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

Technical Progress Report

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**ABSTRACT**

In this reporting period, a study of ultra-fine iron catalyst filtration was initiated to study the behavior of ultra-fine particles during the separation of Fischer-Tropsch Synthesis (FTS) liquids filtration. 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.

The change of particle size during the slurry-phase FTS has monitored by withdrawing catalyst sample at different TOS. The measurement of dimension of the HRTEM images of samples showed a tremendous growth of the particles. Carbon rims of thickness 3-6 nm around the particles were observed. This growth in particle size was not due to carbon deposition on the catalyst.

A conceptual design and operating philosophy was developed for an integrated wax filtration system for a 4 liter slurry bubble column reactor to be used in Phase II of this research program. The system will utilize a primary inertial hydroclone followed by a Pall Accusep cross-flow membrane. Provisions for cleaned permeate back-pulsing will be included to as a flux maintenance measure.

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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 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 researched under simulated FTS conditions at flowrates from 4 to 20 lpm. The crossflow filtration modules are zirconia-coated steel membranes having a nominal pore size of 0.1  $\mu\text{m}$ . In year 3 of the program, a prototype filtration system will be retrofitted to an existing SBCR to test the efficacy of the filtration procedures developed using the filtration test platform.

For the current reporting period, the change of catalyst particle size of the iron nano-catalyst during the FTS in a CSTR has been monitored. Catalyst samples were withdrawn at different TOS using a dip-tube and HRTEM images of the particles were taken. It was found that rims of carbon with a thickness 3-6 nm grows around the particles. Measurement of particle dimension revealed growth of particle during the reaction and formation of hexagonal and rectangular structures. It was found that starting with a catalyst with size 5-8 nm, particles with dimension as high as 110 nm can be observed after 475 h of reaction. This tremendous increase in dimension is not due to carbon deposition on the particles. Fundamental study is required to identify morphology and the mechanism of growth of such big particles.

In preparation for the pilot-scale study in Phase II of this program, a conceptual design and operating philosophy was developed for integrated a catalyst slurry filtration system

for a 4 liter slurry bubble column reactor. The system will utilize a primary inertial hydroclone followed by a Pall Accusep cross-flow membrane. Provisions for cleaned permeate back-pulsing of the crossflow module will be included to as a flux maintenance measure. A progressive cavity pump, installed in the filtration loop will circulate the FT slurry through both the hydroclone and cross-flow elements. The hydroclone shall be designed to lower the catalyst concentration to below 1wt% solids while the cross-flow element will further “polish” the wax below 10 ppm as Fe. The flowrate through the cross-flow filter element will be measured by a coriolis flow meter. Quantifying the flow will be important because the slurry velocity is crucial in cross-flow filtration. The wax permeate flow from the filter shall be limited by a control valve actuated by a reactor level controller. Hence, a constant inventory of slurry will be maintained within the SBCR system as long as the superficial gas velocity remains constant. Changes in the gas hold-up due to a variable gas velocity will need to be calculated so that the space velocity can be accurately quantified. 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.

**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. (*subtask completed*)

## **Task 1.4. Ultra-fine Iron Filtration**

# **Fischer-Tropsch Synthesis with Ultrafine Iron Nano-Catalyst in a CSTR – Growth of Catalyst Particle with Reaction Time**

## **Introduction**

Fischer-Tropsch synthesis (FTS) is a major route for producing a wide variety of hydrocarbons and oxygenates from synthesis gas ( $CO + H_2$ ) made from coal or natural gas (Anderson, 1984; Steynberg and Dry, 2004). Iron catalysts are the preferred catalysts for FTS utilizing synthesis gas derived from coal because of their excellent activity in water gas shift reaction (WGSR) which allow using a synthesis gas with a low  $H_2 / CO$  ratio directly without an external shift step (Dry, 1981). The use of iron-based catalysts is also attractive in view of their low cost and as they produce desired range of higher hydrocarbons (wax) at elevated pressure (10-15 atmospheres). All these features make the use of iron-based FTS catalyst extremely desirable.

Because of the non-selective nature of the FTS, a large amount of waxy material is produced when the catalyst and reactor operation favor long chain growth. This wax can be refined to produce premium transportation fuels. The catalyst fines, suspended in the Fischer-Tropsch (F-T) reactor liquid phase withdrawn from the reactor, must be separated and recycled back to the reactor to maintain required conversion and to avoid catalyst loss (Zhou and Srivastava, 1991). Catalyst/wax separation is also necessary from the standpoint of wax upgrading, since the catalyst fines may foul the equipment and/or catalyst in subsequent wax processing.

Slurry-phase FTS using ultra-fine iron catalyst particles in slurry bubble column reactor (SBCR) is advantageous for efficient control and utilization of highly exothermic heat of reaction for FTS and enhanced mass transfer rate of gaseous reactants to the solid catalysts surface (Kölbel and Ralek, 1980). The advantages of slurry bubble column FTS reactors, such as effective heat-transfer, uniform temperature control, insignificant local-overheating of catalyst particles, and lower capital cost, can be realized commercially



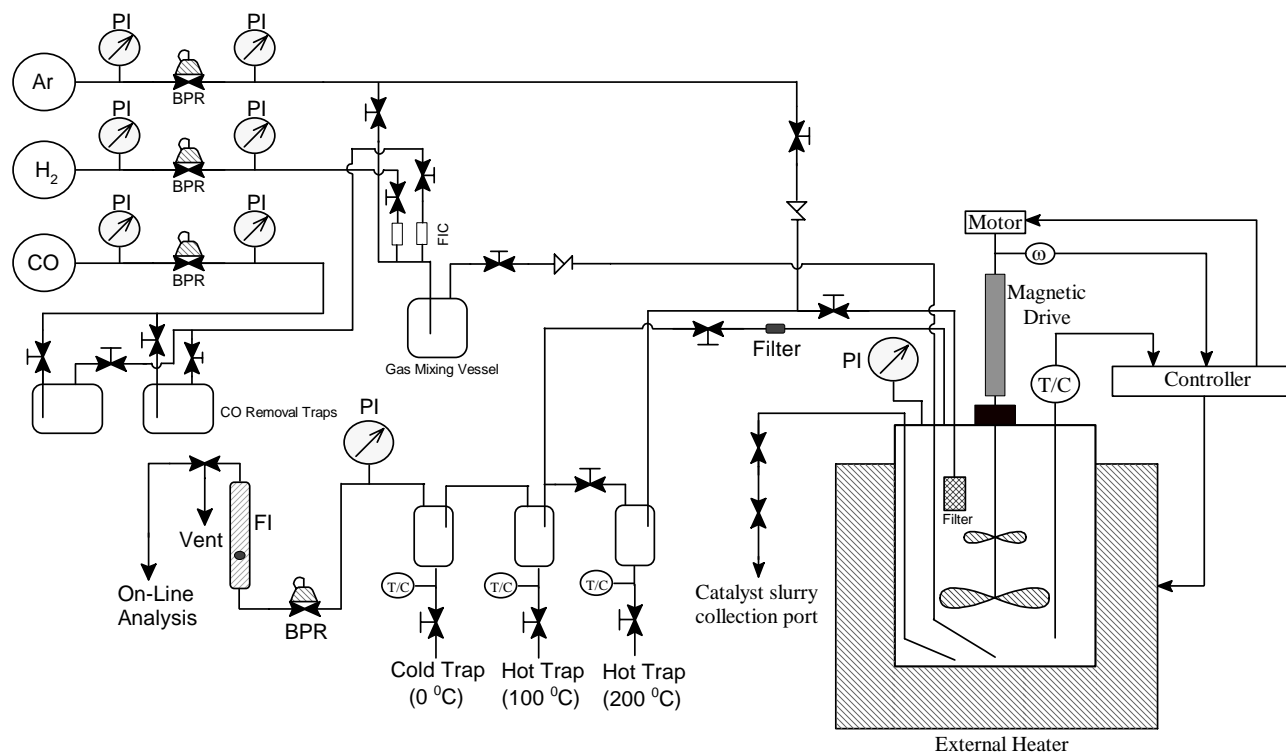
only if a continuous and cost-effective technique for catalyst/wax separation can be developed. A serious problem in the use of iron catalysts in the slurry-phase FTS is their tendency to undergo attrition during the reactions which cause fouling of downstream filters as well as make separation of the catalyst particle from product mixture extremely difficult (Bhatt, 1995). Thus, a continuous and cost-effective catalyst/wax separation technique is an absolute necessity for the commercial-scale operation of slurry bubble column FT reactors.

As a requirement of the downstream wax processing, the solid content of the slurry-phase FT wax should be limited to 2-5 ppm (Zhou and Srivastava, 1991). The difficulties in separation of slurry-phase FT wax/catalyst arise from two major facts: (1) in high viscosity of wax in the range of 4-8 cP (at about 200 °C), and (2) very small particle size of the iron catalyst – generally in the submicron range.

It is known that the iron oxide catalyst undergoes phase-transformation during activation/reaction and the resulting phase transformation play an important role in determining the attrition resistance of this catalyst. During activation (using either CO or synthesis gas), the iron oxide transforms from hematite to magnetite and finally to an iron carbide phase. It was concluded that carbide formation was necessary before iron oxide FT catalyst can exhibit any activity (Shroff et al., 1995; Zhao et al., 2001). It has been reported that in a slurry phase reactor the carbide particles break away leading to catalyst attrition (Pham and Datye, 2003, Zhao et al., 2002) which makes the catalyst/wax separation more difficult. A detailed knowledge of the catalyst particle size is therefore necessary for design of any mechanical liquid/solid separation system.

Various studies on the size reduction of catalyst particles were reported by different researchers (Pham and Datye, 2003, Srinivasan et al., 1996). However, only Kuo et al. (Kuo et al., 1985) have reported so far an increase in apparent particle size during the slurry-phase FTS which is contrary to what generally observed/reported in literature. In one (Kuo et al., 1985), it was suggested as a strong possibility that the catalyst particles might have increased in size either by agglomeration or by the growth of heavy polymers on the outside of the catalyst particles. The TEM pictures of fresh and end-of run catalysts shown revealed that the larger particles do appear to be aggregates, but a mechanism of their formation remained unknown till date.

