Development of Attrition Resistant Iron-Based Fischer-Tropsch Catalysts

Type of Report:	Technical Progress Report, Report Number: 2
Reporting Period:	September 1, 2000 – August 31, 2001
Project Manager:	Adeyinka A. Adeyiga
Date:	September 1, 2001
DOE Award Number:	DE-FG26-99FT40619
Name and Address:	Hampton University Department of Chemical Engineering Hampton, VA 23668
DOE Project Officer:	Dr. Udaya Rao

Disclaimer

Abstract

The Fischer-Tropsch (F-T) reaction provides a way of converting coal-derived synthesis gas ($CO+H_2$) to liquid fuels. Since the reaction is highly exothermic, one of the major problems in control of the reaction is heat removal. Recent work has shown that the use of slurry bubble column reactors (SBCRs) can largely solve this problem. The use of iron-based catalysts is attractive not only due to their low cost and ready availability, but also due to their high water-gas shift activity which makes it possible to use these catalysts with low H_2/CO ratios. However, a serious problem with use of Fe catalysts in a SBCR is their tendency to undergo attrition. This can cause fouling/plugging of downstream filters and equipment, makes the separation of catalyst from the oil/wax product very difficult if not impossible, and results in a steady loss of catalyst from the reactor.

Recently, fundamental understanding of physical attrition is being addressed by incorporating suitable binders into the catalyst recipe. This has resulted in the preparation of a spray dried Fe-based catalyst having aps of 70 μm with high attrition resistance. This Fe-based attrition resistant, active and selective catalyst gave 95% CO conversion through 125 hours of testing in a fixed-bed at 270°C, 1.48 MPa, $H_2/CO=0.67$ and 2.0 NL/g-cat/h with C_5^+ selectivity of >78% and methane selectivity of <5%. However, further development of the catalyst is needed to address the chemical attrition due to phase changes that any Fe-catalyst goes through potentially causing internal stresses within the particle and resulting in weakening, spalling or cracking.

The objective of this research is to develop robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry bubble column reactor. Specifically we aim to develop to: (i) improve the performance and preparation procedure of the high activity, high attrition resistant, high alpha iron-based catalysts synthesized at Hampton University, (ii) seek improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in catalyst preparation steps and (iii) investigate the performance in a slurry reactor.

The effort during the reporting period has been devoted to attition study of the iron-based catalysts. Precipitated silica appeared to decrease attrition resistance of spray-dried iron FT catalysts. It was found that the catalyst with precipitated silica content at around 12wt% showed the lowest attrition resistance. The results of net change in volume moment and catalyst morphology showed supporting evidences to the attrition results. Catalysts with low attrition resistance generated more fines loss, had higher net change in volume moment and showed more breakage of particles. BET surface area and pore volume of this catalyst series fluctuated; therefore no conclusion can be drawn from the data obtained. However, catalyst with no precipitated silica showed the lowest in BET surface area and pore volume, as expected. Addition of precipitated silica to the catalysts had no effect to the phase changes of iron that could have significant influence to catalyst attrition. The presence of precipitated silica is needed for enhancing catalyst surface area; however, the amount of silica added should be compromising with attrition resistance of catalysts.

Table of Contents

Disclaimer……………………………………………………………..…………….... **2**
Abstract……………………………………………………………..……………… **3**
Table of Contents……………………………………………………………….. **4**
Introduction……………………………………………………….…………... **5**
Results And Discussion……………………………………………………………….. **8**
Task 1. Catalyst Preparation………………………………………………… **8**
Task 2. Catalyst Performance Evaluation……………………….………….. **8**
Task 3. Catalyst Characterization…………………………………………… **8**
Task 4. Slurry Reactor Testing……………………………………………… **14**
Future Work ……………………………………………………………………… **14**

Development of Attrition Resistant Iron-Based Fischer-Tropsch Catalysts

Introduction

Fischer-Tropsch Synthesis (FTS) is the reaction of CO and H_2 (syngas) to form a wide variety of hydrocarbons, typically using iron- or cobalt-based catalysts. Currently there are two commercial FTS plants: SASTECH produces synthetic fuels and chemicals from coal (including recent expansions), and Shell is using FTS to convert natural gas to high value products in Malaysia. There are other units in the planning or construction stage: China plans to make town gas via FTS; Williams Company is constructing a pilot plant to determine the economics of underground coal gasification; and Exxon is evaluating the possibility of locating a large natural gas-based FTS plant in Quatar. These activities clearly show that improvements and innovations in FTS are underway. This process is also strategically important to the U.S. because of its vast coal reserves, and because FTS represents the best means to make high quality transportation fuels and liquid products from coal. In addition to other technical challenges, one of the major problems in control of the reaction is heat removal. Recent progress in this area has focused on the use of a slurry bubble column reactor (SBCR). These reactors offer simple designs and low costs while still permitting high catalyst and reactor productivity. It is generally thought that this will be the reactor of choice for commercial, coal-based FTS in the United States.

