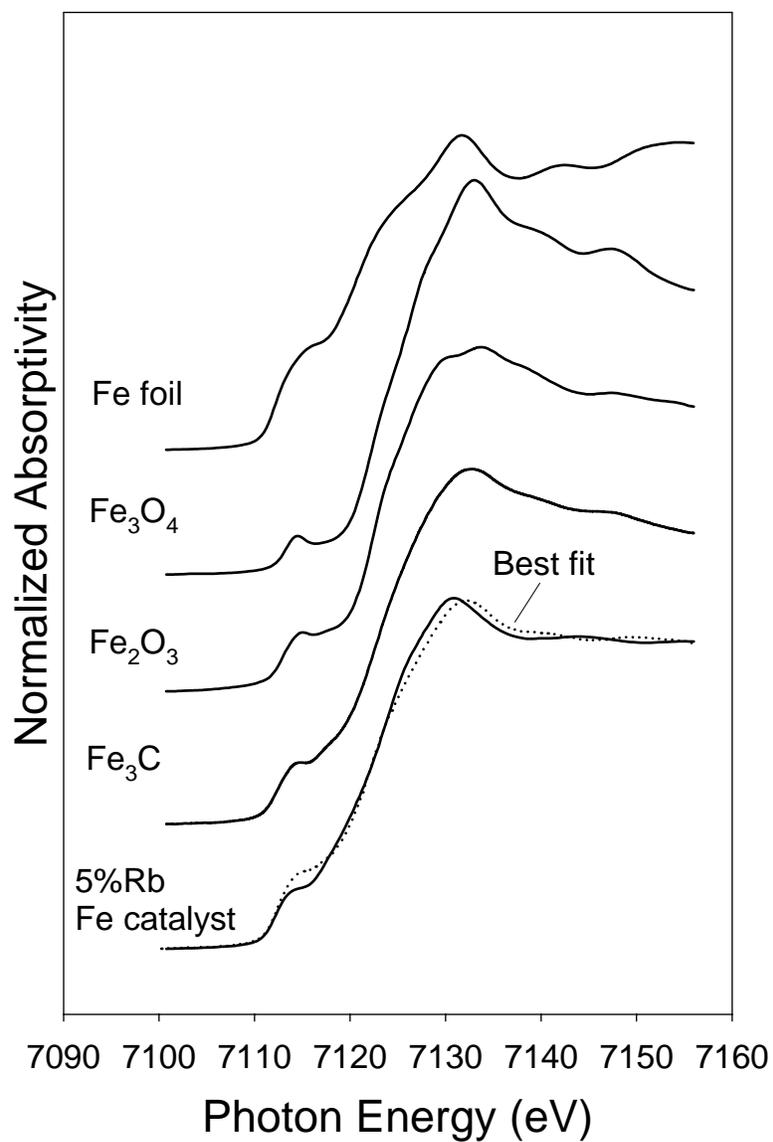


Figure 12: Fe K-edge results. Normalized XANES spectra of references and the used 5% Rb promoted catalyst.

