Task 4. Wax/Catalyst Separation

The objective of this task is to develop techniques for the separation of catalysts from FT reactor slurries.

A.   A Summary of the CAER Experience with Catalyst/Wax Filtration

For the use of an iron Fischer-Tropsch synthesis catalyst in a continuous bubble column slurry reactor, a serious problem is the continuous separation of the heavy wax product from the catalyst slurry. Various approaches have been utilized to separate wax from the catalyst slurry. These include gravity settling with removal of the clean wax, centrifugation, and either external or internal filtration.

While the separation of wax from the catalyst slurry is a problem at the commercial scale, it usually becomes even more difficult as one reduces the scale to one that is practical at the laboratory level. In the following we describe some results obtained at the laboratory scale.

The surface area of our precipitated iron catalysts is of the order of 300 m^2/g. TEM examinations show that the individual particles have nearly spherical shape. Both TEM and surface area measurements indicate that the individual particles are about 3.0 nm (30 Å) in diameter. These small particles agglomerate into clusters that are in the 1-3 micron size range. Spray drying of the slurry allows the individual agglomerates to be formed into spherically shaped particles which have an average diameter that depends upon the variables utilized during spray drying. The SEM pictures at four magnifications of a typical product from the spray drying of the precipitated iron catalyst are shown in Figure 1. At the lower magnification, one can readily see that very uniform spheres are produced by spray drying and that they have the appearance of a good catalyst as defined by Sasol (1). At the highest magnification of one of these spheres, it is evident that the spheres consist of 1-3 micron particles.

Using the 2"x6' bubble column reactor, four activations were performed with a spray dried iron catalyst batch that was prepared by United Catalyst Inc. The activation consisted of treating in flowing carbon monoxide for twenty-four hours, ramping the temperature to 200°C in nitrogen and then to 280°C during three hours. At the end of the twenty-four hour activation period, the shape and size of the catalyst particles were identical to the initial catalyst spheres (2). A sample of the activated catalyst was placed in an oil and tumbled at room temperature for increasing periods of time. It was found that, under these conditions, the iron spherical particles attritted by a gradual removal of the outer layers of the sphere rather than by fracturing the product into two or more fragments (schematically illustrated in Figure 2).

There are two properties of the iron/carbon system that contribute to the problem. The first is the change in volume as the iron oxide is converted to the iron carbide form that is needed to have an active catalyst. As the iron oxide is converted to the carbide, there is merely 100% decrease in the density as determined from X-ray diffraction. Likewise, if the iron carbide is oxidized during usage, there will be a nearly 100% expansion in size. This expansion/contraction exerts severe strain on the particle and leads to loss of the integrity of the catalyst particle that was formed by spray drying. There are two extreme views of the impact of the contraction/expansion: in one instance the spherical catalyst particle would remain the same size and any volume change would be restricted to the smaller particles that make up the primary catalyst sphere and in the other instance the entire catalyst sphere would undergo shrinkage to nearly one-half in size as the carbide was formed (schematically shown in Figure 3). The limited data obtained in the 2" diameter slurry bubble column reactor show that the catalyst sphere remains the same size after carbiding as it had in the oxide form. This means that the size of the individual particles making up the catalyst sphere undergoes a volume contraction during carbide formation and that this will significantly increase the void space between the individual

particles and, at the same time, greatly reduce the contact area between individual particles that serve to hold the sphere together.

A second factor is the hardness of the iron oxide. An empirical relationship has been established between strength, hardness and melting-point of inorganic solids with respect to the ability to form pellets. As illustrated in Figure 4, the properties of iron oxide cause it to fall in a region where it would be unpelletable. Thus, the forces that develop during drying that are caused by the presence of water at the points of contact are not sufficiently strong to overcome the hardness of the iron oxide particle. The result of this is that the agglomerate that forms during spray drying is held together by very weak forces, and is therefore easily broken down to the 1-3 micron sized individual particles. To alleviate this problem, some component needs to be present that will assist in making a stronger bond between the individual particles as the spherical particle is formed during the spray drying operation.

Summary of Filtration with Different Catalysts

We have utilized a variety of catalysts for Fischer-Tropsch synthesis in the CSTR using internal filters. Our experience with many runs with each type of catalyst is summarized in Table 1.

Our filtration experience with alumina and silica supported cobalt catalysts, with a few instances when the alumina support did not possess attrition resistance, have been successful. We have run for periods of three months without encountering problems with filtration. This has been the case even when the catalyst loading was so large that the amount of wax produced required us to filter two times per day.

Our limited experience with iron supported catalysts (silica, alumina, magnesium silicate and magnesium aluminate) has, in general, not been reproducible. All four supports show attrition resistance during the CSTR runs. Thus, it appears that the filtration problems, when

encountered, are due to the iron particles being removed from the support and interfering with the filtration and/or separation by gravity settling. More work needs to be done to confirm this.

Problems are not encountered in removing the small amount of reactor wax from the reactor when using the low-alpha precipitated, unsupported iron catalyst. With intermediate iron catalysts, filtration problems are encountered in some runs but not in others. These runs may be of 1,000 hours duration or longer. For the high alpha, precipitated, unsupported iron catalyst we almost always encounter filtration problems at some point in the run; however, the point at which this occurs is very variable.

Estimation of Filtration Rate at Sasol

One approach to evaluate the needed filtration rate is to try to estimate one that is realized in a commercial operation. In the following we utilize the published data for the size of the Sasol slurry reactor (5m x 22m) and the productivity of the reactor (2,500 bbl/day). Assuming that the reactor is only 2/3rds filled with slurry and that the hydrocarbon has a density of one, one can calculate that the productivity is 57.8 kg/hr/m^3 reactor volume. It is further assumed that the filter has a cylindrical shape and occupies 1% of the reactor volume; that is, the reactor volume would be reduced by 1% by the filter. It is assumed that 75% of the total product is removed from the reactor through the filter and the remainder goes overhead. One m^3 of reactor volume will contain 1.36 m^2 of filter area. With these assumptions, the filtration rate is 0.53 kg/min/m^2 of filter area. It is realized that there may be significant errors introduced in the assumptions leading to this calculated value; however, attempts have been made to make assumptions on the conservative side so that the value should be viewed as a conservative estimate.

In operating the CAER CSTRs we have made estimates of the rate of filtration through Mott sintered metal filters. In making this estimate, it has been assumed that the filter is

completely immersed in the slurry and that the total filter area is utilized. In actual practice, it is likely that during part of the filtration time the filter is only partially immersed, and this will make the measured rate be lower than the actual filtration rate. Likewise, it is assumed that the removal of wax occurs during the entire draining period. In actual practice, the wax removal will occur during the earlier portion of the time the valve is open, and this will also make the measured value be lower than the actual value under optimum operation. During one of the runs the measured rate was 2.4 kg/min./m^2 filter area. Thus, the sintered metal filter will easily provide the filtration rate, and much higher, than is estimated for the Sasol commercial operation. If this is the case, then the filtration problems are associated with technique, and not with the initial capacity of the sintered metal filter.

CAER Filtration Procedure

A schematic of the CSTR system is shown in Figure 5. Two paths are available for the reactor products to exit, depending on the configuration/arrangement of the valves associated with the sample traps. The components of interest are the hot (or rewax) letdown valve and trap, the warm (or wax) letdown valve and trap, and the equalizing valve between the hot/rewax and warm/wax traps).

The primary path for products to exit the reactor is via a line that connects a port on the upper, inner surface of the reactor head to the warm/wax trap. Ideally, these products are in the vapor phase. After exiting the reactor head, they pass through a 7µm sintered stainless steel filter and then through the warm/wax trap letdown valve to pass through the warm/wax product trap (typically set for a temperature of 100ºC). The reactor effluent then flows to the oil trap to condense the oil fraction (usually set for 0ºC). The remaining product gas passes through the back pressure regulator, where the pressure is reduced to a value slightly above atmospheric, and then to either an on-line gc or to the vent line.

An alternate path for the products to exit the reactor is via the rewax filter. This filter has been positioned at several levels below the inner top surface of the reactor head, ranging from the liquid-gas interface to being immersed in liquid near the bottom of the reactor. The porosity of the rewax filters have ranged from 0.5 to 2µm. The material exiting the rewax filter then passes through the hot trap letdown valve and then on into the hot/rewax product trap (normally set to 200°C). The products then pass through an "equalizing" valve located between the rewax and wax traps and then passes in turn through the wax and oil traps and finally through the back pressure regulator to either the gc or the vent line. Note that in this configuration the wax trap letdown valve is closed, thus eliminating a short circuited path for the reactor effluent. This ensures that the reactor effluent flows through the series arrangement of first the rewax trap, then the wax trap, and finally the oil trap.

Ideally, the system should be operated to have a continuous gas plus liquid products exit the reactor. To accomplish this the reactor product should continuously exit the reactor through the rewax filter and pass through the series arrangement of the rewax, wax, and oil traps. In this mode of product removal the wax trap letdown valve would be closed so that no product could be shunted around the rewax trap. In theory, utilizing this mode of operation for product letdown would allow for an accumulation of reactor contents to a fixed level, which would be determined by the positioning of the rewax filter. Once the slurry level had increased to the level of the rewax filter, both gas and liquid product would be continuously at the slurry-gas interface from the reactor through the rewax filter (thereby achieving a volumetric steady state condition). If the slurry level did rise to completely submerge the rewax filter, the reactor inlet gas pressure would temporarily rise and this should be sufficient enough to force the excess liquid product out through the filter, allowing the pressure to return to the desired setting once gas breakthrough occurred. This mode of operation is appealing in theory, in that a fixed volumetric inventory

could be maintained. Unfortunately, the accumulation and build up of product/catalyst with time on the rewax filter causes a pressure drop across the rewax filter to increase; this results in an increase in the reactor pressure. In fact, in the past, the increased pressure drop across the rewax filter has resulted in the reactor pressure attaining a value equal to the inlet pressure of the mass flow controllers, resulting in no flow into the reactor.