Since modern coal gasification plants produce a syngas that is relatively lean in H_2 ($H_2/CO = 0.5-0.7$), a catalyst which is active for the FTS reaction ($CO + 2\ H_2 \rightarrow -CH_2- + H_2O$) and the water-gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is required. The overall reaction on these catalysts is thus $2CO + H_2 \rightarrow -CH_2- + CO_2$. This allows the efficient use of low H_2/CO syn gas. Iron-based catalysts, which are active shift catalysts, are thus preferred over cobalt-based catalysts, which are not. Iron is also much less expensive than cobalt.

F-T products are very desirable from an environmental point of view. Because F-T catalysts are very sulfur sensitive, the feed must be completely sulfur free which means that the product is also sulfur free. In addition to being sulfur free, the product is also nitrogen and aromatics free. F-T diesel fuel has a very high cetane number. Although raw F-T naphtha has a low octane number, it can be processed into high quality gasoline. F-T distillate also makes excellent ethylene plant feedstock.

Catalyst development activities have involved an extensive effort to improve the performance of iron catalysts. Iron catalyst development work has been carried out by the Center for Advanced Energy Research (CAER) and FETC's Office of Science and Technology (OST). These efforts have resulted in iron catalysts with much higher activities than previous catalysts. A problem with iron catalysts is that they tend to have low structural strength with the result that attrition tends to produce very small catalyst particles during slurry operations. This attrition causes plugging, fouling, difficulty in separating the catalyst from the wax product, and loss of the catalyst. This is due to the low attrition resistance of the Fe catalyst and the significant breakage of the Fe particles. Fe catalysts are subject to both chemical as well as physical attrition in a SBCR. Chemical attrition can be caused due to phase changes that any Fe catalyst goes through ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe \rightarrow$ Fe carbides) potentially causing internal stresses within the particle and resulting in weakening, spalling or cracking. Physical attrition can result due to collisions between catalyst particles and with reactor wall. Catalyst particles of irregular shapes and non-uniform sizes produces by conventional methods are subject to greater physical attrition.

Another inherent complication associated with the iron-based catalyst is the catalyst pretreatment. Before synthesis, a catalyst precursor is pretreated to convert the catalyst into an active form. The pretreatment of Fe is not as straight forward as that for Ru, Co or Ni. Although pretreatment includes reduction of the iron particles, other processes are also involved. The pretreatment of iron FT catalysts is not clearly understood. Part of the confusion stems from the fact that the nature and composition of iron catalysts change during reaction. These changes depend on the temperature, time of exposure to the reactant feed, nature of the reactor system, and composition of the feed, and activation conditions (time and temperature). The common pretreatment conditions employed in the case of iron catalysts are H_2 reduction, CO reduction (and carbiding), or reduction in the reactant syngas. Work at the Federal Energy Technology Center has focused on the effect of catalyst pretreatment and the impact of the liquid starting medium on syngas conversion in a stirred tank slurry reactor.

Several phases of iron are known to exist when iron-based catalysts are subjected to F-T synthesis conditions. These include metallic iron (α -Fe), iron oxides (hematite, α-Fe_2O_3; magnetite, Fe_3O_4 and Fe_xO), and iron carbides, of which at least five different forms are known to exist. These include O-carbides (carbides with carbon atoms in octahedral interstices, ε-Fe_2C, ε'-$Fe_{2.2}C$, and Fe_xC) and TP-carbides (carbides with carbon atoms in trigonal prismatic interstices, χ -$Fe_{2.5}C$ and Fe_3C). The formation and distribution of these phases depend on the reaction conditions, reaction times, and state of the catalyst (reduced/unreduced, supported/unsupported, etc.). However, the role of each of these phases during the reaction has not been resolved.