The purpose of the present study is to monitor the change of catalyst particle size of an ultrafine iron nano-catalyst during the FTS in a CSTR. Catalyst samples from the reactor will be withdrawn at times using a dip-tube and particle size will be evaluated using high-resolution TEM. The information on the change of particle size can be utilized for design and optimization of a filtration unit for wax/catalyst separation.



**Figure 1:** A simplified schematic of the CSTR set-up used for FTS in the present study.

## Experimental

**Materials:** A commercial ultrafine iron oxide catalyst (NANOCAT® Superfine Iron Oxide, Mach I, Inc.) was used for all experiments. The reported average particle size of the catalyst = 3 nm, surface area = 250 m<sup>2</sup>/g, and bulk density = 0.05 g/cm<sup>3</sup>. Polywax 850 (polyethylene fraction with average molecular weight of 850) purchased from Baker Petrolite, Inc. was used as start-up solvent.

**Methods:** The FTS experiments were conducted in a 1 L CSTR equipped with a magnetically driven stirrer with turbine impeller, a gas-inlet line, and a vapor outlet line

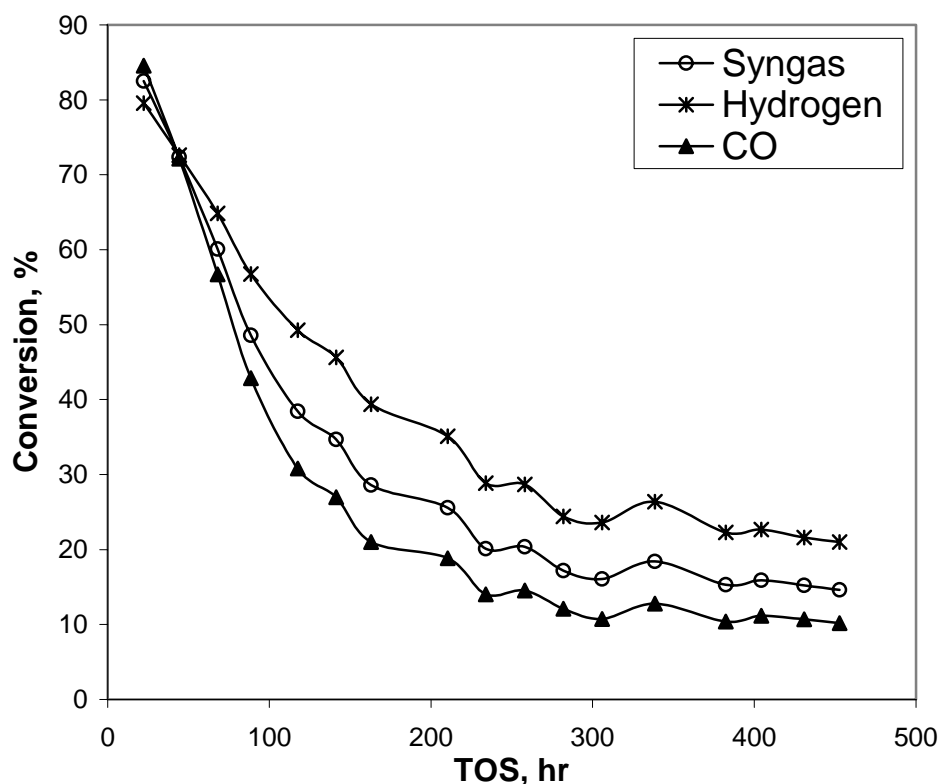
with a SS fritted filter (2 micron) placed external to the reactor. A tube fitted with a SS fritted filter (0.5 micron opening) extends below the liquid level of the reactor for withdrawing reactor wax (rewax) maintains a constant liquid level in the reactor. Another SS dip-tube (1/8" OD) extends to the bottom of the reactor was used to withdraw catalyst/wax slurry from the reactor at times. A simplified schematic of the reactor set-up is presented in Figure 1. Separate mass flow controllers were used to control the flow of hydrogen and carbon monoxide at the desired rate. The gases were premixed in a mixing vessel before entering to the reactor. Carbon monoxide was passed through a vessel containing lead oxide-alumina to remove any traces of iron carbonyl. The mixed gases entered the CSTR below the stirrer operated at 750 rpm. The reactor temperature was maintained ( $\pm 1$  °C) by a temperature controller.

The as-received ultrafine iron oxide catalyst (54.7 g) was added to melted (150 °C) Polywax 850 (300 g) in the CSTR to produce a slurry that contained about 15 wt% iron oxide. The reactor temperature was then raised to 270 °C at a rate of 1 °C/min. The catalyst was activated using CO at a space velocity of 3.0 sl/h/g Fe at 270 °C and 175 psig for 24 h. At the end of activation a sample of activated catalyst (Sample S1) was withdrawn via the dip-tube. The FTS was then started by adding synthesis gas mixture to the reactor at a space velocity of 3.0 sl/h/g Fe and a  $H_2/CO$  ratio of 0.7. The conversions of CO and  $H_2$  were obtained by gas-chromatography analysis of the exit gas. The reaction products were collected in three traps maintained at different temperatures – a hot trap (200 °C), a warm trap (100 °C) and a cold trap (0 °C). The products were separated into different fractions (rewax, wax, oil and aqueous) for quantification. However, the oil and the wax fraction were mixed prior to GC analysis.

**Table 1:** The schedule of withdrawal of catalyst samples via the dip-tube from the CSTR during Fischer-Tropsch synthesis. The counting of TOS started from the start of CO activation of the fresh catalyst.

<b>TOS, hr (counted from the start of CO activation)</b>	<b>Sample Number</b>
0	S-0
24	S-1
112.6	S-2
258.3	S-3
406.8	S-4
505.6	S-5
620.8	S-6

Catalyst/rewax slurry was withdrawn at different reaction times via the dip-tube. The withdrawal schedule is presented in Table 1. The withdrawn samples were diluted with hot (about 65 °C) o-xylene to remove the high molecular weight FT-wax fractions. However, it was found that it is not possible to completely remove the FT-wax from the catalyst particles by this method. Solution of relatively clean catalyst particles in o-xylene were prepared for use in high resolution transmission electron microscopy (HRTEM). An optimum ratio of o-xylene to catalyst slurry was used so that the catalyst particles formed a slightly turbid suspension. HRTEM pictures were obtained using a JEOL 2010F microscope operating at 200 kV. A drop of the suspension was placed with a syringe onto a lacey carbon film on 200 mesh copper grid. After the o-xylene evaporated, the grid was loaded into the microscope for analysis.



**Figure 2:** Variation of conversion of synthesis gas, hydrogen and carbon monoxide during the FTS using ultrafine iron nano-catalyst in a CSTR (270°C, 175 psig, space velocity 3.0 sl/h/g and H<sub>2</sub>/CO ratio of 0.7).

## Results and Discussions

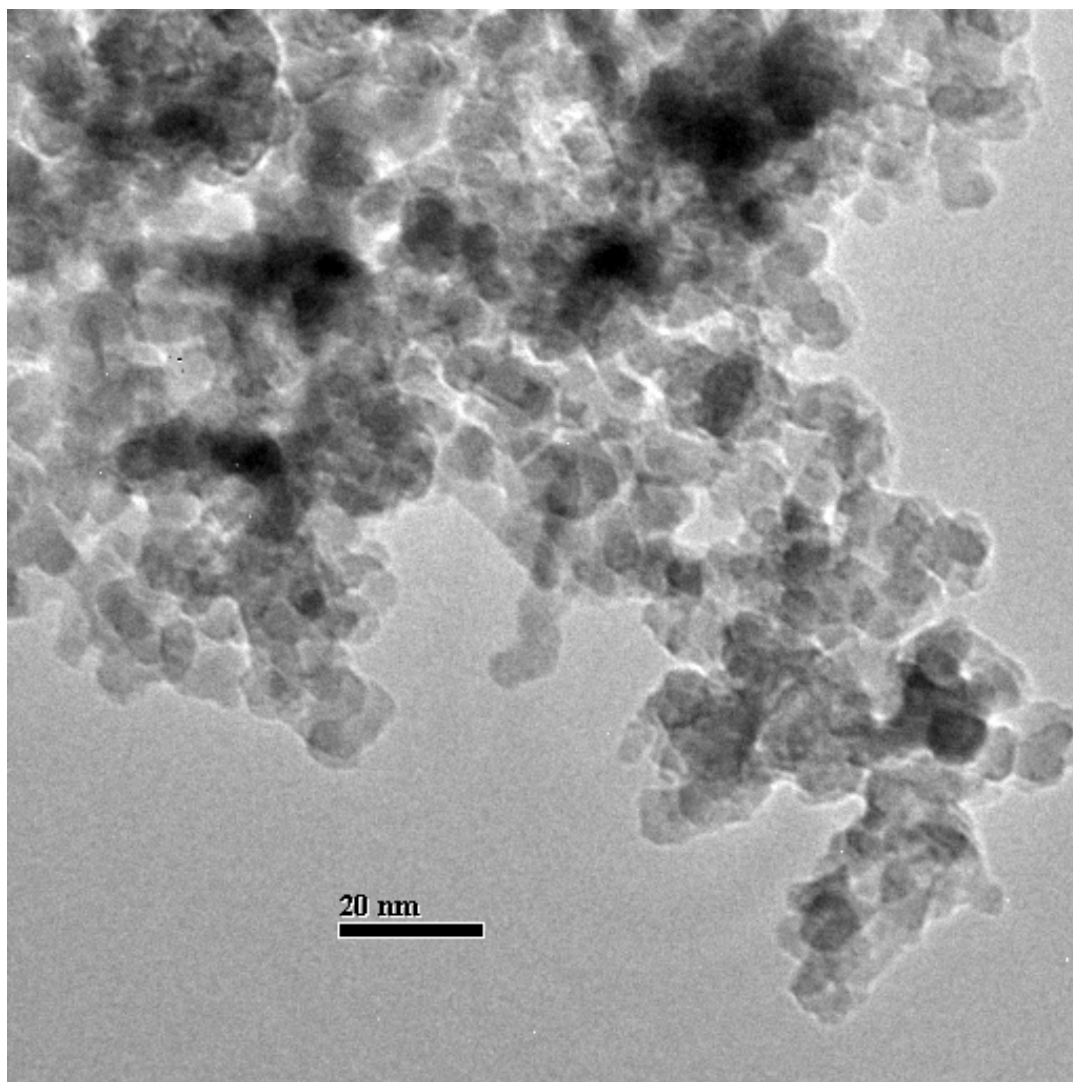
The catalytic activity of the ultrafine catalyst showed a slow and gradual decrease during a total time-on-stream (TOS) of over 475 h. The TOS in this case has been counted from the starting of FTS using synthesis gas. The variation of conversion of synthesis gas, hydrogen and CO, calculated from gas analysis, against TOS is shown in Figure 2. It should be noted that the withdrawal of the catalyst particles during the experiment also caused the conversion to decrease.