Due to the inability to operate in the continuous mode mentioned above, a different technique for the letdown of reactor products was developed. The continuous method was modified by allowing the rewax trap to be bypassed for the majority of the sample period. Sample periods are typically one day in duration, with the exception of those following weekends and holidays when longer periods are encountered. The valving arrangement for this modified technique has the rewax trap letdown valve in the closed position and with both the wax trap letdown and the wax/rewax trap equalizing valve in the open position, for the majority of the time. In this configuration, the slurry in the reactor can increase to levels above that of the rewax filter, resulting in an unsteady state volumetric condition. Usually, several hours prior to the daily collection of trap products, the rewax letdown valve would be opened and the wax trap letdown valve would be closed, while the wax/rewax trap equalizing valve would remain in the open position. This permitted the reactor product (gas and/or liquid) to exit exclusively through the rewax filter (either 0.5 or 2 µm filter) as opposed to essentially an open port in the top of the reactor head (which does have the 7 wax filter). In this configuration, it was expected and realized that the reactor pressure would increase, particularly if the level of the reactors contents was sufficient to completely immerse the rewax filter. To insure that the reactor pressure did not increase to values much higher than that of the specified pressure for FTS or to pressures that would stall out the mass flow controllers, required continual monitoring of the reactor pressure. If and when the reactor pressure increased to an unacceptable level, the wax letdown valve

would be opened slightly to allow venting down of the pressure build up in the reactor, and then the wax letdown valve would be closed to continue the reactor liquid product letdown procedure.

Not only did this procedure result in pressure swings during the liquid letdown period, but at best, the reactor inventory would oscillate about some level, neither of which to be considered steady state. In fact, there was no guarantee that the amount of liquid reactor product withdrawn was equivalent to that which was being produced in the reactor for a given sample period. Later, a technique was adopted that utilized a computerized mass balance method designed to predict the day-to-day reactor accumulation of product.

Another valving modification and letdown technique that was tried was to have all the valves associated with the sample traps (i.e., the letdown valve for the rewax trap, the wax trap , and the equalizing valve between the rewax and wax traps) in the open position at all times. It was thought that the two parallel paths for the reactor products to exit the reactor, which recombine at the inlet to the wax trap, would allow for the continuous removal of both the gaseous and liquid products to exit without variations in the reactor pressure. The reactor pressure did in fact remain constant as there was always a path for the overhead condensable gaseous products to exit the reactor via the wax discharge line (through the 7μ-wax filter and then through the letdown valve leading to the wax trap). The second of the two parallel paths for products to exit, which is for the removal of the accumulated liquid reactor product, incorporates the 0.5 or 2 μm rewax filter, which is internal to the reactor, and the letdown valve leading to the rewax trap. As mentioned, the discharge line from the rewax trap feeds through a "wax/rewax trap equalizing" valve into the inlet of the wax trap. The pressure difference across the path for removal of the accumulated liquid product is at least equal to, or slightly greater than, that of the pressure difference that exists across the discharge path for the condensable gas products. It was thought that the force that was generated as a result of this pressure difference, although small in

value, would be sufficient to provide the necessary driving force to aid in the removal of the accumulated liquid reactor product.   In practice, this was not the case and liquid would accumulate in the reactor more rapidly than it was removed through the rewax filter.

Experimental Data-Process Operations

The initial runs effected separation of reactor product from catalyst slurry using a 0.5μ Mott Metallurgical Corporation sintered stainless steel filter (0.5 " O.D. and 1"in length for a surface area of 0.0109 ft^2). This filter was positioned so that the bottom surface is about 3 inches from the upper internal surface of the head of the one-liter CSTR, which has an internal diameter of 3" and an internal height of 10¼," with a hemispherical bottom and a cylindrical shaped top. Since using the Polywax PWR3000 high molecular weight wax (average molecular weight of 3,000) as a reactor solvent, problems have persisted in that the filter was increasingly being blinded off, resulting in an increasing inability to remove the reactor product (i.e., the heavy liquid product at reactor temperature and pressure we refer to as 'rewax'), allowing the reactor to ultimately fill up, resulting in aborting the runs. Potential solutions to this problem have been suggested and/or implemented.

The first attempt, which has been incorporated, was to lower the filter to insure that it is completely immersed in the catalyst slurry. This allows the filter to be continually washed by the slurry and eliminate or at least minimize the blinding off of the filter. To accomplish, the filter is lowered at an elevation so that it's bottom surface is about seven inches below the upper surface of the reactor; that is, the bottom of the filter is positioned about 1/4 inch above the upper surface of the gaspersator blades.

The first run using this lowered filter configuration was LGX263 using a low-alpha catalyst (100Fe:4.60Si/2.72Cu/0.00K). As shown in Figure 6 (i.e., Rewax Flux Density vs Sample Day for Run LGX263), problems were encountered in attempting to remove the rewax

for the first 12 days of operation. This was due to the fact that the line from the reactor head to

the rewax trap was heated at a too low of a temperature, specifically lower than the melting point

of the Polywax PWR3000 (130°C). When additional heat tracing was applied to the line, rewax

removal was then permitted as can be seen for sample days 13-17. The rewax collected during

this run showed no visible traces of iron. The filtration rate was about 0.06 gallon/min/ft^2 filter

area/min., a value that compares favorably with that estimated for the Sasol commercial plant.

Another run that also incorporated the lowered filter utilized a high alpha iron catalyst

(LGX266; (100Fe:4.60Si/2.72Cu/7.52K). Figure 7 shows the performance of the filter, as

measured by flux density (gpm/ft^2), decreased with time. The implication is that blinding of the

filter increases with subsequent rewax letdown periods. As in run LGX263, the rewax product

showed no visible evidence of iron catalyst content. Two rewax samples, LGX266-005 and

LGX266-007, were analyzed for iron content and showed 0.03wt% Fe and 0.01wt% Fe,

respectively. Also, note that on this figure there is reference to the Regimesh Filter that has a

flux density of 0.13-0.20 gpm/ft, surface area of 0.175 ft^2, and a porosity of 18μ (corresponding

to about 16 times the area and an increase of 36 times the porosity of the Mott SS-filter that we

were using). With the maximum pressure drop across the Mott SS-filter at 75 psi and the

pressure drop across the Regimesh filter unknown, a comparison of the performance of the filters

is not possible. From the liquid flow characteristic graphs supplied with the Mott product

catalog, by changing the μ-grade from 0.5 to 20μ (while holding the viscosity and pressure drop

constant) the flux density should increase about 100-fold. However, if the pressure difference is

varied and the μ-grade and viscosity held constant, the relationship between the flux density and

pressure drop is linear.

After the completion of run LGX266, an attempt was made to test a 2μ Mott SS-filter.

This was accomplished by opening up the reactor after it had cooled to 130°C and replacing the

0.5 μ-filter with a 2μ-grade filter. Comparing the liquid flow media charts in the Mott catalog

for the 0.5μ and 2μ filters, at equal pressure differences and viscosities, the average flux density

should increase by a factor of seven. Once the reactor was back to normal operating conditions,

the rewax valve was opened for a rewax letdown period of one hour. About 300g of reactor

contents were removed. The collected product contained catalyst but it was not possible to

decide if:

1)   the wax/catalyst leaked through an improperly tightened filter fitting,

2)   had it passed straight through the 2μ filter,

3)   was due to the fact that the level had dropped so much that the filter was exposed

        to the gas/froth space that may contain finely ebullated catalyst particles, or

4)   possibly a combination of the above.

Since the results of the 2 μ filter at the end of Run LGX266 were inconclusive, another 2μ

filtration test was attempted after Run LGX268 was completed (LGX268 used the

100Fe:4.60Al/2.72Cu/3.66K as well as a 0.5μ filter). The results from this series of rewax

letdowns was more promising since the rewax product collected appeared catalyst free. Thus, a

run was made with the installation of a 2μ filter prior to the start of a run (LGX271;

(100Fe:4.60Al/2.72Cu/15.87K). During a 240 hour run, with CO conversion at about 30%,

rewax could be removed that did not contain catalyst. The run was terminated because of the

low catalytic activity.

        The second of the potential solutions to address the problem of rewax removal and

reactor overfilling was to develop a mass balance for the system to allow for the prediction of the

amount of rewax to be removed so that a constant reactor inventory could be maintained.

Simply stated,

Reactor Accumulation(g) = Gas in(g) - Gas out(g) - Trap Products out(g).

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Two versions of this mass balance were developed. The first just accounts for the mass of the gas out based on the Carle Series 400 AGC chromatographic data and is referred to as the simplified mass balance. The second, and certainly more sophisticated, utilizes chromatographic data from the HP-5790 as well as the AGC data. By adding either reactor accumulation terms to the starting weight of the wax/catalyst slurry, a predicted reactor inventory is determined. Runs LGX's 267, 269, and 270 have had either one or both of these mass balances applied to them, with mixed results. Figure 8 shows run LGX267 (100Fe:4.60Al/2.72Cu/0.00K) using the second mass balance which predicted that there was about 127g remaining in the reactor, while in fact the reactor contents were measured at 92g after the completion of the run. Note that the dashed line across the graph indicates the starting weight of the of the reactor slurry, which was 318.68g. Figure 9 is for run LGX269 (100Fe:4.60Al/2.72Cu/7.52K), which also had a staring weight of 318.68g. Both mass balances are presented and up until run hour 144, agree rather well with one another. After run hour 144 there is a divergence of predicted reactor contents in which there is an approximate 50g difference in values. At the end of the run the disagreement was at about 40g, but the actual measured amount of wax/catalyst in the reactor for this run was at 598g, 55% more than the second mass balance predicts and 73% more than the first, i.e., the simplified mass balance prediction. These discrepancies have yet to be resolved. A final application of the mass balances, to date, was used for run LGX270 (100Fe:4.60Al/2.72Cu/11.58K) shown in Figure 10. For this run the predicted reactor contents agree to within about 20 g of one another, 384.8g for the simplified and 363.2g for the second method (within 6% of each other), as well as both prediction models compared to the final measured wax/catalyst weight of 310g (24% high for the simplified method and 17% high for the second method). Although there is some disagreement with either method and the final actual weight of the reactor contents, this is potentially a very useful technique for maintaining and

predicting reactor inventory, as well as predicting the amount of rewax to be removed from the reactor on a daily basis.

The third of the solutions for addressing the problem of reactor rewax removal and that of avoiding reactor overfilling involves the installation of a liquid back flush bomb for the rewax filter. Presently, the rewax bomb itself can be used as a gas charging vessel by closing the rewax letdown valve and the equalizing valve between the rewax and wax traps. An inert gas can then be introduced into the rewax bomb at a pressure higher than that of the reactor, the rewax valve opened and the gas pressure can force the hydraulic column of rewax (contained in the rewax line and the rewax filter) to back flush the filter. Although this capability does exist and has been used, there is probably not enough rewax present in the line and filter to perform an adequate backflush. In addition, the rewax letdown valve is a flow control/throttling type of valve and does not allow for an instantaneous surge of higher pressure gas to force the rewax material as, for example, a ball valve would allow. With a bomb installed on the branch of a tee (with a ball valve separating the bomb and the branch of the tee) and the run of the tee plumbed between the reactor head rewax discharge port and the existing rewax valve, liquids such as C-30 oil could be used to facilitate this back flush. Such an apparatus will be constructed and tested.