Potassium and copper are typically used as chemical promoters for iron FT catalysts. The adsorption of CO on iron results in a net withdrawal of electrons from the metal, whereas hydrogen adsorption tends to donate electrons to the metal. Potassium and the associated O^{2-} donate electrons to the metal, enhancing CO adsorption while weakening H_2 adsorption. This leads to decreased hydrogenation and increased chain growth during the synthesis reaction, yielding higher molecular weight products (i.e., a higher α). More lower olefins are also produced. Potassium also decreased CH_4 production and increases WGS activity. Copper on the other hand is introduced to facilitate reduction of the iron itself. Copper is more effective in increasing the FTS reaction rate than potassium. Also the average molecular weight is increased in the presence of copper.

The objective of this research is to develop robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry bubble column reactor. Specifically we aim to develop to: (i) improve the performance and preparation procedure of the high activity, high attrition resistant, high alpha iron-based catalysts synthesized at Hampton University, (ii) seek improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modification in catalyst preparation steps and (iii) investigate the performance in a slurry reactor.

Results And Discussions

The project consists of four experimental tasks (Tasks 1-4) addressing the contract objectives described above:

Task 1: Catalyst Preparation
Task 2: Catalyst Performance Evaluation
Task 3: Catalyst Characterization
Task 4: Slurry Reactor Testing

Task 1. Catalyst Preparation

Attrition resistant Fe-based catalysts (100Fe/5Cu/4.2K/10SiO_2 on a mass basis) were prepared using precipitation methods. The resultant catalyst precursor was spray dried to produce micro-spheroidal particles (>50 μm) followed by air-calcination at 300°C to produce attrition-resistant spheroidal catalysts.

Task 3. Catalyst Characterization

This task provides support to each of the previous tasks. The following analytical techniques are used to characterize the fresh, pretreated and used catalysts. 1) Total surface area measurement using BET method. 2) Hg-porosimetry for pore volume and pore size distributions. 3) X-ray Diffraction (XRD) for the bulk phases of the catalysts. 4) CO chemisorption on the reduced iron catalysts to measure the available active Fe surface area. 5) The reducibility of the catalysts by TPR. 6) Elemental analysis using atomic absorption (AA) spectrometry.

Attrition

From the attrition results (Table 1), the catalyst composition without precipitated silica showed clearly the lowest amount of fines loss, in other words, the highest attrition resistance. Attrition resistance seemed to decrease (fines loss increase), as the amount of precipitated silica increased (Figures 1 & 2). However, the catalyst with 15wt% precipitated silica showed an increase in attrition resistance, which made the lowest attrition resistance of the whole series appeared to be at the composition with approximately 12wt% silica. Although it could not clearly tell the difference among the attrition results for catalysts with SiO_2 9, 12 and 15wt%, these results are found to be reproducible.

Based on the results, the addition of precipitated silica is found to decrease attrition resistance of catalyst. However, high surface areas of silica are needed to enhance the active surface area of catalyst. From this point of view the compromise between activity and attrition resistance have to be considered for the development of attrition resistant catalyst.

Change in volume moment

The volume moment of catalyst particles before jet cup test was measured as a representative of the average particle size of the whole batch before the test (Table 2). After a jet cup test the catalyst particles were collected separately as “bottom” and “fines” particles in which the volume moment of each one was evaluated separately before combining them as an average volume moment after attrition (Figures 3 & 4). The relation between the volume moment change and concentration of precipitated silica showed the same tendency as that of attrition results. This was shown to be consistent since the more the particles were broken, the larger the net change in average particle size was expected.

Particle morphology

Catalyst particles with precipitated silica were round in shape whereas the ones without precipitated silica looked like small rocks. Each picture was chosen in such a way that it well represented the whole batch of testing particles. The micrographs illustrated clearly the more breakage of catalyst particles with precipitated silica than that of the ones without silica, as consistent with the attrition and net change in volume moment results.

BET surface area and pore volume

Results of BET surface area and pore volume, presented in Figures 5 & 6, fluctuated. However, they varied with precipitated silica content with similar tendency; the results were reproducible. From the figure the lowest BET surface area as well as the lowest pore volume are shown at the precipitated silica content around 0 wt% while the highest ones appear at around 6wt%.

Phase and crystallinity

By comparing XRD patterns between iron catalyst without precipitated silica and the one with precipitated silica, the addition of silica did not affect the phase change of iron catalyst. As seen from Figure 7, the XRD peaks are identical, representing the hematite phase. Effect of phase change due to attrition was not needed to evaluate since attrition process had impacts only on physical properties of catalyst, but not the chemical ones.

Table 1: Weight Percentage of Fines Loss of Each Catalyst Composition.