For TEM analyses, to represent the “true representative size” of the irregular shaped catalyst particles, some approximations are required. In general the ‘particle diameter’ can be specified for any equi-dimensional particles. Particles that are not equidimensional, i.e. that are longer in one direction than in others, are often

characterized by the second longest major dimension. Hence an arithmetic average of the first two large dimension of an irregular-shaped particle has been taken as the “representative particle diameter” for the present study.

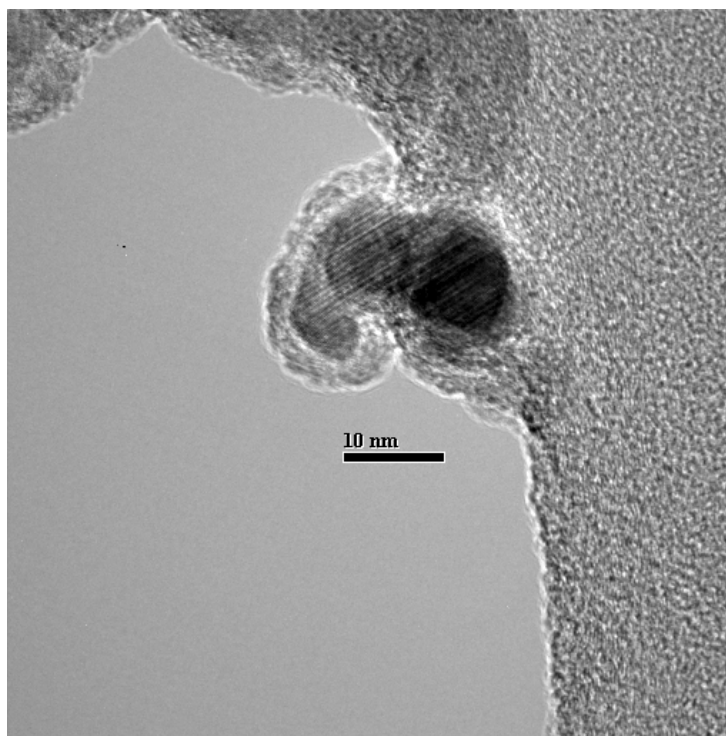
The distribution of size of particle in a sample can be suitably expressed by a combination of one or more statistical distribution functions. The main statistical analysis of the size distribution consists of a measure of central tendency (including median, mode, and mean), a measure of the degree of scatter or sorting, kurtosis (the degree of peakedness) and skewness (the lop-sidedness of the curve).

In the case of ultrafine, sub-micron scale particles, the size distribution is generally viewed by the HRTEM images. It was found that the derivation of the statistical size distribution function for the samples needs to be done by the manual measurement of the dimensions of the HRTEM images. Hence, instead of getting the true distribution function, there is a high chance of getting a “biased” distribution function. Since the main objective of this study is to monitor the growth (if any) of the iron nano-catalyst particles during FTS; the identification of any larger particle and evaluation of its representative diameter will be sufficient. Thus, we report the “Largest Observed Particle Size, nm” which is the arithmetic average of the first two large dimensions of the particle. This representative dimension has been manually measured for the particles clearly visible in the HRTEM image of each sample. The arithmetic average of this representative diameter (denoted as the “average diameter”) of the measured particles has been also been reported here. This “average diameter” is not the “true representative average diameter” of the particles, but it reflects the central tendency of the actual size distribution.

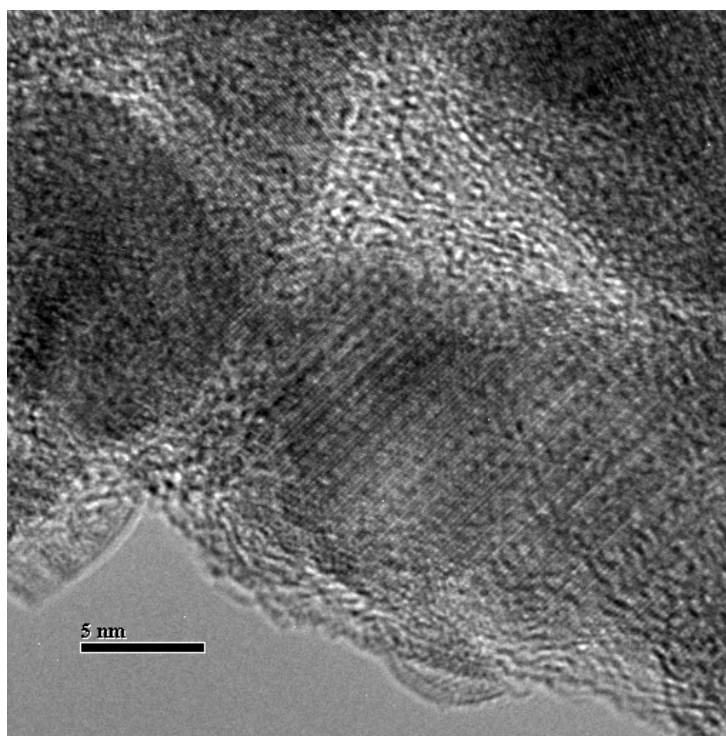


**Figure 3:** HRTEM image of fresh ultrafine iron nano-catalyst (Sample: S-1; TOS = 0 h).

The HRTEM image of the fresh ultrafine catalyst is shown in Figure 3 which reveals a particle size in the range of (4-8) nm. The HRTEM image of CO activated catalyst with TOS = 24 h (i.e., sample S-1) is presented in Figure 4. The TOS for the HRTEM samples were counted from the time of start of CO activation and this TOS is different than the TOS presented in Figure 2. The observed particle size in this sample varied between 8-15 nm. The average diameter of the particles in this sample was 12.5 nm and a 2-3 nm rim of carbon around the iron particle was visible.



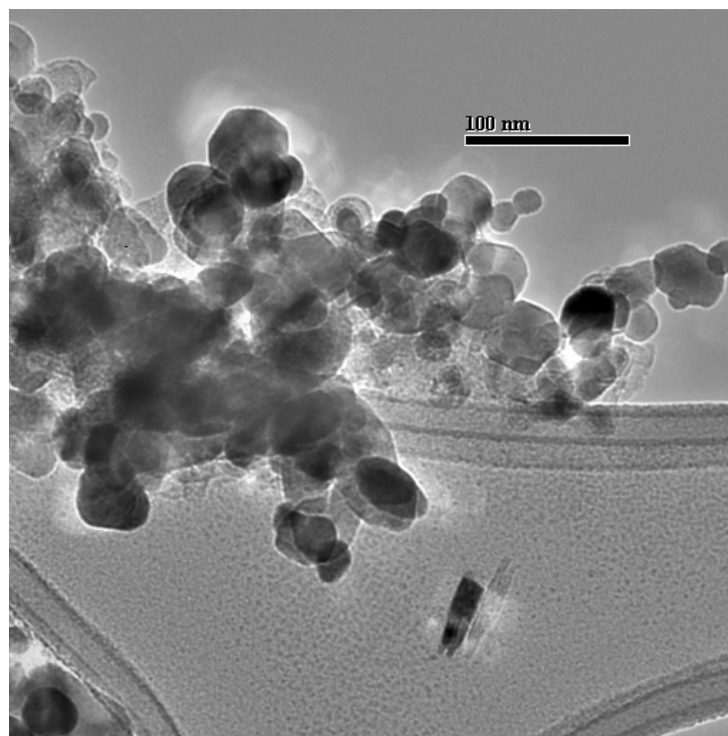
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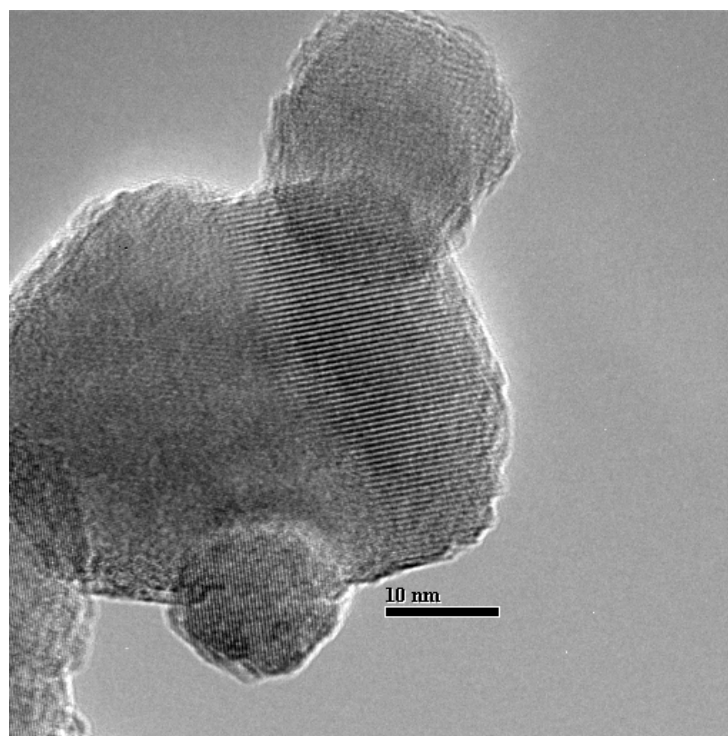
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**Figure 4:** HRTEM image of CO activated ultrafine iron nano-catalyst (TOS = 24 h).