The most recent method/technique used in assisting the removal of reactor liquid product involves isolating and charging the hot/wax trap (see Figure 5) to a pressure about 75 psi lower than that of the reactor. Once the trap is at the desired pressure, the hot trap letdown valve can be opened to allow the pressure difference to force out the reactor liquid product. A variation of this technique uses the gas law to predict the pre-letdown pressure for a desired volume of reactor liquid removal.

The importance of cleaning the filter cannot be understated, and can be demonstrated by returning to Figure 7. It is seen that as time progresses, the flux density decreases, requiring

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longer periods of letdown time to remove the desired amounts of rewax, which are determined

by using either of the reactor mass balance techniques. This was experienced for FTS runs

LGXs 267, 269, and 270. The situation was such, that to remove the necessary amount of rewax,

the letdown periods were approaching six to seven hours in duration.

References

1.   B. Jager and R. Espinoza, *Catal. Today*, **23**, 17 (1995).

2.   R. Srinivisan, L. Xu, R. L. Spicer, F. L. Tungate and B. H. Davis, Fischer-Tropsch

catalysts. Attrition of carbided iron catalyst in the slurry phase, *Fuel Sci. & Tech. Intl.*,

14, 1337 (1996).

Table 1			
Summary of Filtration with Iron and Cobalt Catalysts			
Alpha	**Iron, Unsupported**	**Iron, Supported**	**Cobalt, Supported**
Low ($< \approx 0.7$)	No Problem	No Problem	---
Intermediate (0.7 to 0.85)	Problems in some runs	-----	No Problem
High (> 0.85)	Problems	Problems	No Problem
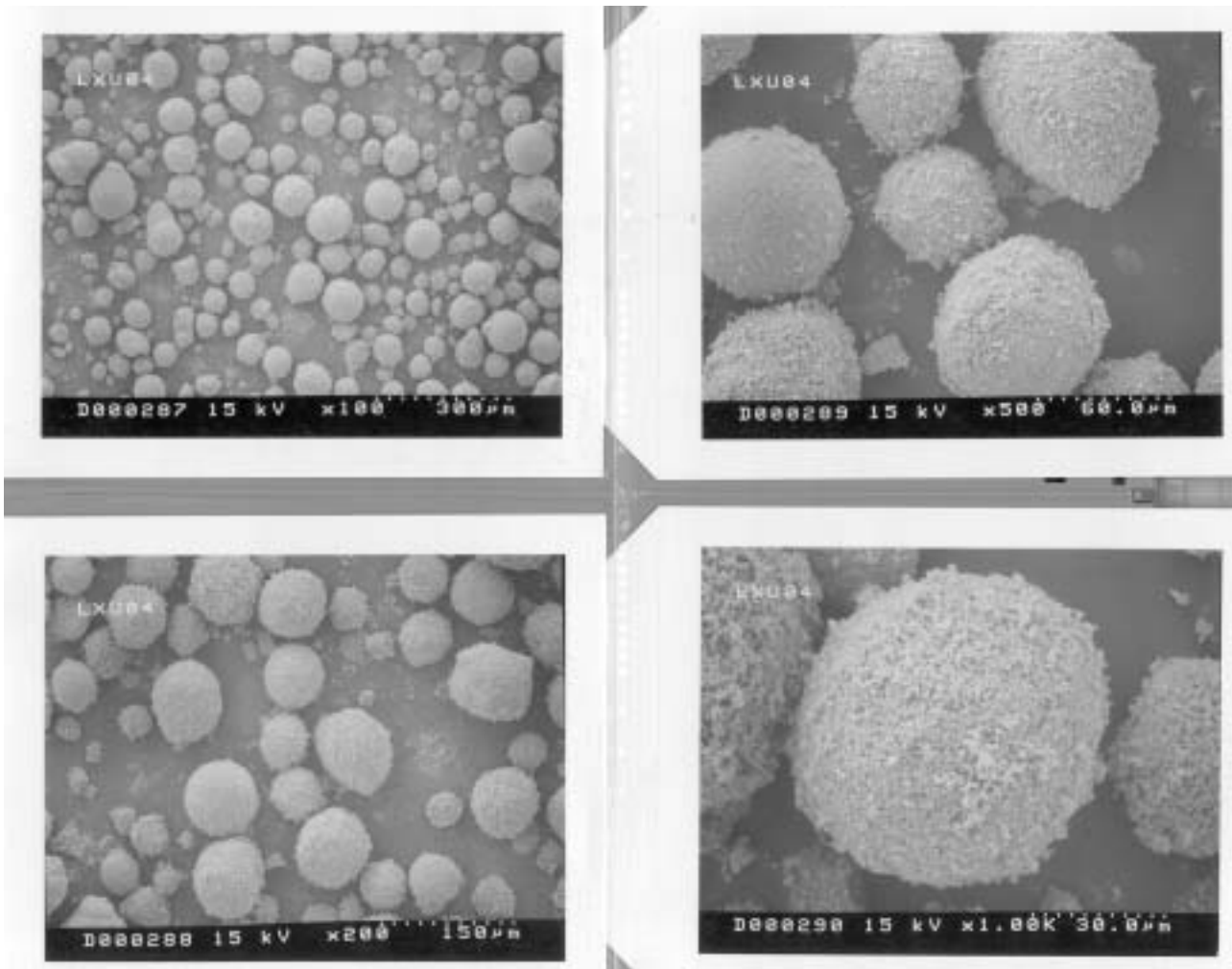
Figure 1.   Scanning electron microscope pictures of spray-dried, precipitated, iron catalyst at four increasing magnifications (x100, 200, 500, 1,000; size scale indicated in picture).
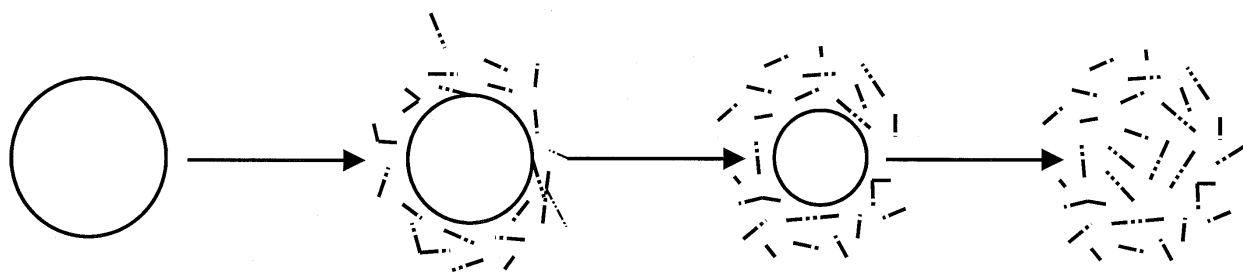
Figure 2. Schematic of attrition of spray-dried precipitated iron catalyst by a gradual decrease in size of the primary particle.