Catalyst Composition	SiO_2 wt% (based on Fe)	SiO_2Conc.[(a)] (wt%)	Fines Loss[(b,c)] (wt%)
100Fe/5Cu/4.2K	0	0.0	3.2
	3	2.7	6.4
	6	5.2	7.5
	9	7.6	8.6
	12	9.9	9.3
	15	12.1	7.7

(a) Calculated based on total weight of catalyst.

(b) Error = ±10% of the value measured.

(c) Wt% fines = weight of fines collected/weight of total catalyst recovered x 100%.

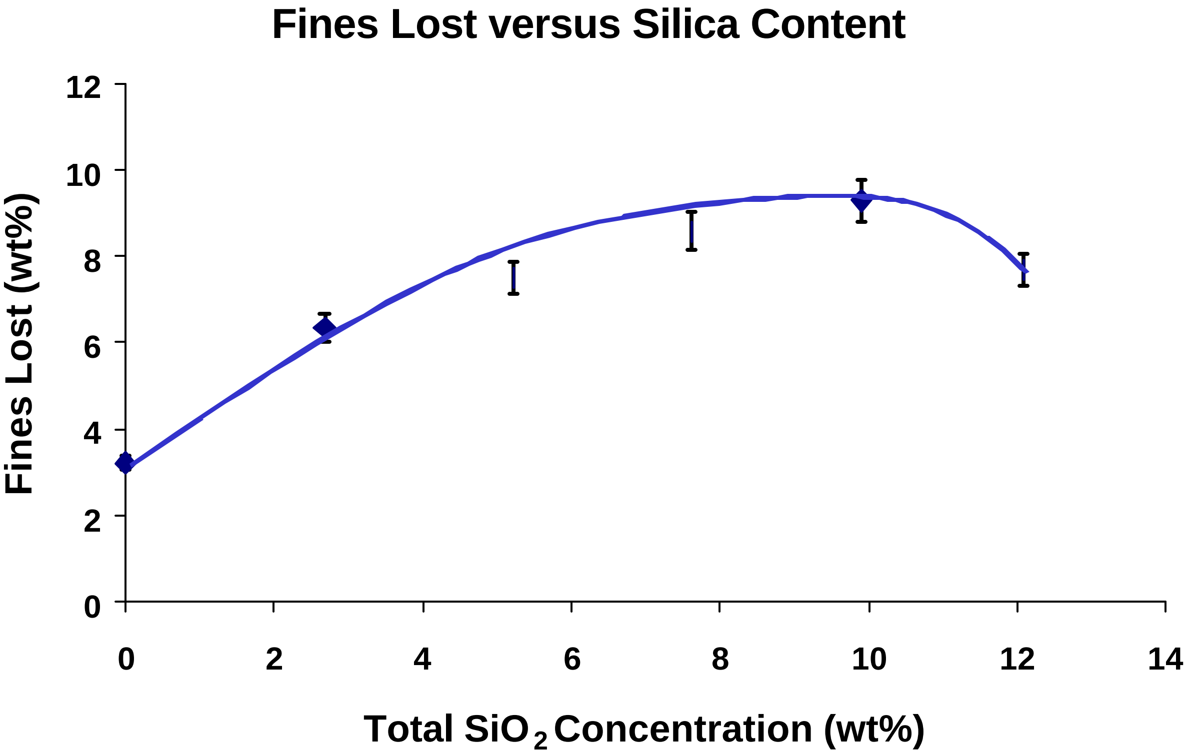

Figure 1. Plot of attrition results from Table 1.