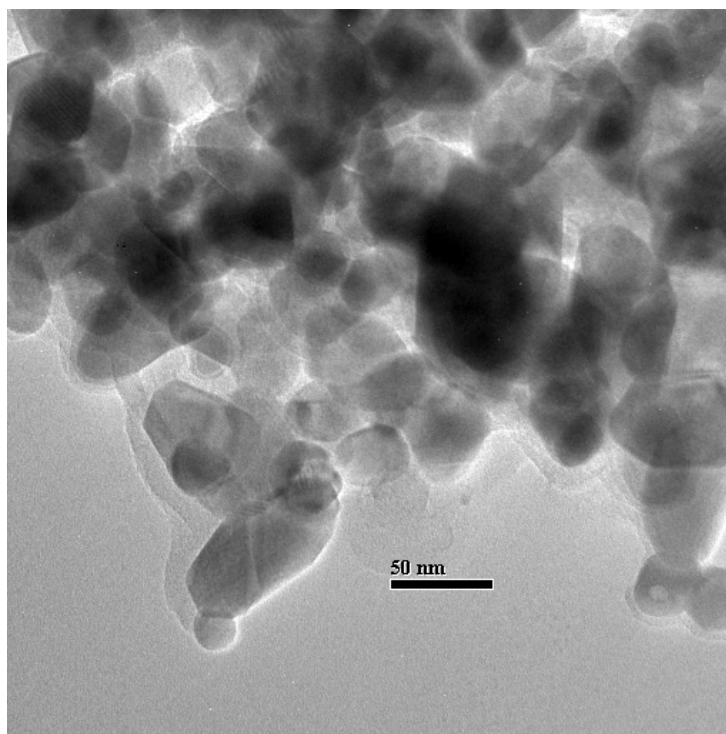


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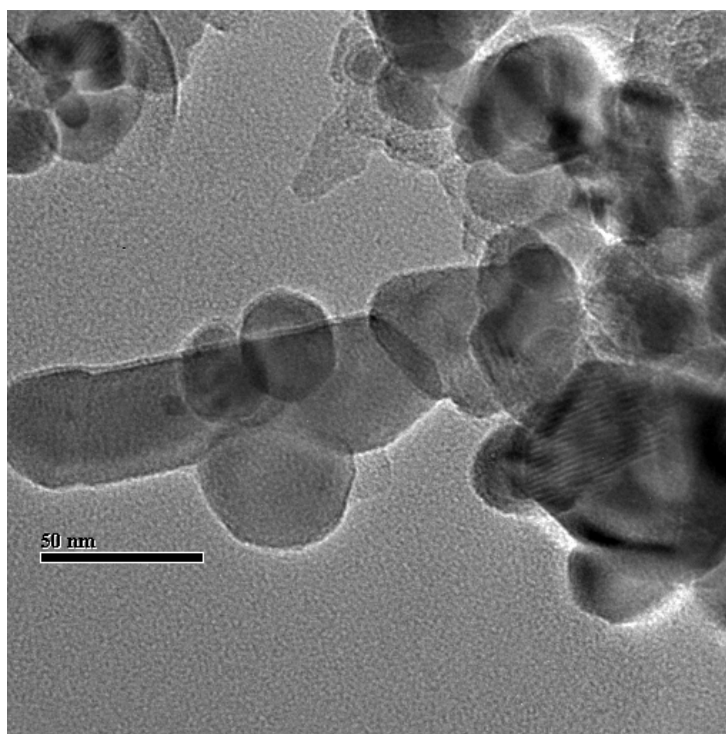


(b)

**Figure 5:** HRTEM image of ultrafine iron nano-catalyst sample at TOS = 112.6 h.

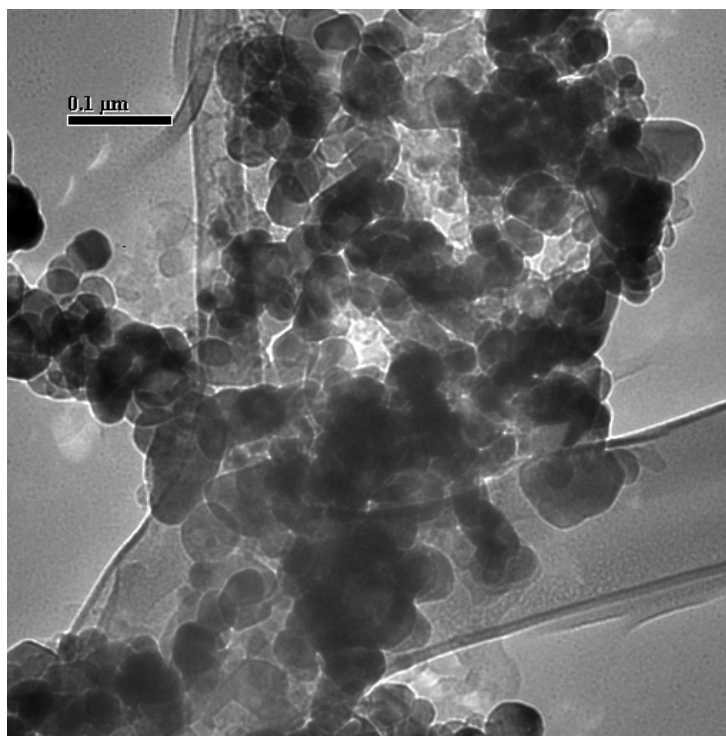


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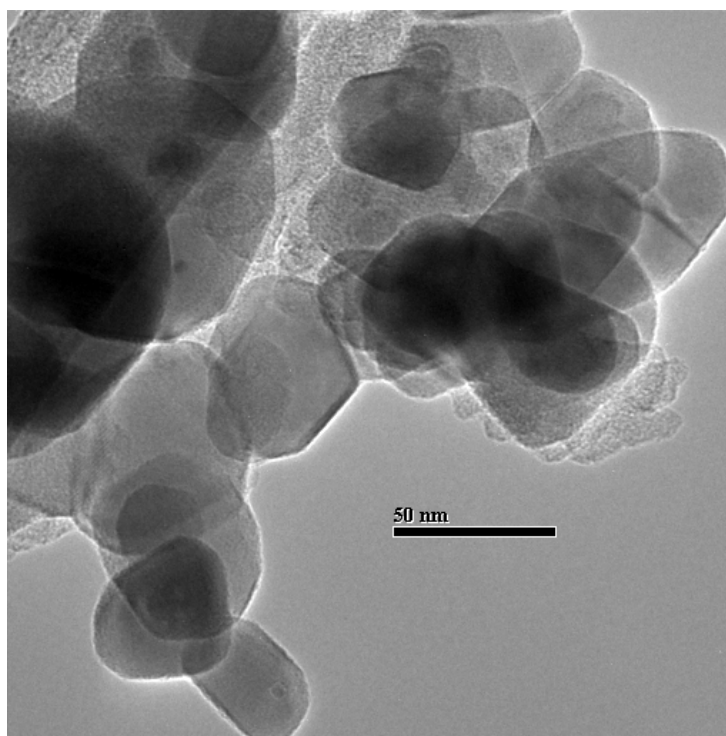


(b)

**Figure 6:** HRTEM image of ultrafine iron nano-catalyst sample at TOS = 258.3 h.

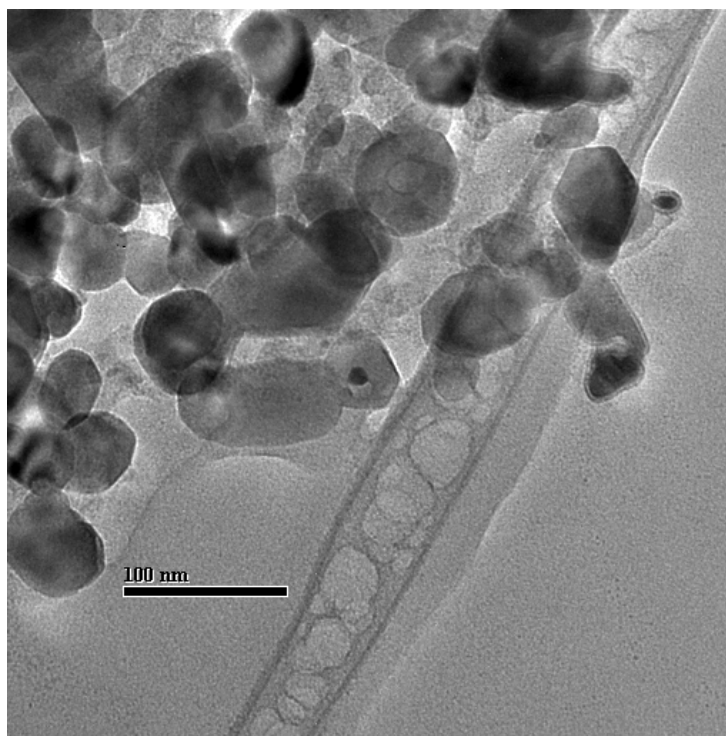


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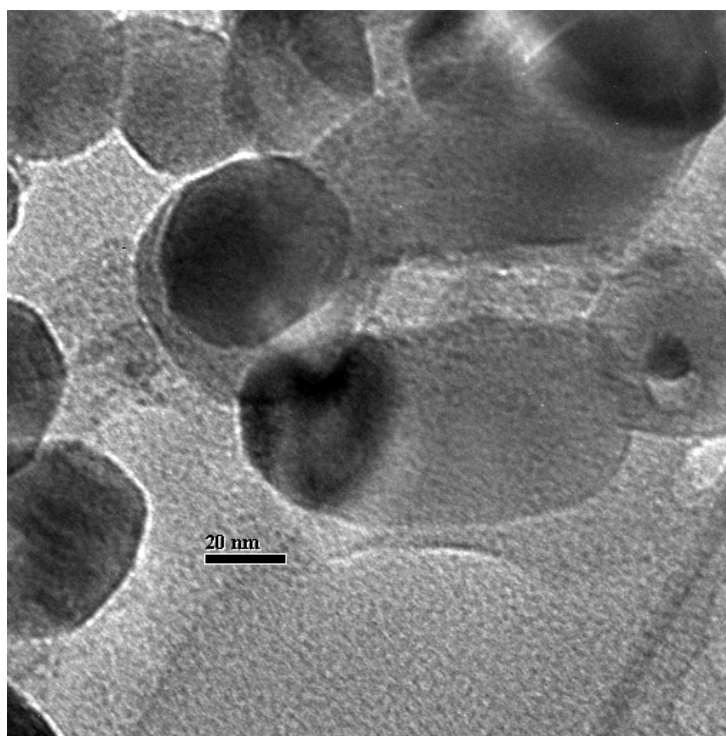