Particle Contraction / Expansion

Particle size of B is 55 % of A

Particle size of C is the same size of A

Particle size of A = B = C
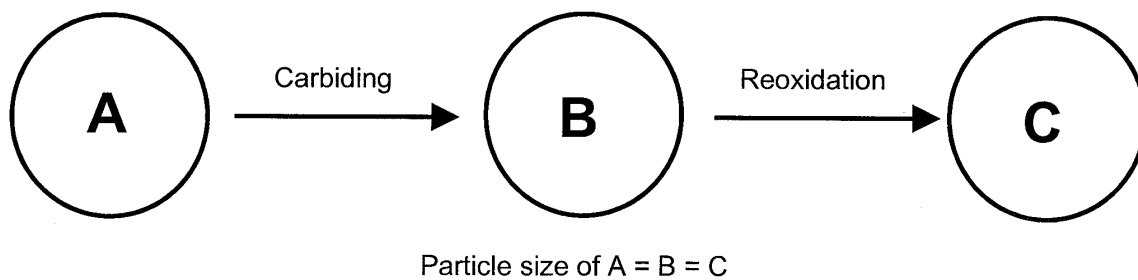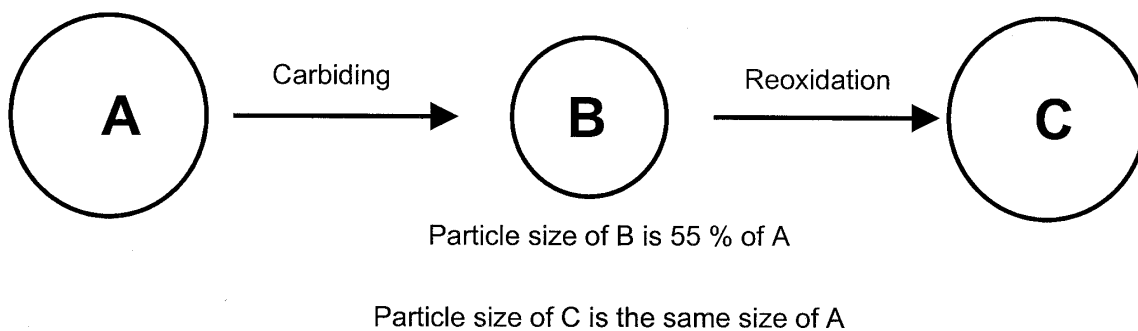
Figure 3.   Schematics of size changes in activation of an iron catalyst and then reoxidation for: (top) whole particle charges size and (bottom) whole particle remains same size and individual units of particle changes size.
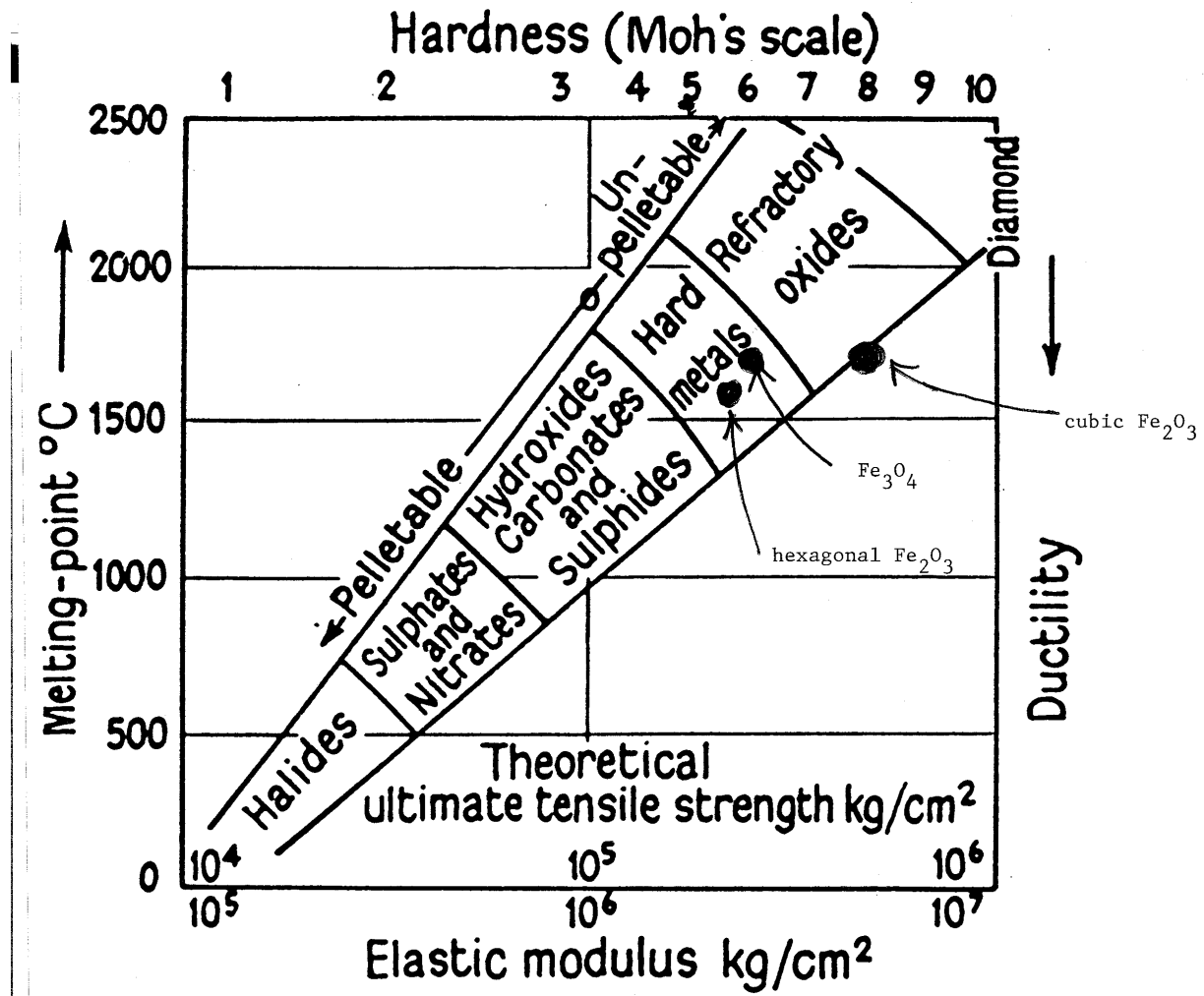
Figure 4.   Relationship of physical properties and pelletability of compound classes.
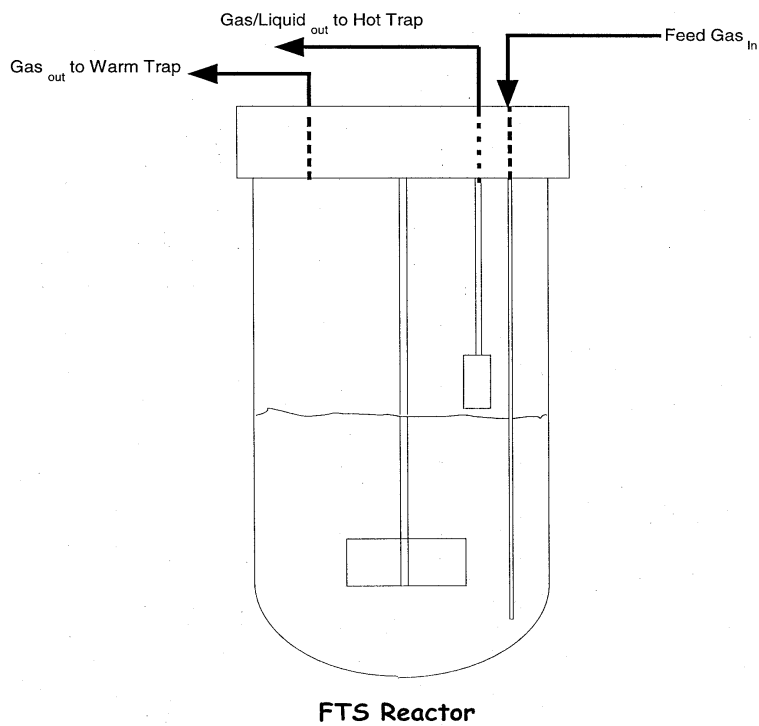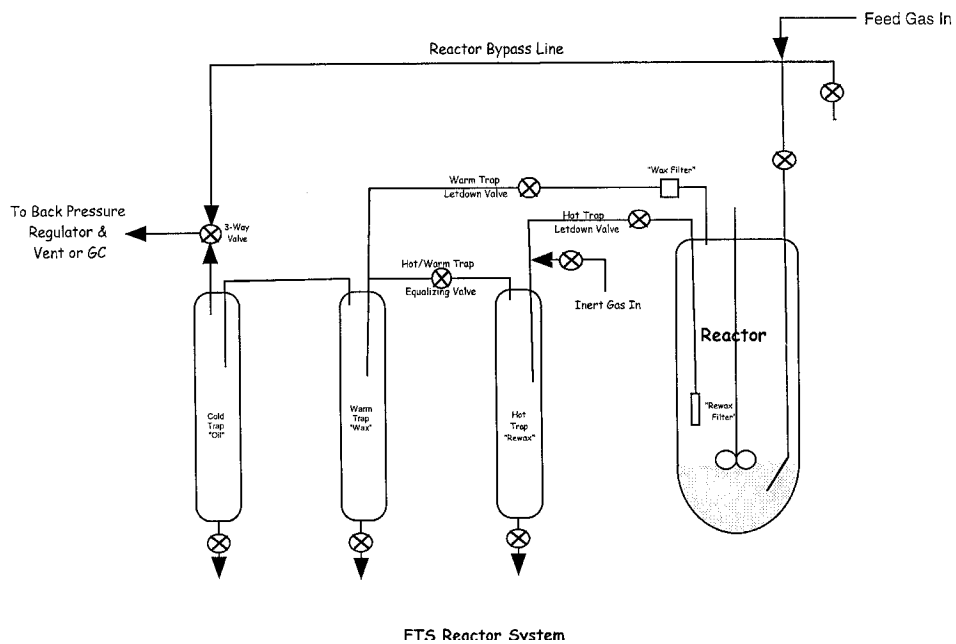
Figure 5.   Schematic of CAER reactor system (top) and CSTR (bottom).