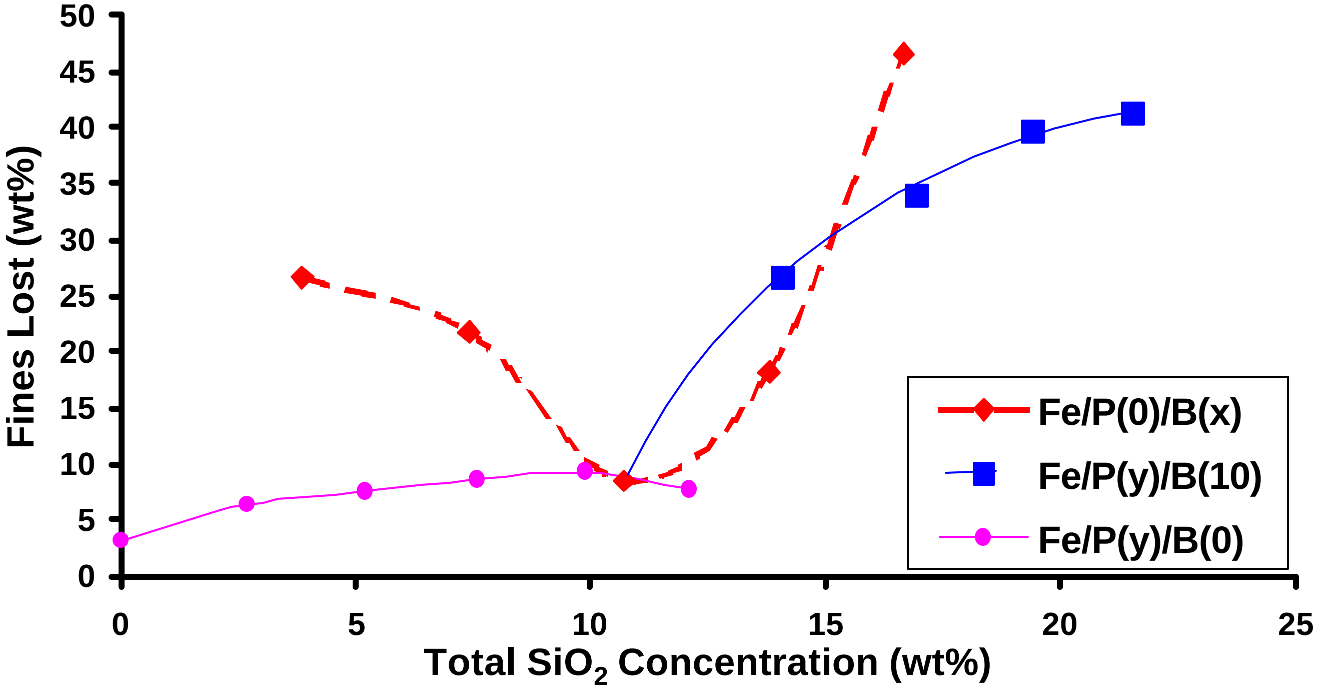

Figure 2. Plot of Figure 1 with the earlier study by Zhao and Goodwin on the same scale.

Table 2: Net Change in Volume Moment after Attrition Test.

Catalyst Composition	SiO_2 wt% (based on Fe)	SiO_2Conc.[(a)] (wt%)	Net Change in Volume Moment[(b,c)] (%)
100Fe/5Cu/4.2K	0	0.0	5.95
	3	2.7	18.4
	6	5.2	23.4
	9	7.6	27.1
	12	9.9	30.1
	15	12.1	27.8

(a) Calculated based on total weight of catalyst.
(b) Average of 3 particle size distribution measurements, error = ±5% of the value measured
(c) Volume moment is a volume mean diameter of the particles

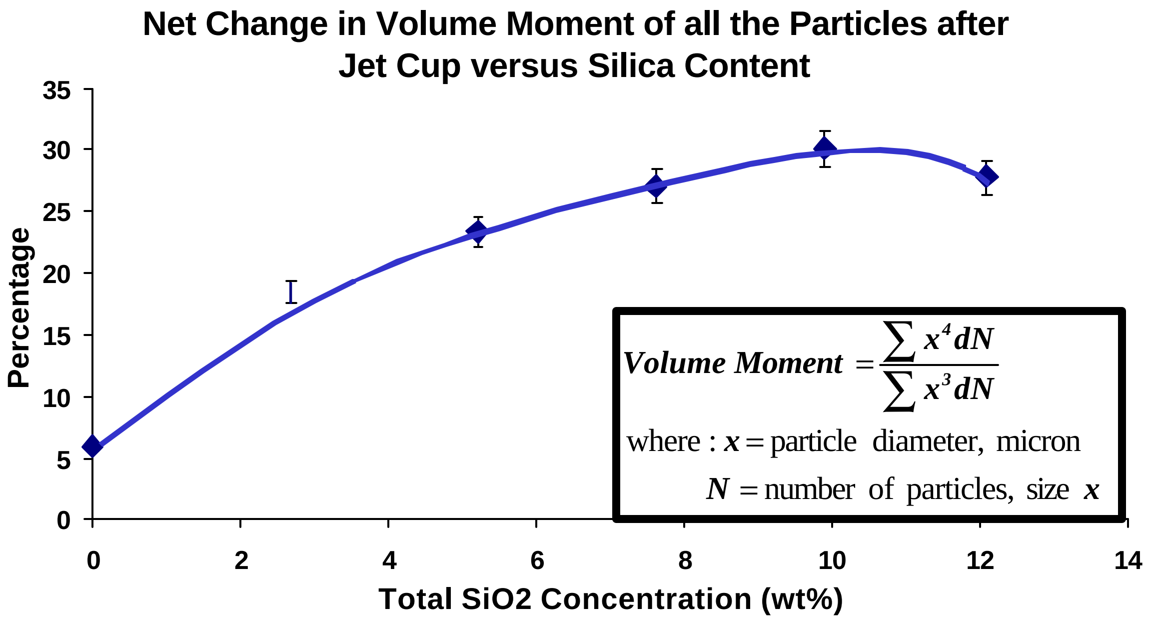

Figure 3. Net change in volume moment after jet cup test, data from Table 2.