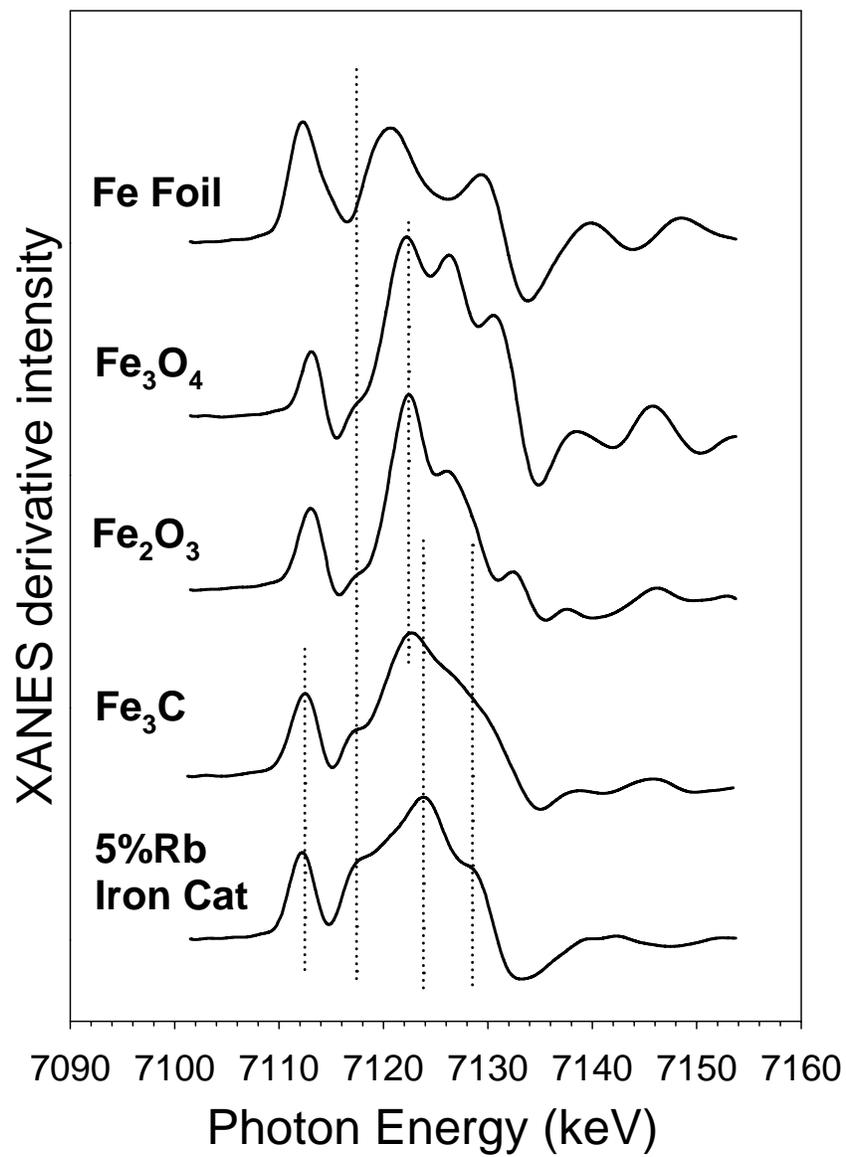


Figure 13: Fe K-edge results. XANES derivative spectra of references and the used 5% Rb promoted catalyst.

CONCLUSIONS

Preliminary characterization by XANES confirmed our previous results of Mossbauer and EXAFS spectroscopy that a major component of the reduced, activated 5%Rb promoted Fe-based catalyst is Fe carbide. This conclusion was made on the basis of qualitative comparisons between the catalyst and the reference materials using not only the normalized XANES spectra as a basis for comparison, but also in considering the XANES derivative spectra. The latter give much more precise detail on the inflections in the absorptivity profiles. XANES fitting of the spectrum of the working catalyst with a linear combination of the reference spectra confirmed that Fe carbides were a major constituent. The results confirm that, in conjunction with Mossbauer and EXAFS results, XANES is an appropriate technique for extracting chemical information on the Fe phases present in the working catalyst.

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Task 2. Phase II Bubble Column Pilot Plant Studies

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

PATENTS, PRESENTATIONS AND PUBLICATIONS

Patents Issued 2004/2005

James K. Neathery and Burtron H. Davis (2004), "Bubble Column Apparatus for Separating Wax from Catalyst Slurry." U.S. Patent 6,762,209.

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Jacobs, G.; Chenu, E.; Patterson, P.M.; Calico-Williams, L.; Sparks, D.E.; Thomas, G.; and Davis, B.H.; "Water-gas Shift: Comparative Screening of Metal Promoters for Metal-ceria Systems and Role of the Metal," Applied Catalysis A: General 258 (2004) 203.

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Jacobs, G.; Chaney, J.A.; Patterson, P.M.; Das, T.K.; and Davis, B.H.; "Fischer-Tropsch Synthesis: Study of the promotion of Re on the reduction property of Co/Al₂O₃ catalysts by in-situ EXAFS of Co K and Re L_{III} Edges," Applied Catalysis A: General 264 (2004) 203.

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Jacobs, G; Patterson, P.M.; Chaney, J.A.; Conner, W.A.; Das, T.K.; Luo, M.; and Davis, B.H.; "Fischer-Tropsch synthesis: Influence of Reduction Promoters on Cluster Size and Stability of Co/Al₂O₃ Catalysts for GTL," Anaheim, CA, Am. Chem. Soc., Div. Petr. Chem. 49, 186, 2004.

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Jacobs, G.; Patterson, P.M.; Crawford, A.C.; Chenu, E.; Sparks, D.E.; and Davis, B.H.; "Low Temperature Water Gas Shift: Comparative study of Pt Promoted Ceria and Thoria," 13th International Congress on Catalysis, July 11-15, Paris, France, 2004.

Jacobs, G.; Patterson, P.M.; Chaney, J.A.; Conner, W.A.; Das, T.K.; and Davis, B.H.; "Fischer-Tropsch Synthesis: Influence of Cluster Size and Promoters on Reoxidation Phenomena Associated with Co/Al₂O₃ Catalysts for GTL," 13th International Congress on Catalysis, July 11-15, Paris, France, 2004.

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Jacobs, G.; Patterson, P.M.; Crawford, A.C.; and Davis, B.H.; "Developing Structural Property Relationships of Pt/Ceria Catalysts for Low Temperature Water Gas Shift," Atlanta, GA, AIChE Spring National Meeting, April 10-14, 2005.

Davis, B.H.; Das, T.K.; Chaudhari, K.; Jacobs, G.; and Luo, M.; "Impact of Water on Iron and Cobalt Catalysts During Synthesis," Atlanta, GA, AIChE Spring National Meeting, April 10-14, 2005.

TRAVEL

March 2004 Anaheim, CA – two oral presentations at ACS Spring National Meeting

April 2004 New Orleans, LA – two oral presentations at AIChE Spring National Meeting

July 2004 Paris, France – two poster presentations at the International Congress on Catalysis

March 2005 San Diego, CA – two oral presentations at the ACS Spring National Meeting

April 2005 Atlanta, GA – two oral presentations at the AIChE Spring National Meeting