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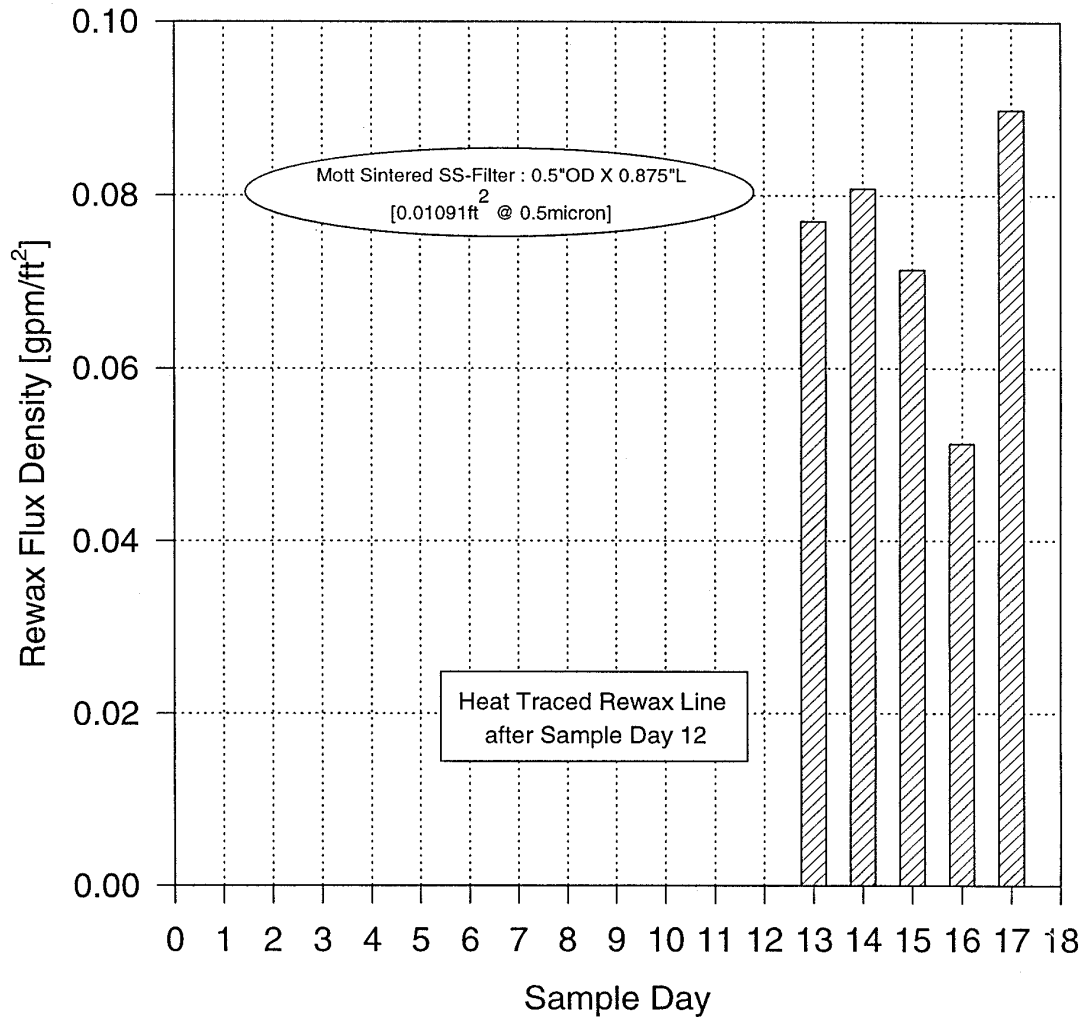
Figure 6.   Rewax flux density vs. sample day for run LGX263$_{R7}$ (100Fe:4.60Al/2.72Cu/0.00K).
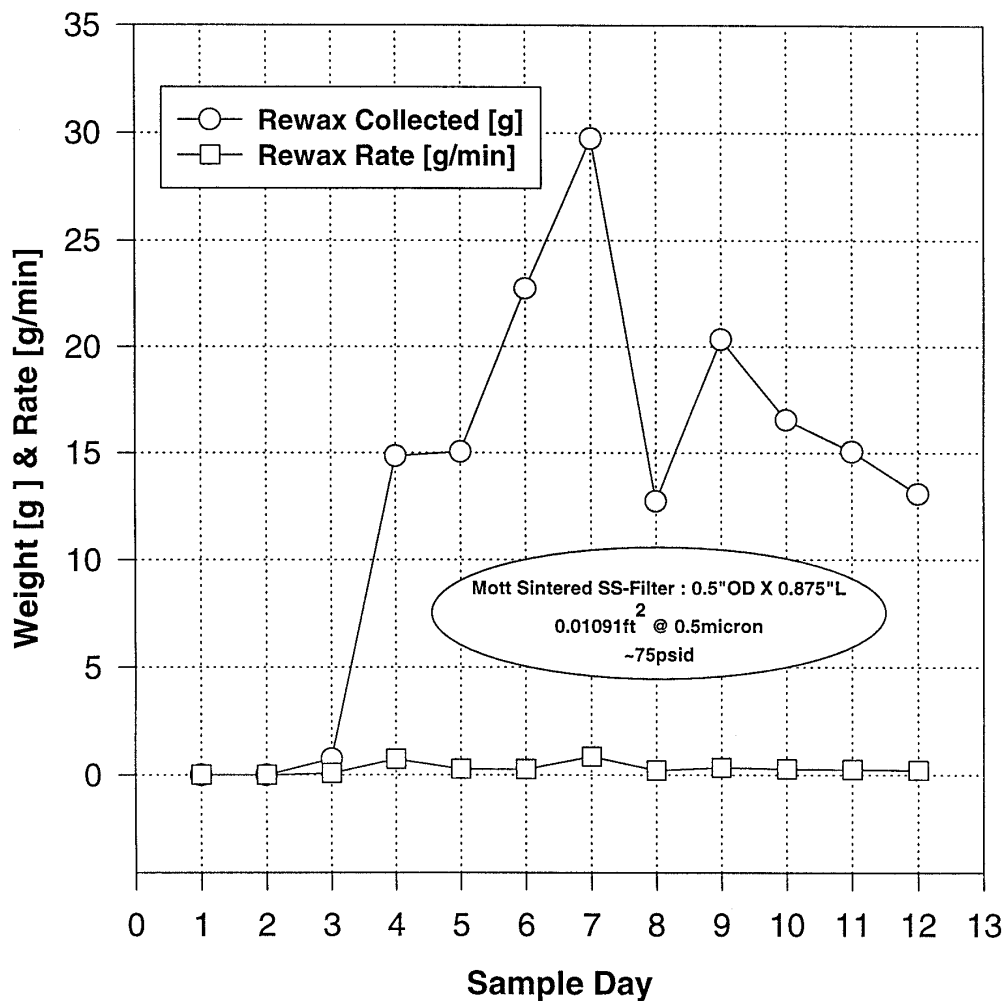
Figure 7.   Rewax withdrawal weight and rate vs. sample day for run LGX266$_{R7}$ (3.0wt.% Cu, 5.0 wt.% K, T_{syn} = 230°C).
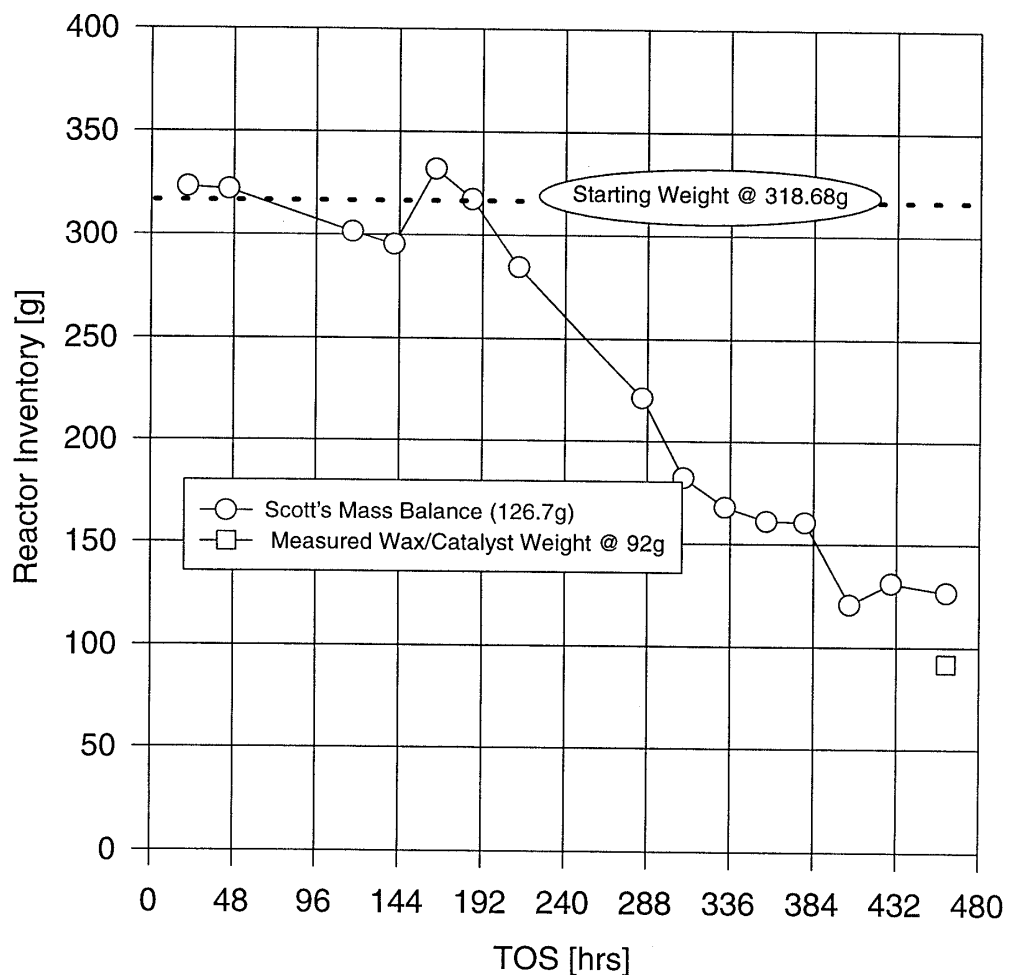
Figure 8.   Predicted reactor inventory vs. time-on-stream for run LGX267$_{R1}$.
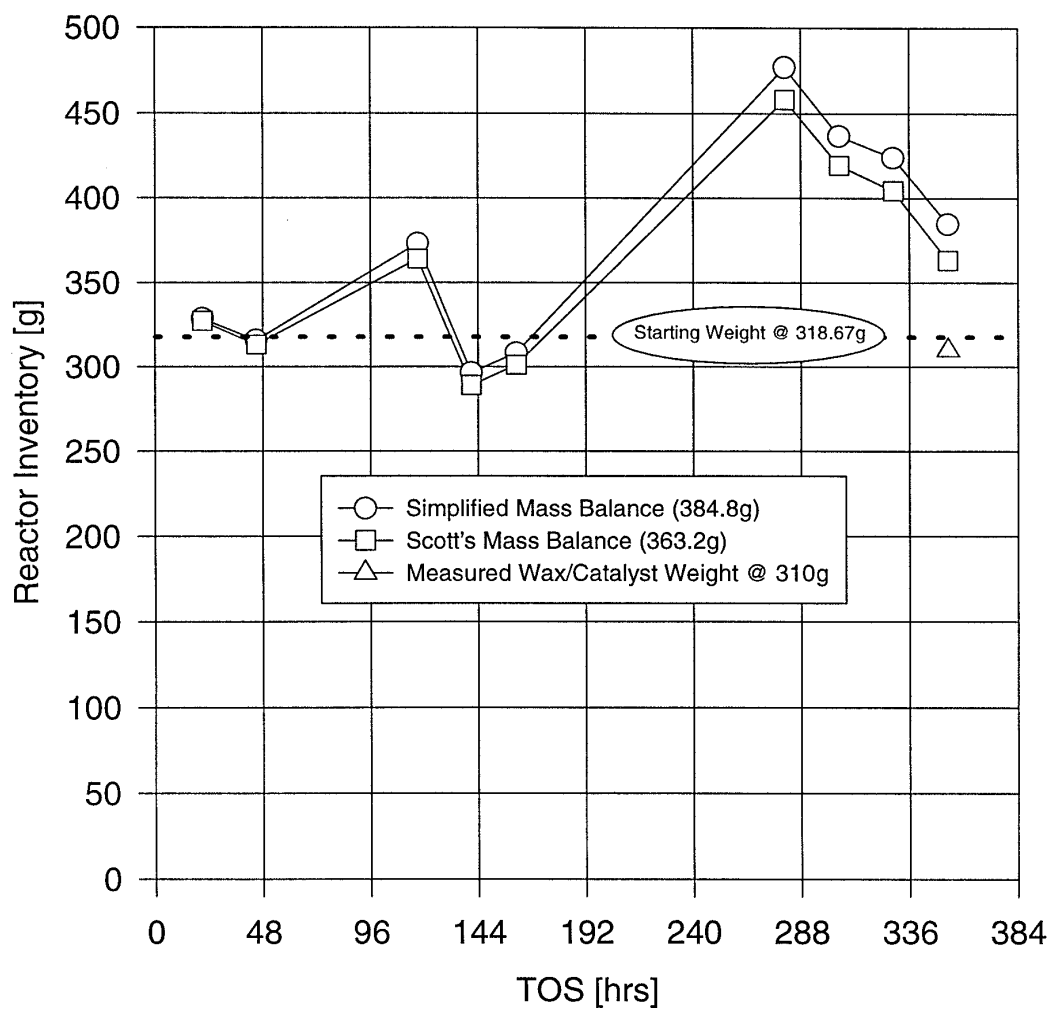
Figure 9.   Predicted reactor inventory vs. time-on-stream for run LGX270$_{R4}$.

B.   Filtration with High Alpha Unsupported Fe Catalysts

The filtration problems need to be addressed from two viewpoints: the ability to operate the CSTRs and the ability to filter at the pilot or commercial plant scale.