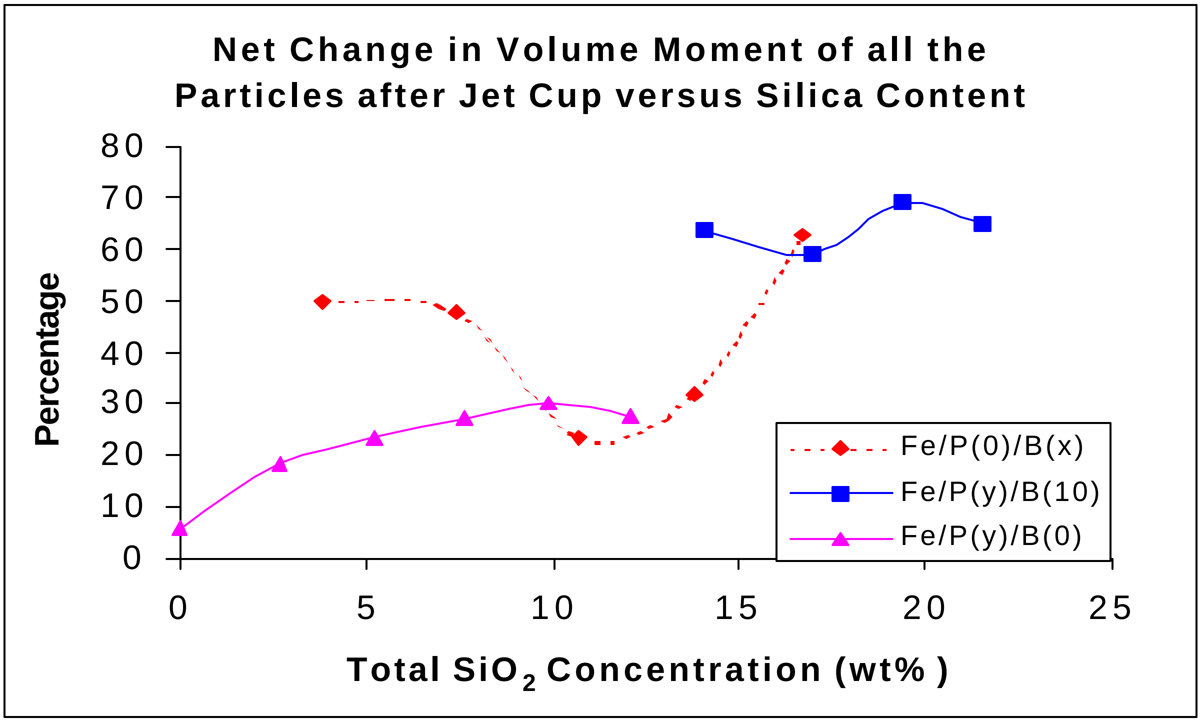

Figure 4. Plot of data from Table 2 with previous study by Zhao and Goodwin on the same scale.