(b)

**Figure 7:** HRTEM image of ultrafine iron nano-catalyst sample at TOS = 406.8 h.

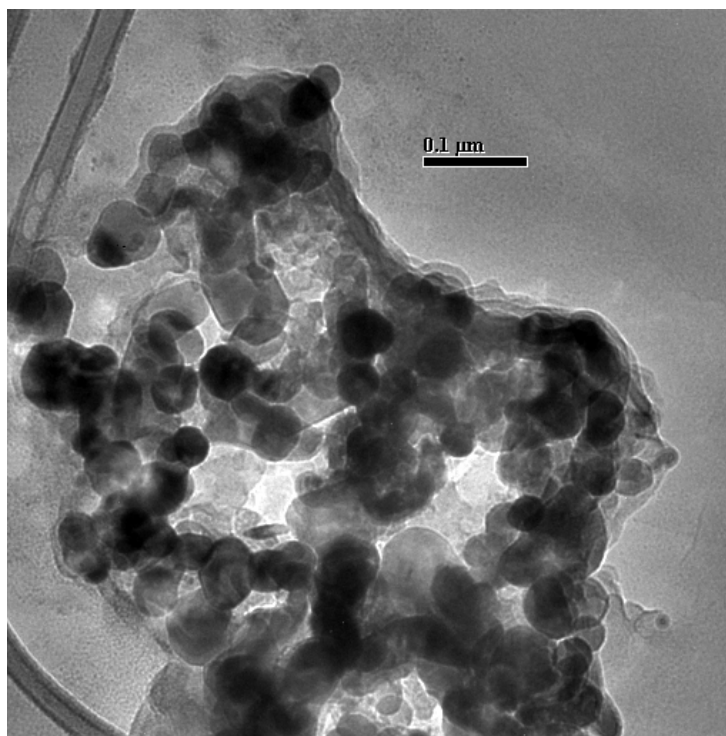


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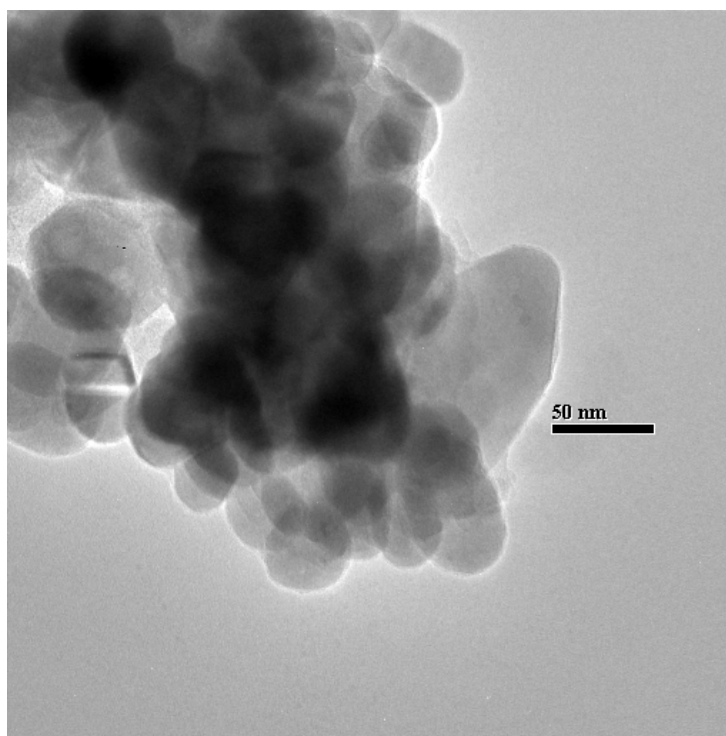


(a)

**Figure 8:** HRTEM image of ultrafine iron nano-catalyst sample at TOS = 505.6 h.

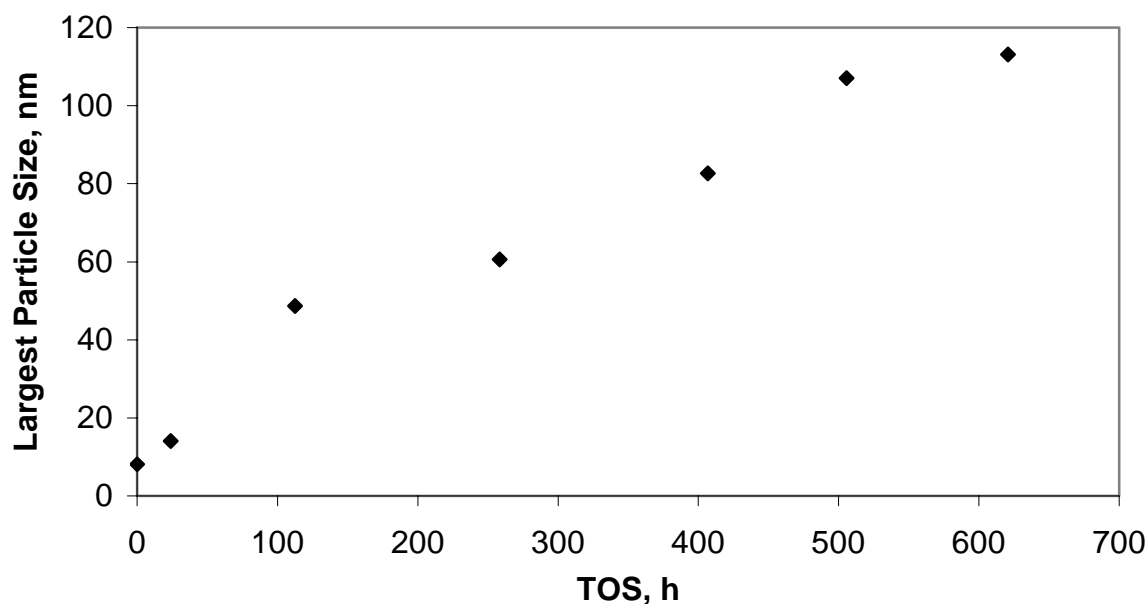


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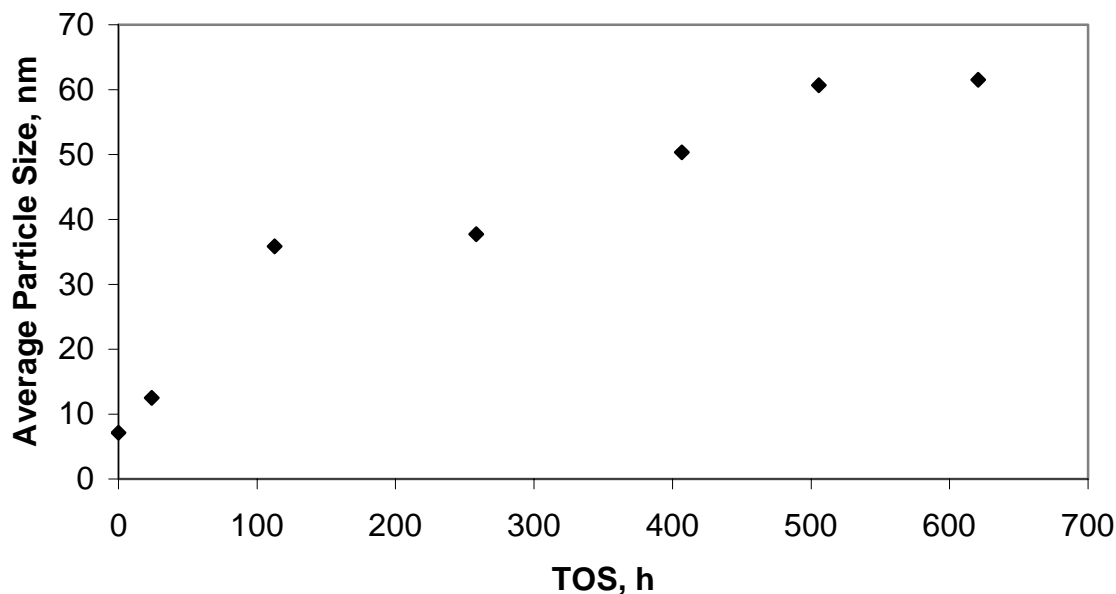
**Figure 9:** HRTEM image of ultrafine iron nano-catalyst sample at TOS = 620.8 h.



**Figure 10:** Plot of variation of largest observed size of catalyst particle in the HRTEM image against TOS during the FTS in a CSTR.