To date we have been able to filter the products from the operation of CSTRs when we operate with cobalt catalysts. In these operations we utilize 10 wt.% catalyst (total catalyst, not cobalt) and have operated for nearly 4,000 hours on occasion. Only on very rare occasions have we encountered problems with filtration. Thus, in 95+% of the runs, the pressure generated when we open the internal filter to remove reactor wax is less than 40 psig and the wax (up to 75 grams) can be removed in less than three hours, and usually in a shorter time period. Thus, from the viewpoint of operating a CSTR with alumina or silica supported cobalt catalysts, we have been able to remove wax and operate the CSTR for extended run periods. We have less experience with a titania supported catalysts but during about 10 runs we have been able to remove the reactor wax. In general, these cobalt catalysts are what we define as intermediate alpha (0.75-0.90) catalysts. Thus, while the wax is highly hydrogenated it does not have the very high molecular weight of a high alpha catalyst (alpha greater than 0.90).

We continue to have problems removing reactor wax from the CSTR when using the unsupported high-alpha iron catalysts. When we operate with a 0.5- or 2.0 micron Mott sintered metal filter, we find that the reactor wax that is withdrawn has a low iron content (30 ppm or less). Thus, the filter functions to retain the precipitated iron catalyst with particles in the 1 to 3 micron size range in the reactor. However, with time the ability to remove wax decreases.

The following data demonstrate the difficulty in quantifying the filtration ability during a run with a high-alpha precipitated iron catalyst. The particular catalyst used for run BAO-029 produced a soft wax that is representative of an intermediate alpha catalyst (alpha approaching 0.90). The filtration rate was obtained from the amount of reactor wax withdrawn and the time

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that the internal, submerged filter was open to the collection vessel. The removal line is fitted

with a pressure gauge that permits us to reduce the pressure in the collection vessel by an amount

that is known and is below that of the reactor in order to provide a driving force for the removal

of wax. At present, we do not have the ability to adjust the pressure in the collector to maintain a

constant head pressure to provide a constant driving force. Thus, as gas passes through the filter

along with the reactor wax, the pressure in the collector increases and this results in a decrease in

the driving force together with a decrease in the filtration rate.

Early in the run, the amount of wax removed was low, presumably because the small

amount of startup solvent and the rate of production of wax did not keep the filter submerged in

the liquid during the entire time that the filter was open to the collector (Figure 1). Thus, for

about 50 hours of operation the filtration rate was increasing to attain a value of about 6,000

g/hr-ft^2 (100 g/min-ft^2), a much higher value than reported in the last quarterly report (0.1 g/min-

ft^2 or lower). During about 100 hours, the filtration rate remained at about 6,000 g/hr-ft^2, then

appeared to gradually decline to about 1,000 g/hr-ft^2 (16 g/min-ft^2) and then remain essentially

constant during 200 hours of operation. The run was terminated because of scheduled

laboratory shut-down, and not due to filtration problems.

Attempts have been made to operate the reactor by calculating, based upon the

experimental values of other samples collected and the gas flows, the amount of reactor wax that

should be withdrawn and then withdrawing that amount of wax. This has had variable success.

The cumulative grams of hydrocarbon products produced during the nearly 400 hour run are

shown in Figure 2 together with the cumulative calculated grams of wax produced and the

cumulative grams of wax withdrawn. According to the data shown in Figure 2 we should have

accumulated about 754 grams of reactor wax but when we opened the reactor the amount was

only about 500 grams. This amounts to less than 4% error in the mass balance during the entire

run. Since some sample is lost due to flashing during the collection of the products from each of the three traps for each collection period, the mass balance is considered to be excellent.

The filtration rate shown in Figure 1 is not a reliable estimate of the actual filtration rate and is therefore impacted upon the sample removal technique. There was concern that too much wax was accumulating in the reactor so that at 216 hours, a large amount of wax was withdrawn during a 7-hour period. The average filtration rate during this 7-hour period was greater than 5,000 g/hr-ft^2 (shown as □ in Figure 1), near the maximum rate obtained earlier in the run. Thus, the low rate shown before and after 216 hours must be due to the sampling technique and this must be defined so that a more quantitative filtration rate can be obtained.
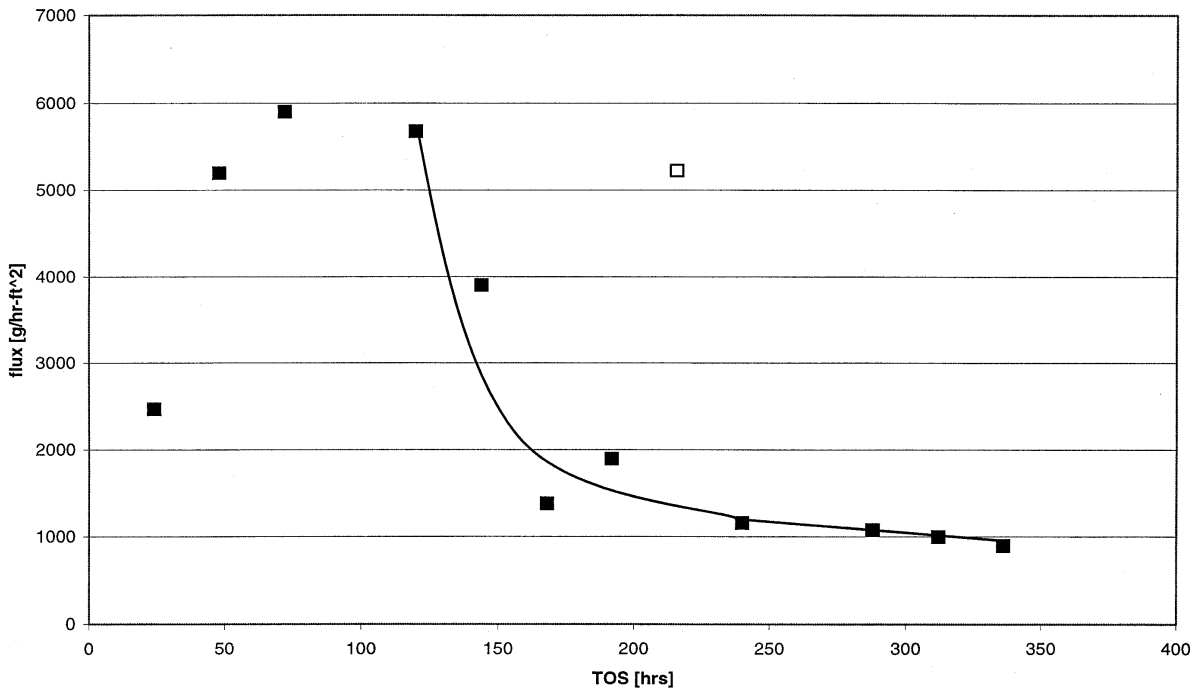
Figure 1.   Filtrate rate as a function of time-on-stream.
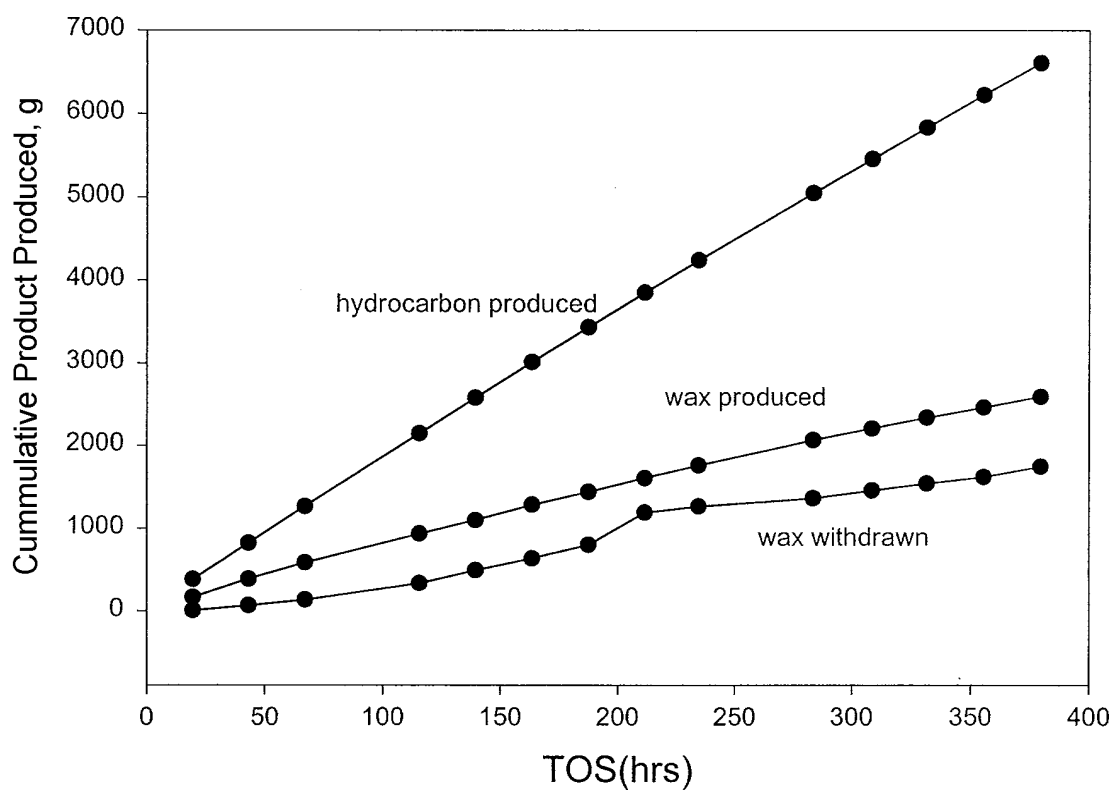
Figure 2.   Cumulative hydrocarbon and wax produced and wax withdrawn as a function of time-on-stream.

C. Initial Filtering Studies with Pall Corporation Filters

Summary of Separation Work

Wax separation from a catalyst slurry for slurry bubble column reactor operation can be viewed from two perspectives:

1. Separation of wax from large (50-100 micron) sized catalyst particles formed by spray drying and made attrition resistant.

2. Separation from small catalyst particles (1-3 micron) and eliminate the need for attrition resistant large particles.

The immediate separation problem to be solved by CAER work is to be able to operate a laboratory reactor to define activity, selectivity and aging characteristics of high alpha iron catalysts. A longer term solution is to develop procedure for the operation of the LaPorte facility and potential commercial operation.