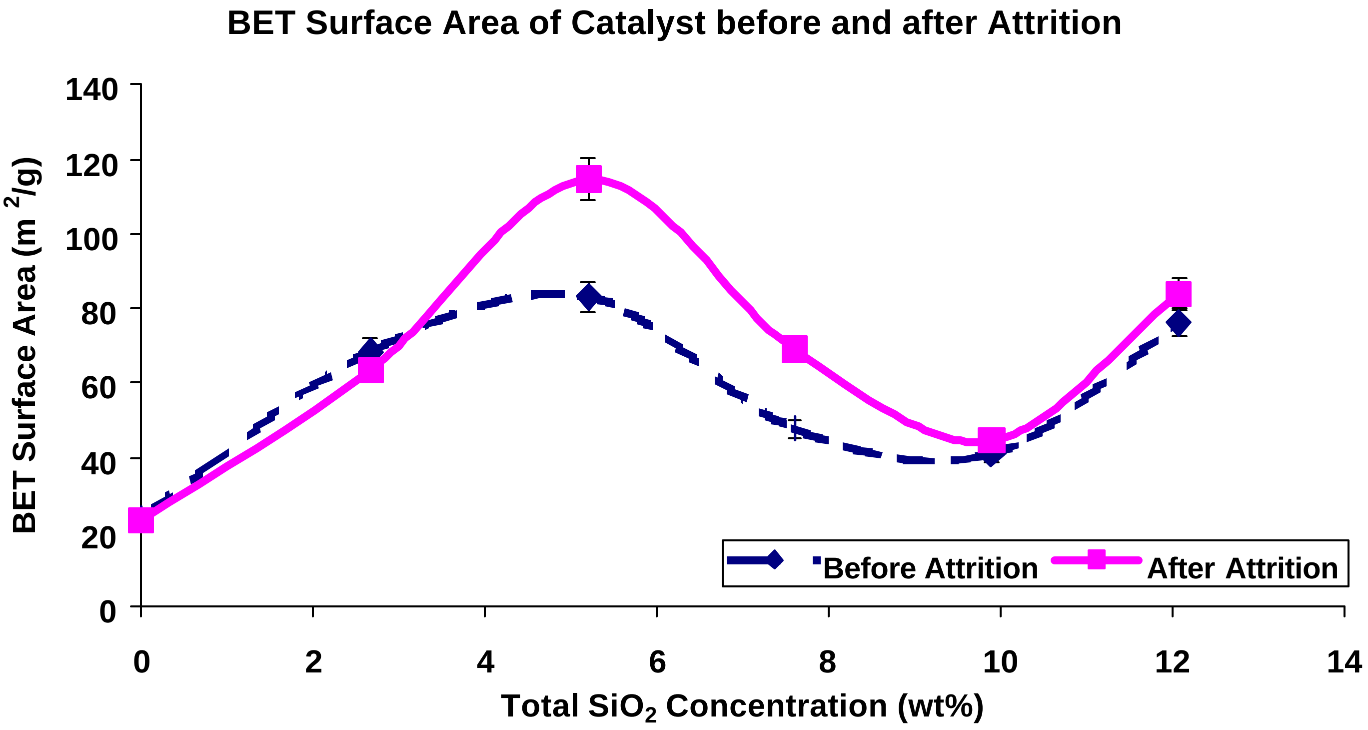

Figure 5. BET surface areas before and after attrition.

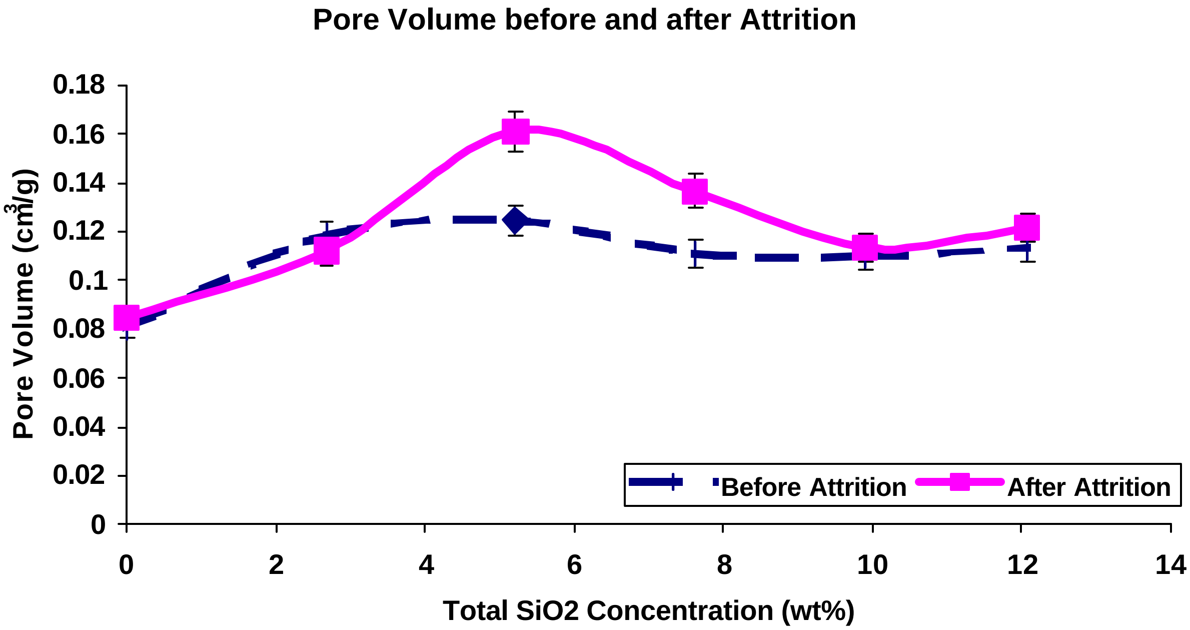

Figure 6. Pore Volume Before and After Attrition.