The HRTEM image of the catalyst sample at TOS = 112.6 h (i.e., sample S-2) is presented in Figure 5. The observed particle size in this sample was varied between 18-50 nm. The average diameter of the particles in this sample was 35.7 nm and a 3-5 nm thick carbon rim around the iron particles were found. Small crystallites with very prominent  $d$ -spacing can also be easily seen.

Figure 6 displays the HRTEM image of the catalyst sample at TOS = 258.3 h (i.e., sample S-3). The observed variation in the particle size range in this sample was 20-60 nm. The average diameter of the particles in this sample was 37.8 nm and carbon rims of thickness 4-6 nm around the iron particles were found. Large growth of some of the particles can be noticed. Some particles also formed hexagonal shaped structure.



**Figure 11:** Plot of variation of arithmetic average size of catalyst particle in the HRTEM image against TOS during the FTS in a CSTR.

Figure 7 represents the HRTEM image of the catalyst sample at TOS = 406.8 h (i.e., sample S-4). The particle size in this sample varied in between 28-83 nm. The average diameter of the particles in this sample was 50.3 nm and carbon rims of thickness 4-6 nm around the iron particles were found. Formation of hexagonal/rectangular shaped particle structure can be identified.

Figures 8 and 9 represent the HRTEM image of the catalyst sample at TOS = 505.6 h (i.e., sample S-5) and at TOS = 620.8 h (i.e., sample S-6), respectively. Getting a clear high-magnification HRTEM image was difficult for these samples because of the presence of leftover high molecular weight hydrocarbons that were not removed during the extraction. The particle size of S-5 sample varied between 28-107 nm and for the S-6 sample the size range was 28-113 nm. The average diameter of the particles in S-5 and S-6 was 60.7 nm and 61.5 nm, respectively. Carbon rims of thickness 4-6 nm around the iron particles were also found.

The formation of larger particles observed in the samples at different TOS definitely originated during FTS as these sized particles were not present initially. The variation of

'largest observed particle size' against TOS is shown in Figure 10 while the variation of 'average particle diameter' with TOS is shown in Figure 11. In both cases, the growth of catalyst particles during the Fischer-Tropsch reaction is clear. It was observed that the carbon rim around the particle grows initially. However, the thickness of the carbon rim does not grow above 5-6 nm. Hence, it can be inferred that the growth of the catalyst particles, as observed in this study, does not originate from the deposition of carbon on the catalyst particles. It is definitely the catalyst particle which grows during the synthesis. However the chemical and morphological nature of this growth is not clear at this moment and further study is required to get more insight into these phenomena.

## Conclusions

The catalytic activity of the ultrafine catalyst exhibited a slow decline during the FTS in a CSTR over 475 h on-stream. The HRTEM images of the catalyst particles withdrawn during the reaction revealed that a rim of carbon is present around the catalyst particles. The maximum thickness of this rim reached about 6 nm. The iron carbide particles grow during the reaction. Starting with an ultrafine catalyst with size 5-8 nm, the formation of hexagonal and rectangular particles with dimension as high as 110 nm was observed after 475 h of reaction. This increase in particle size is not due to carbon deposition on the particles. Fundamental study is required to identify morphology and the mechanism of growth of such big particles.

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

*Subtask Completed.*

**Task 1.6. Chemical and physical characterization of slurry and filtrate****INTRODUCTION**

In temperature programmed oxidation (TPO), a diluted flow of O<sub>2</sub> in inert carrier is passed over the catalyst, and the catalyst is heated to high temperatures. The outlet gas is then routed to a thermal conductivity detector (TCD). Typically, helium is used as both carrier and reference due to the greater difference in thermal conductivity than argon. Consumption of O<sub>2</sub> in the production of CO<sub>2</sub> yields peaks resulting in a TPO profile. Comparison of the reference profile against the profiles of reference compounds, such as iron carbides, can give a wealth of information on the different chemical species present on the catalyst [1-5], either after activation, or after exposure of the activated catalyst to reactant gases for a duration of time, based on the temperature at which the species combusts.

**EXPERIMENTAL**

In this term, the Zeton Altamira system was converted to run TPO, and preliminary testing was carried out on our Fe<sub>3</sub>C reference material. A mixture of 10% O<sub>2</sub>/He was used at a flow rate of 30 ccm. The TCD current was fixed at 50 mA, while the gain was set at 5, and the scan rate was 10.0 sec/pt. The temperature was ramped at 10°C/min from 40°C to 1100°C.

## RESULTS AND DISCUSSION

Results for the iron carbide reference material are presented in Figures 1 and 2. All uptake of O<sub>2</sub> in oxidizing carbonaceous species and evolution of carbon dioxide took place below 450°C. Zooming in on the range between 40 and 450°C, one can ascertain two negative peaks, merged together, with a tail on the low temperature section, situated at 235 and 245°C, respectively. These are likely assigned to uptake of O<sub>2</sub>, most likely due to the two forms of carbide present in the sample, including the lower iron content “Hagg” carbide. At higher temperature, there are two positive peaks, tentatively assigned to carbon dioxide liberation, at 345 and 390°C, respectively.

## CONCLUSIONS

Used iron-based catalyst samples have been withdrawn from the CSTR reactor at different times onstream for study, to attempt to assess how the carbonaceous species evolve on the catalyst surface during Fischer-Tropsch synthesis. Wax was extracted from the pores of the catalyst using xylene. TPO studies will be carried out on these samples during the following six month period, for analysis. The iron carbide material characterized in this study will serve as a reference for those tests.

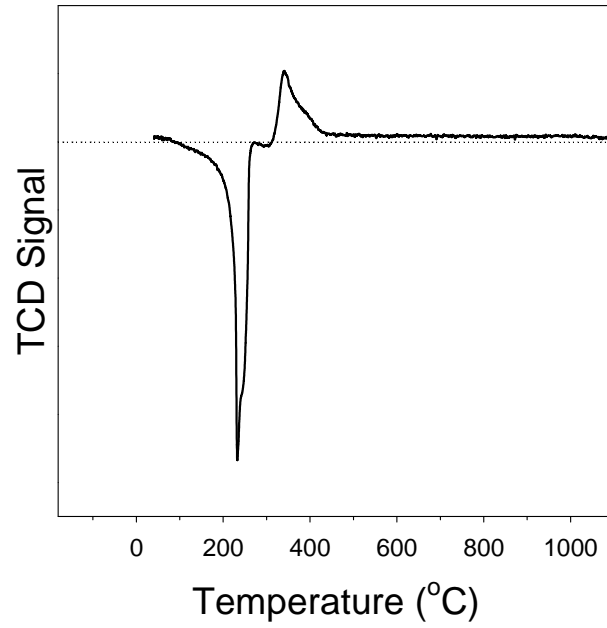


Figure 1: Temperature programmed oxidation profile of an iron carbide reference material.

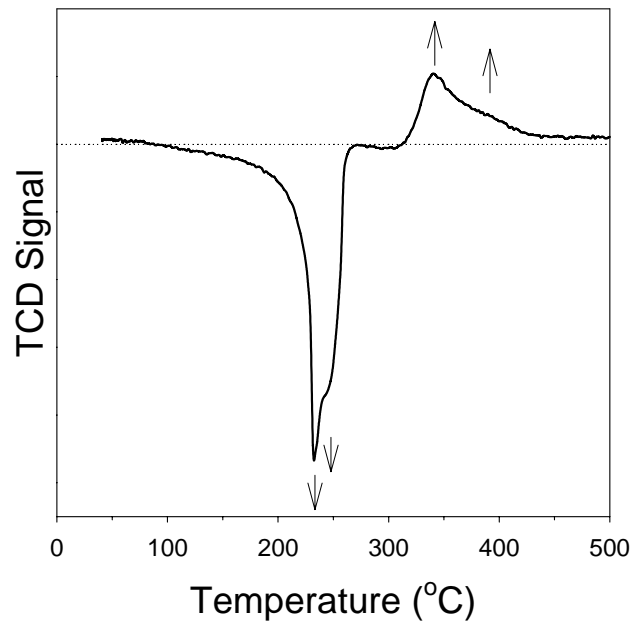


Figure 2: Zoom in on the temperature programmed oxidation profile of an iron carbide reference material.

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## **Task 2. Phase II Bubble Column Pilot Plant Studies**

### **INTRODUCTION**

In the second phase of the current program, a pilot-scale SBCR system is to be integrated with a filtration scheme with procedures and equipment developed in Phase I. In Phase-I, filtration properties of various iron-based catalyst slurries were correlated with the chemical and physical changes occurring during activation and FTS synthesis. Our research has focused on understanding of the phase changes during activation/reduction and their associated effects on filtration properties. Additionally, cleaning/flux maintenance procedures were optimized for the various filter media types test in the research program.

In Phase II, our objective is to address the technical barriers associated with integrating an improved filtration strategy into commercial FTS unit. A series of pilot plant runs will obtain the data needed for the F-T filter system scale-up. Laboratory evaluations will also be used to support the pilot tests help to optimize both the F-T catalyst and the overall process.

#### *Existing Filtration Technologies for FTS Catalyst*

Heavy wax products must be continuously separated from catalyst slurry before being removed from the reactor system. This insures that a steady-state operation and nominal reactor liquid levels are maintained. Achieving an efficient wax product separation from the catalyst is one of the most challenging technical problems associated with slurry-phase F-T.

Wax products obtained from internal filters (primary separation) still contain more than .01-1 wt% of iron (Zhou, 1991). Further processing or “polishing” is required to achieve an acceptable wax quality. The processing equipment located downstream determines the specifications for wax purity. For hydrocracking, the concentration of iron in the wax feed should be less than 2 ppm. Lowering iron content of the wax will reduce fouling of downstream hydrocracking catalyst, thus reducing product-upgrading costs. Achieving a high level of wax purity also minimizes the FTS catalyst make-up requirements. Accordingly, employing an efficient wax/separation process will improve the economic viability of FTS for both coal and natural gas-based systems.