The CAER efforts apply for two catalyst systems: cobalt and iron.

Cobalt Catalysts

CAER personnel have prepared supported cobalt catalysts based on alumina, silica and titania support material. The supports have sufficient attrition resistance to retain their physical shape and size during weeks of operation in a CSTR.

CAER personnel have successfully removed wax from the reactor during operations of up to five months using supported cobalt catalysts. The only wax separation problem with cobalt catalysts was when testing for a company (work outside DOE contract) due to attrition of a poor support.

Conclusion

Wax separations from catalyst slurry is not a problem using a fine (2 to 5 micron) porous metal filter. Operations of laboratory reactions with wax production of 100g/day or higher can

be accomplished. Wax removal is therefore not a problem with supported cobalt catalysts in the laboratory setting. For Run 4 at LaPorte, it has been reported that filtration was not a problem but was a problem for Run 3 with a similar catalyst.

Iron Catalysts

All spray dried iron catalysts that have been tested at CAER have attrited to 1-3 micron sized particles during the activation period. Supported iron catalysts can be utilized without attrition of the support.

Using a porous metal filter with the small (1-3 micron) sized iron catalyst, operates with a 10 wt.% slurry of a high-alpha unsupported iron catalyst had to be terminated after 200-400 hours due to filter plugging, resulting in the reactor filling with wax. With the supported high-alpha iron catalysts, the support did not attrite but the filter plugged; it is assumed that this was due to the small iron particles being released from the support.

Wax removal has now been accomplished when the small (1-3 micron) high-alpha (0.92) iron catalysts are used in a laboratory reactor containing 10 wt.% slurry. A Rigimesh filter permitted operation for 1450 hours (2 months) without having the filter plug. When the run was voluntarily terminated, the filtration rate had not declined. The run was terminated in order to make a run that contained a higher wt.% catalyst slurry. Using the same catalyst with finer pore openings resulted in filter plugging after 100 hours (very fine filter) and 1000 hours (medium porosity filter). Using the Rigimesh filter, the catalyst loss with the withdrawn wax was about 1%/week; the catalyst activity also declined at about 1%/week.

Conclusion

The Rigimesh filter can be utilized to permit the operation of the laboratory reactor to define the long-term activity and selectivity of intermediate and high-alpha iron catalysts. The wax removal flux is lower than desired for commercial operation; however, the rate obtained

during the CAER initial work should be viewed as the minimum. Should this initial success continue, we will be able to operate laboratory reactors without the need to develop attrition resistant iron catalysts.

Detailed Description of Filtration Study with Pall Filter

Two filters manufactured by Pall Corporation were installed in 1000 mL continuous stirred tank reactors. The filters had the same geometrical external surface area as the Mott Metallurgical sintered filters used previously. Two types of filtering media were used. One filter used a material called Rigimesh (filter A). Rigimesh is a sintered woven wire mesh which Pall Corp. reports as having the greatest permeability for comparable removal efficiency. Sintering increases the strength of the mesh by bonding the wire at each point of contact which prevents shifting of the wires and maintains a constant pore size. The filter used in this study was a multilayer composite of different mesh sizes. The other filter tested is composed of PMM medium (filter B). PMM medium is a thin sintered matrix of stainless steel powder within the pores of sintered stainless steel mesh. The sintered powder allows for filtration down to µm and the stainless steel mesh provides strength.

Each filter was tested with the same high alpha catalyst. The catalyst was prepared by standard continuous precipitation techniques and impregnated with KNO_3 and $Cu(NO_3)_2 \bullet 3H_2O$ to give an atomic composition of 100Fe/4.6Si/2.0Cu/5.0K. The reactor was loaded with 32.2 g of catalyst and 310 g of decene trimer. The catalyst was activated with CO at 270°C, 175 psig for 24 hours. Following activation, syngas (H_2/CO = 0.67) was started at a space velocity of 3.1 sl h^{-1} g-Fe^{-1}. The temperature and pressure were maintained at 230°C and 175 psig, respectively.

A schematic of the reactor, traps and filtering system is shown in Figure 1. Reactor effluent (vapor phase) exited through valve 1 which was open at all times, unless the filters were being purged. Valve 2 was normally closed. Wax removal was accomplished by venting the

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wax trap to 125 psig (50 psi less than reactor pressure) with valve 3 closed (wax trap isolated from reactor and 60°C trap) followed by slowly opening valve 3. Wax removal was considered to be finished when the pressure of the wax trap was equal to the reactor pressure. Accumulated reactor wax was removed approximately every 24 hours. The first wax samples appeared black due to catalyst penetrating the filters. After a few days the wax samples appeared clean, presumably due to the formation of a filter cake on the filter. The amount of wax removed during the first 5 minutes that valve 3 was open was determined on most days to calculate the rate of filtration and determine if the filters were plugging. The initial filtration rates for the two types of filters are shown in Figure 2. The filtration rate of the PMM filter was higher than the Rigimesh filter for the first 380 hours. It is emphasized that these are minimum filtration rates.

The reactor plumbing was arranged such that the filter could be periodically purged with Ar in order to clean the filtering medium and prolong filter life. To purge the filter, valves 1, 2 and 3 were closed. Valve 4 was opened to pressurize the wax trap with Ar up to 250 to 400 psig. Valve 3 was opened slowly to allow Ar to flow back into the reactor through the filter. The first time the filter back purge was done was at approximately 390 hours of the run with the Rigimesh filter. The filter was purged with 300 psig Ar and showed no signs of plugging because the reactor pressure rose immediately and within seconds the wax trap and reactor pressures were identical. A wax sample was taken 30 minutes after purging the filter and it appeared black due to catalyst penetrating the filter (just like the wax samples at the beginning of the run). Twenty-four hours after purging the filter the wax withdrawn through the filter appeared clean. Once again, the clean wax was probably due to better filtration from the build-up of a cake on the filter. The PMM filter was also purged after approximately 510 hours on stream. This filter seemed to be partially plugged because it needed to be purged 6 times with Ar pressure ranging from 250 to 400 psig; however, it was successfully cleaned by the back purges. The cumulative

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wax yield for each run is shown in Figures 3-5. The cumulative wax yield was the same for each run and after 700 hours, and about 1.4 kg of wax had been removed from each reactor (Figure 3).

Syngas conversion as a function of time on stream is shown in Figure 6 for both runs. The conversion was nearly superimposable for the two runs, indicating excellent reproducibility of catalyst activation and activity measurements. There was an induction period of about 3-5 days in which the conversion increased from about 17% to 49%. After the conversion peaked, the catalysts deactivated at the rate of 3.4% syngas conversion (absolute, not relative) per week. Methane selectivity for the two runs decreased to below 2% after 100 hours (Figure 7) on stream which is indicative of high alpha catalysts (alpha-2 was 0.92 for both catalysts).

These runs represent the first time that a high loading of precipitated iron catalyst was run at the CAER under high alpha conditions with 10 wt.% slurry for an extended time (> 800 h). Typically with the Mott Metallurgical filters, high alpha runs were terminated after approximately one week due to filter plugging and subsequent filling of the reactor with wax.

The cumulative iron in the products from run BAO 36 (using the filter A) and BAO 35 (using filter B) are shown in Figures 8 and 9, respectively. During the period up to about 150 hours very little reactor wax was removed as the reactor filled to the filter level. For the period of about 150 to 200 hours the first significant reactor wax was removed from the reactor (Figure 4). During this same period a significant amount of iron (about 1 g) was removed using filter A (Figure 8). This is a clear demonstration of iron leakage through the filter during the initial wax withdrawal period. From the period of about 200 to 390 hours on stream, the removal of iron was slower and at a nearly constant rate of about 0.22 g Fe/week. At run hour 390 the filter was backflushed using argon. After the backflushing, there was a period of rapid iron removal (about 0.4 g Fe in one day). This conclusively shows that the backflush was effective in partially, or completely, cleaning the "cake" of iron deposited on the filter. Following this backflush, the

filter was operated without backflushing. From 400 to 1,000 hours on stream the iron and reactor wax was removed at a constant rate. During this 600 hour period, the slope of the line in Figure 8 indicates that iron was removed at a rate of 0.18 g Fe/week. The values of 0.22 and 0.18 g Fe/week for the two periods of constant iron removal are in excellent agreement considering the length of time for the run. Since the reactor was loaded with 20 g of iron, the filter permitted the passage of about one percent per week of the iron. The run was terminated after almost 1500 hours (2 months) of continuous operation. The filter was operating as well at the end of the run as it was during the course of the run. The termination with this filter was voluntary, and not due to filter plugging. **Thus, we consider this to be a demonstration of our ability to operate the CSTR so that we can now define the activity, selectivity and catalyst deactivation characteristics for both the intermediate and high alpha catalyst.**

The run (BAO 35) using filter B was less effective that for filter A. The run had to be terminated after about 1,000 hours on stream due to the filter plugging. This allowed the reactor to fill with reactor wax. This filter has been sent to be cleaned by a commercial organization recommended by Pall to learn whether it can be reused after cleansing or whether the plugging is so severe that the filter must be discarded. Filter B has a component that has finer openings that filter A; thus, it is assumed that the plugging is due to the finer average pore opening.

The alkali content of the high-alpha, low-temperature catalyst has a significant impact upon the conversion that is attained. The alkali content of the catalyst utilized in these two runs was about 5 wt%, and this is below the level that should give the maximum conversion. Even so, the conversion is in the range of 30-45% and the hydrocarbon productivity rate is 0.22-0.35 g hydrocarbon/g Fe/hr. This productivity rate compares favorably with those reported for the productivity of cobalt catalysts when the cobalt productivity is based on g hydrocarbon/g

catalyst/hr). Early indications are that the catalyst formulation with 7.5 wt.% potassium has about twice the productivity of the catalyst containing 5 wt% potassium.