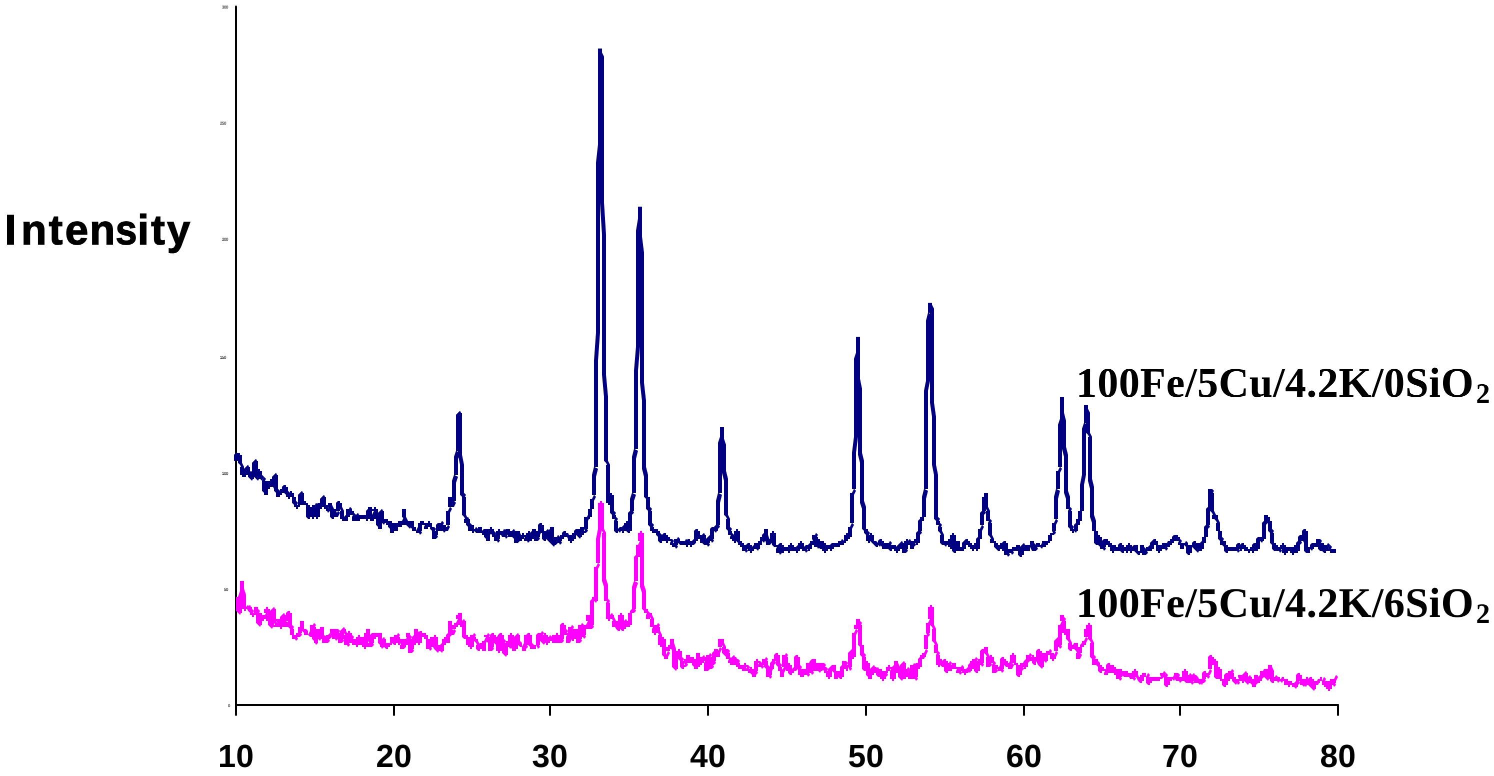

Figure 7. XRD results.

Task 4. Slurry Reactor Testing

New CSTR was purchased. Currently, we are in the process of installing the CSTR reactor.

Future Work

Work will continue developing and testing robust iron-based F-T catalysts that have suitable activity, selectivity and stability in the slurry bubble column reactor.