A number of processes have been proposed in the literature to separate heavy wax liquids from catalyst slurries (Zhou, 1991). Most of these techniques can be classified as “primary” and “secondary” filtration. The former is to remove up to 90-99.5% of the catalyst while the latter is a polishing method that provides wax clarity sufficient for upgrading (less than 2 ppm as Fe). These methods can be further categorized as either internal (filter elements located inside the reactor vessel) or external.

Internal methods, usually primary in nature, have the disadvantage of being inaccessible during normal operation of the reactor. Therefore, in anticipation of plugging problems, duplicate filtration systems must be installed to achieve high reliability in commercial settings. External filtration systems have the advantage of being more accessible for maintenance purposes; however, they usually require external pumps that could accelerate catalyst attrition. External piping circuits also tend to add to the complexity of the filter system design.

### *Internal Filtration Methods*

Sasol (Jager, 1997) patented an internal filtration system for F-T SBCRs. Their filtration process consists of a plurality of wire mesh filter units connected in parallel within the BCR vessel. Critical parameters such as filtration and back-flushing rates per unit area of filter are specified in the patent. This system has the advantage of minimizing the hold-up of catalyst slurry outside the reactor vessel. However, internal systems are difficult if or sometimes impractical to service without taking the reactor vessel off-line.

Lorentzen (Lorentzen, 1996) developed and patented a process in which liquid products are separated from a slurry phase containing catalyst particles using a series of vertical reaction tubes in parallel. A separate filter member ring is provided near the top of each tube. The filtrate from each ring overflowed into a weir and centrally collected for further processing. Several configurations of the filtration zone are described in detail.

### *External Filtration Methods*

A simple method commonly used for F-T catalyst/wax separation is sedimentation by gravity and/or centrifugal force. The practicality of sedimentation is quite limited due to the low terminal velocity of submicron particles that are abundant in the catalyst fines. Large settling chambers with residence times exceeding 3 hours are needed to achieve a reactor wax of less than 0.1 wt%. Many of the new separation techniques described in the literature employ simple hydroclones or dynamic settlers as



“primary” separation device before undergoing secondary “polishing” of the wax product.

ConocoPhillips (Espinoza et al., 2004) patented a simple settling device reported to produce a “sub-particle rich” stream and a catalyst-lean stream that removed from the SBCR system. The settling device relies on laminar “Stokes Law” gravitational settling where large particles, partially impeded by a baffle, exit near the bottom of the device. The catalyst-lean stream exits near the top of the settling chamber after flowing under the baffle. Here, catalyst-lean is defined as “A stream of slurry from which the majority of the catalyst particles have been removed”.

Rentech (Benham, 2000 and Bohn, 2004) patented a dynamic settler that in one embodiment utilizes the momentum of catalyst particles exiting an enclosed nozzle to force solids to exit near the bottom of settling chamber enclosure. Clarity of the wax exiting the top of the settler depends on the superficial velocity of the wax in the annular region above the nozzle. Thus, a larger settler diameter results in a clearer wax. Typically, the wax concentration of the clarified wax is less than 0.5 wt% with an entering slurry concentration of 10-20wt%. The dynamic settler was further refined by the addition of several parallel channels (or a “honeycomb” type structure) that minimizes turbulence in the clarified wax region. Thus the mixing of the clarified wax with the slurry exiting the nozzle jet is limited. They report in their patent that with particle sizes greater than 6  $\mu\text{m}$ , a clarified wax purity of less than 0.5wt% can be achieved.

Mobil patented a process for removing catalyst fines from wax slurry using a magnetic separator (Brennan, et al., 1986). Catalyst fines are held by a magnetized filter

element while the wax passes unabated. Two external pumps are used in the system; one pump extracts a portion of the reactor slurry while another pump returns the captured catalyst particles to the BCR. The operational cost of their system is relatively low; however, the capital costs of the magnet assemblies are reported to be expensive.

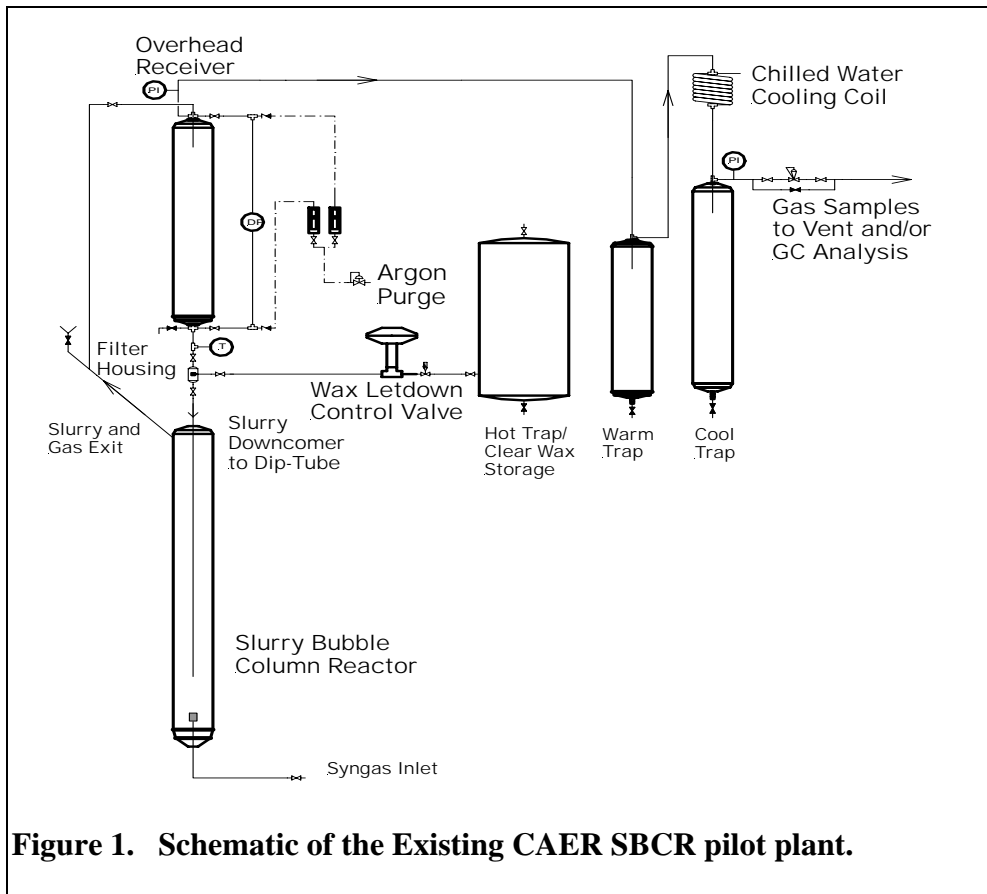
Shell Oil (Engel, et al., 1999), outlined a cross-flow filtration process in a U.S. Patent. Their system extracts gas and catalyst slurry from a BCR column via an external pump. The slurry is degassed by a hydroclone and is directed to a cross-flow inertial filter. A slurry velocity of 1 to 6 m/s must be maintained for efficient filter operation. The system has the disadvantage of requiring an external pump that could accelerate catalyst attrition.

## **EXPERIMENTAL**

### *Current SBCR Apparatus*

In the current configuration, the CAER bubble column has a 5.08 cm diameter and a 2 m height with an effective reactor volume of 3.7 liters (Figure 1). The synthesis gas passes continuously through the reactor and is distributed by a sparger near the bottom of the reactor vessel. The product gas and slurry exit the top of the reactor and pass through an overhead receiver vessel where the slurry was disengaged from the gas-phase. Vapor products and unreacted syngas exit the overhead vessel, enter a warm trap (333 K) followed by a cold trap (273 K). A dry flow meter down stream of the cold trap measures the exit gas flow rate.

A dip tube, inserted into the reactor vessel, recycles the F-T catalyst slurry via a natural convection loop. The unreacted syngas, F-T products, and slurry exit into a side port near the top of the reactor vessel and enter a riser tube. The driving force for the



recirculation flow is essentially the difference in density between the fluid column in the riser (slurry and gas) and that of the dip-tube (slurry only). The dip tube provides a downward flow path for the slurry without interfering with the upward flow of the turbulent syngas slurry mixture. Thus, to some degree, back mixing of the slurry phase and wall effects in the narrow reactor tube are minimized.

An automatic level controller is located in the overhead slurry/gas separation tank. This insures a constant inventory of catalyst particles is being maintained in the reactor vessel as long as the superficial gas velocity within the column is constant.

A sintered metal cross-flow filter tube is located in the liquid down comer between the overhead separation vessel and the reactor. Currently, the filter is a flow-

through device having a sintered metal tube in a shell. Filtered wax is extracted radially through the tube while slurry flows downward in the axial direction. The shear force of the axial slurry flow prevented excessive caking of the catalyst around the filter media. Filtered wax is metered into a storage tank through a letdown valve operated by the overhead liquid level controller. Pressure drop across the filter media (or trans-membrane pressure) is varied manually by varying the wax storage tank pressure. The filter assembly is configured such that the filter media could be replaced on-line, without aborting or interrupting the reactor run.

The level or volume of the slurry within the receiver is continuously monitored by measuring the differential pressure across the height of the vessel. Argon is purged through each of the pressure legs to keep the lines free of slurry. Slurry volume within the receiver is controlled to be no more than 1.3 liters by removing wax from the reactor system via the level control valve. The unfiltered slurry flows back to the reactor via a natural convection loop through a dip-tube exiting near the bottom of a reactor.

## **DISCUSSION**

### *Preliminary Findings in Phase I*

In the early stages of this research program, our objective was to develop a single-stage filtration scheme that would produce a wax with clarity of less than 5 ppm. Based on our operating experience and analytical information gathered with the pilot filtration rig in Phase I, this objective was, in hindsight, overly optimistic. A two-stage system is required because of the combined stresses of catalyst loading and the formation of nano-scale carbide particles formed during activation and synthesis.

For commercial FTS reactor systems, it is economically advantageous to operate with highest feasible catalyst slurry concentration. Typically for commercial iron-based units, the catalyst slurry concentration can range from 15-20 wt%. Our results have shown that the fouling rate of the filter media is directly proportional to catalyst slurry concentration. As expected, the permeation flux is inversely proportional to catalyst slurry concentration. Additionally, flux maintenance for cross-flow filtration such as back pulsing was found to be more effective for lower catalyst loadings (from 0.5 to 1.0 wt% as Fe).

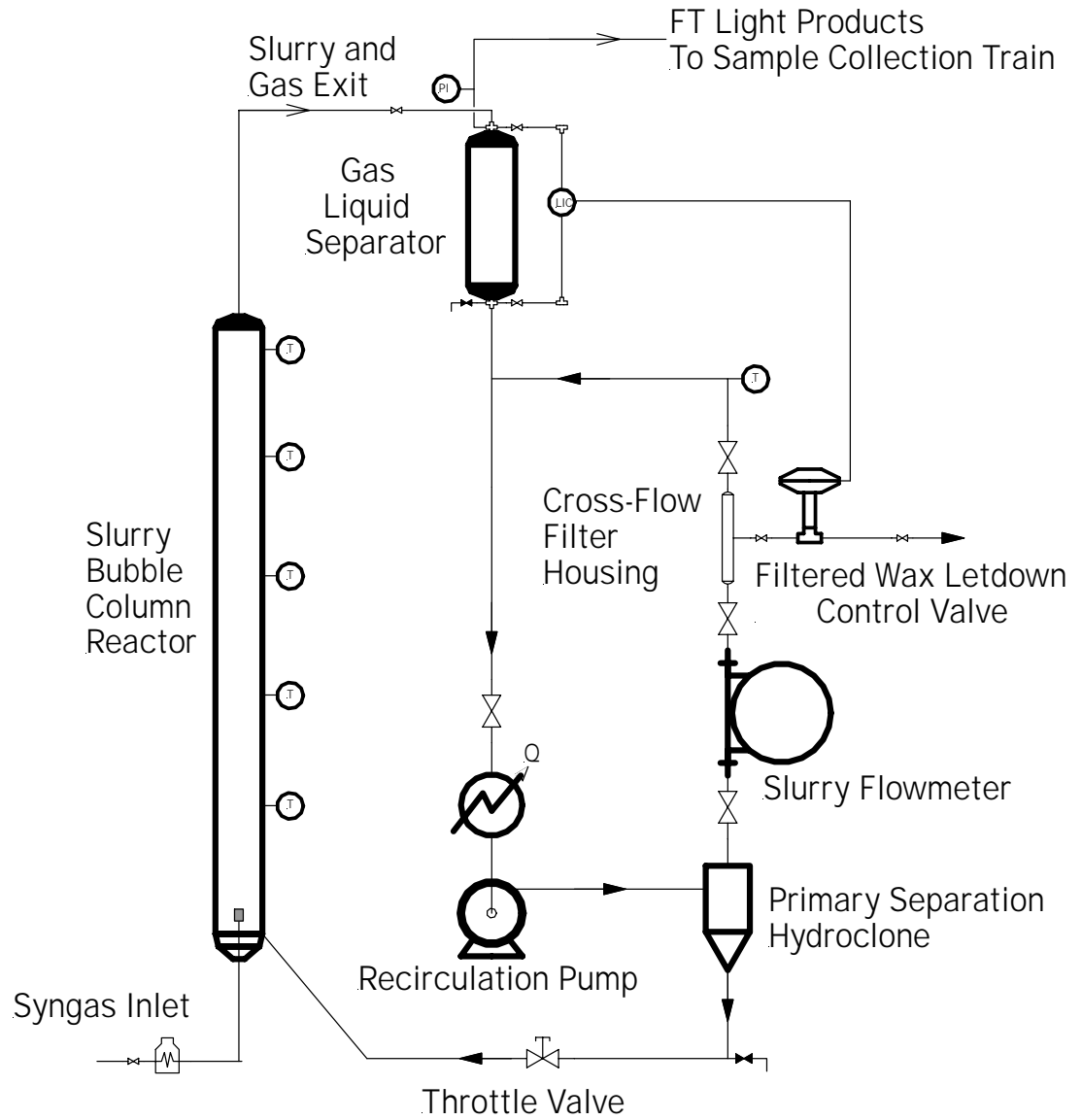
#### *Modified 2-Stage Filtration System for the SBCR Pilot Plant*

The proposed SBCR filtration scheme for Phase II is shown schematically in Figure 2. As with the previously mentioned SBCR configuration, the modified unit will consist of a gas/liquid separator to be located above the reactor vessel. The internal liquid downcomer will be removed. Instead, the downcomer will be moved outside the reactor vessel and will be connected to the suction side of a recirculation pump. The pump discharge will be connected to a primary separation device; a catalyst rich stream will be recycled to the reactor vessel while the clarified wax stream will be diverted to a secondary filtration loop.

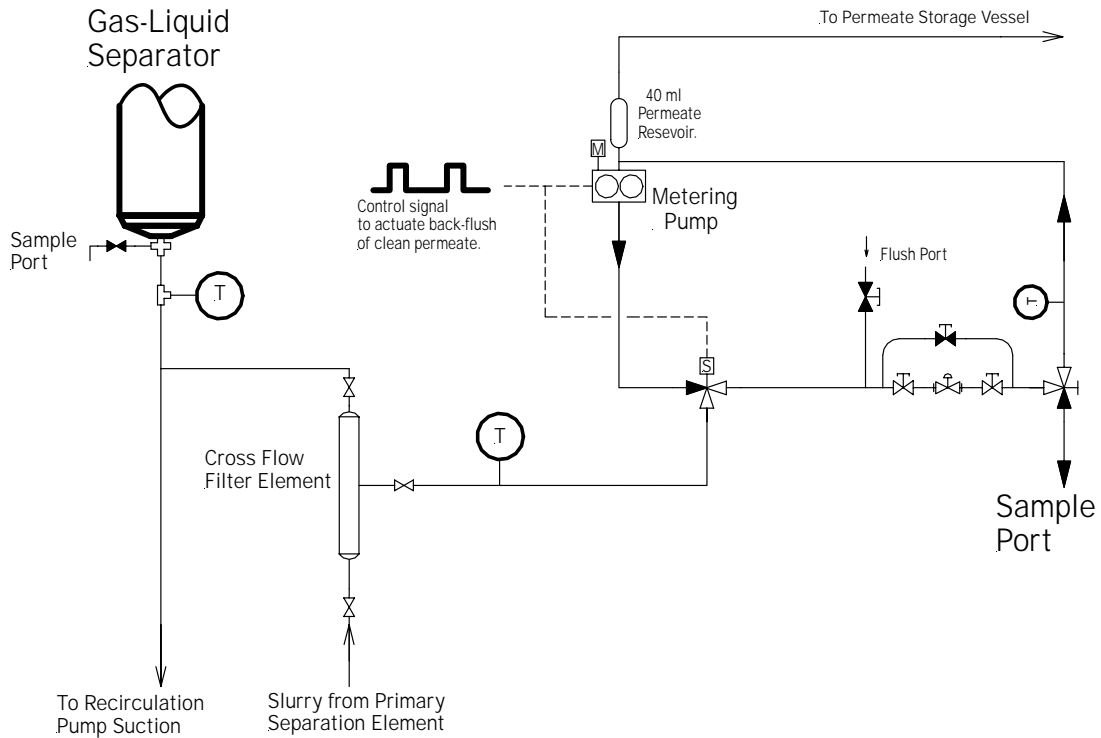
The fraction of clarified slurry entering the secondary loop will be controlled via a throttle valve. The secondary flow rate will be measured by a coriolis flow meter. Quantifying the flow will be important because the slurry velocity is crucial in cross-flow filtration. Polishing of the clarified slurry will be by a cross-flow filter element( eg, Aucusep), similar to the type supplied by Pall Filtration in Phase I. The wax permeate flow from the filter shall be limited by a control valve actuated by a reactor level

controller. Hence, a constant inventory of slurry will be maintained within the SBCR system as long as the superficial gas velocity remains constant. Changes in the gas hold-up due to a variable gas velocity will need to be calculated so that the space velocity can be accurately quantified.

The flux maintenance system developed in Phase I will be added to the permeate side of the filtration system. As shown in Figure 3, 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.



**Figure 2. Modified SBCR with Improved Filtration Scheme.**



**Figure 3. Proposed Flux Maintenance System for the Phase II SBCR**

## CONCLUSIONS

The Phase I test program has provided the information and operational experience to integrate an improved filtration system for providing ultra-clean product wax. A series of pilot plant runs in Phase II will obtain all the necessary data needed for the F-T filter system scale-up. The proposed 2-stage filtration system will incorporate a hydroclone-type device in series with a polishing cross-flow filter. A flux maintenance systems, developed in Phase I, will also be added to provide regular back-pulses of cleaned permeate to the cross-flow membrane.



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1. Patterson, P.M.; Sparks, D.E.; Jacobs, G.; Tackett, A.; Chaney, J.A.; and Crocker, M.; "Supported Bismuth Oxide Catalysts for NO<sub>x</sub> Reduction Using Hydrocarbon Reductants," 19th North American Meeting of The Catalysis Society, May 22-27, Philadelphia, PA 2005.
2. Jacobs, G.; Patterson, P.M., and Davis, B.H.; "Low Temperature Water-Gas Shift: Isotopic Tracer and Kinetic Isotope Effect Investigations Over Pt/ceria," 19th North American Meeting of The Catalysis Society, May 22-27, Philadelphia, PA 2005.

### **TRAVEL**

May 2005 Philadelphia, PA – three presentations at the 19<sup>th</sup> North American Meeting of The Catalysis Society.

June 2005 Frankfurt, Germany – One paper presented at the 4<sup>th</sup> International Conference on Environmental Catalysis.

Sept. 2005 Cincinnati, OH – Tri-State Catalysis workshop.