There is a reasonably long induction period in which the activity increases, then attains a maximum which is followed by a period where the activity gradually declines to a nearly constant activity after about 500 hours on stream. During the period between 800 and 1463 hours, the activity declines at a rate of 0.8% CO conversion/week. During this period the iron catalyst in the reactor is declining at a rate of about 1%/week. **Thus, the activity decline is at approximately at the same rate as the loss of catalyst, and the catalyst activity decline is clearly lower that the DOE target of 1% CO conversion/week.**

The catalyst with 5 wt% potassium is a high-alpha catalyst with the second alpha being about 0.92. The methane make is consistent with a high alpha catalyst and is about 1.5 wt% of the total hydrocarbon fraction (Figure 7).   The fraction of the C_2 fraction (Figure 10) that is represented by ethylene (about 85%) is representative of a high-alpha catalyst, as is the C_3 (Figure 11) and C_4 (Figure 12) olefin fractions. The fraction of CO converted by the water-gas-shift reaction is about 0.35; thus, about 65% of the CO that is converted is to hydrocarbons.
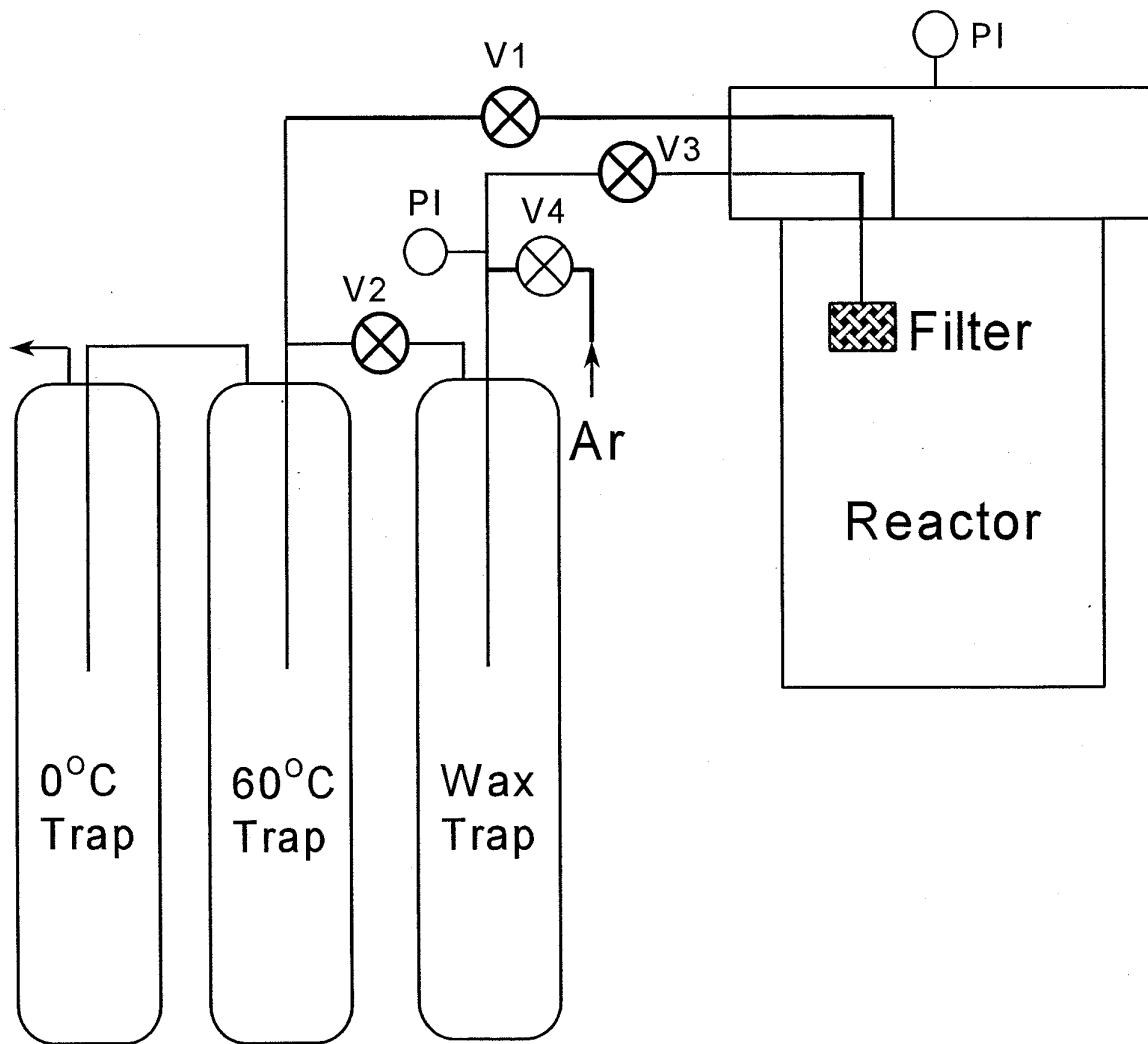
Figure 1.   Schematic of the reactor, traps and filtering system.
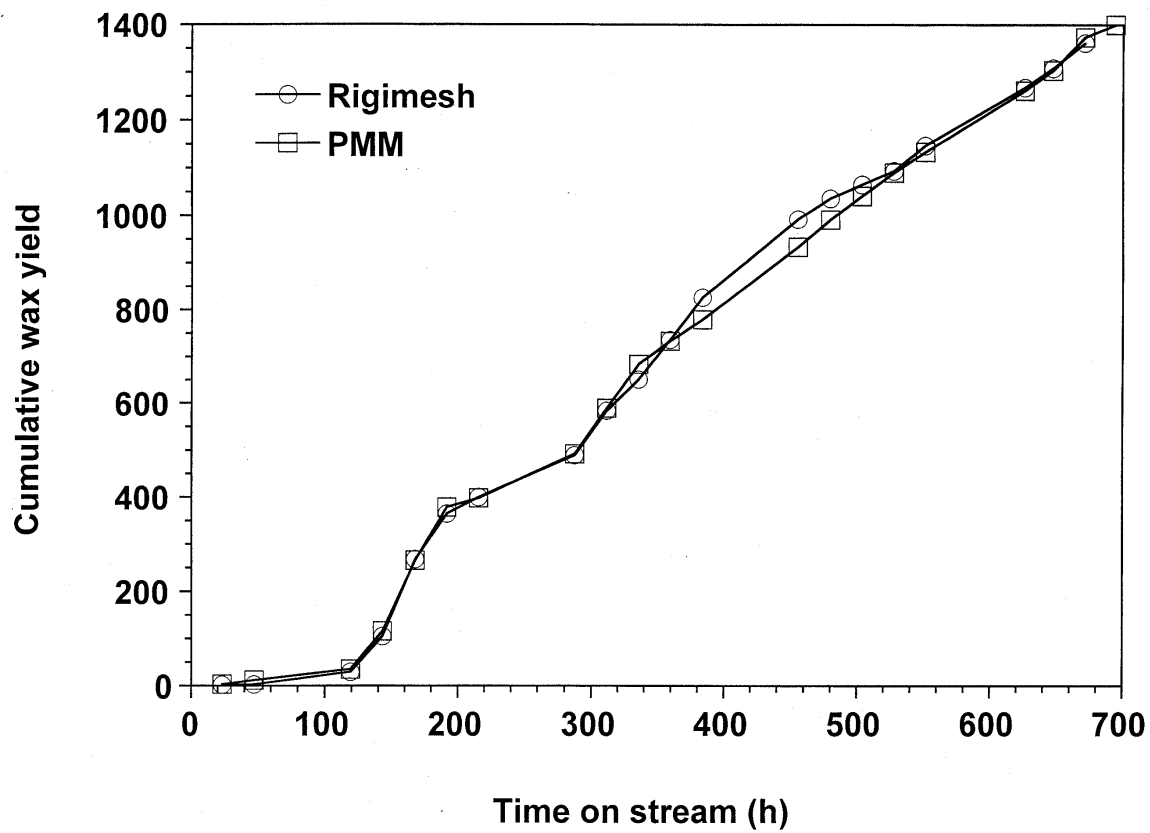
Figure 2.   Cumulative wax yield rates for two types of filters.
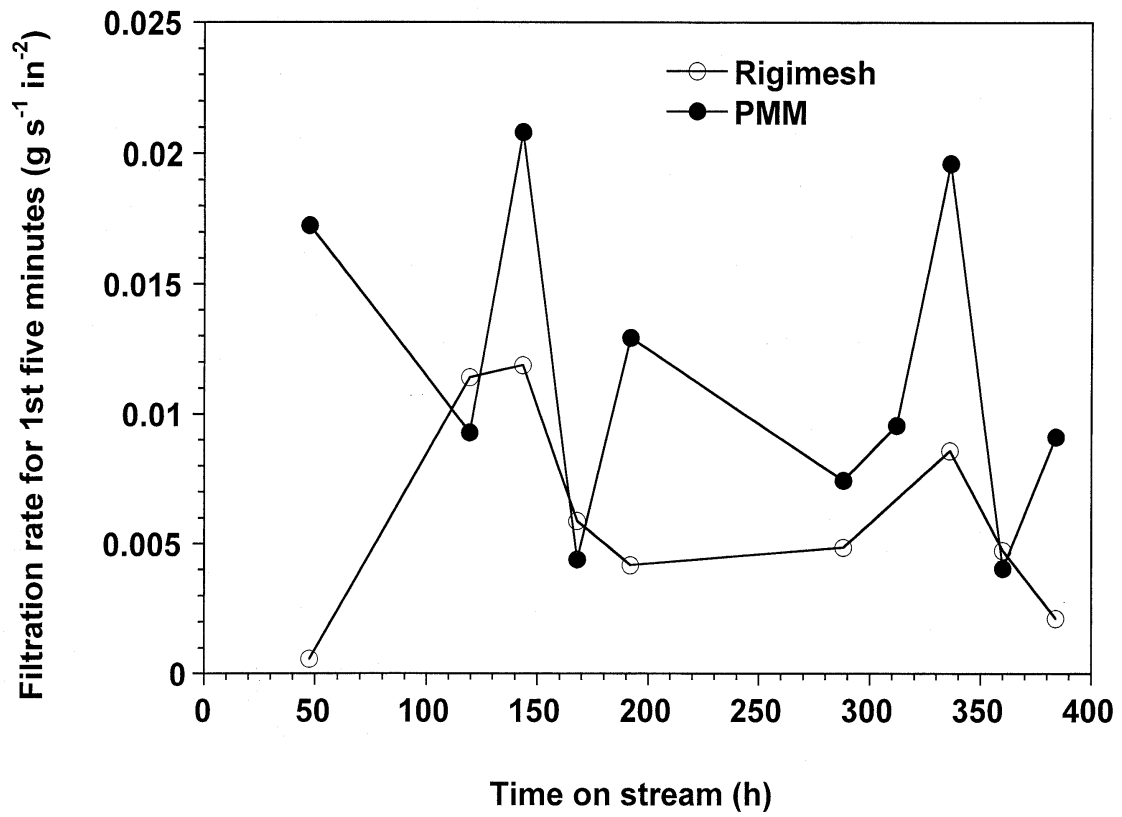
Figure 3.   Filtration rate (first 5 min.) For two types of filters.
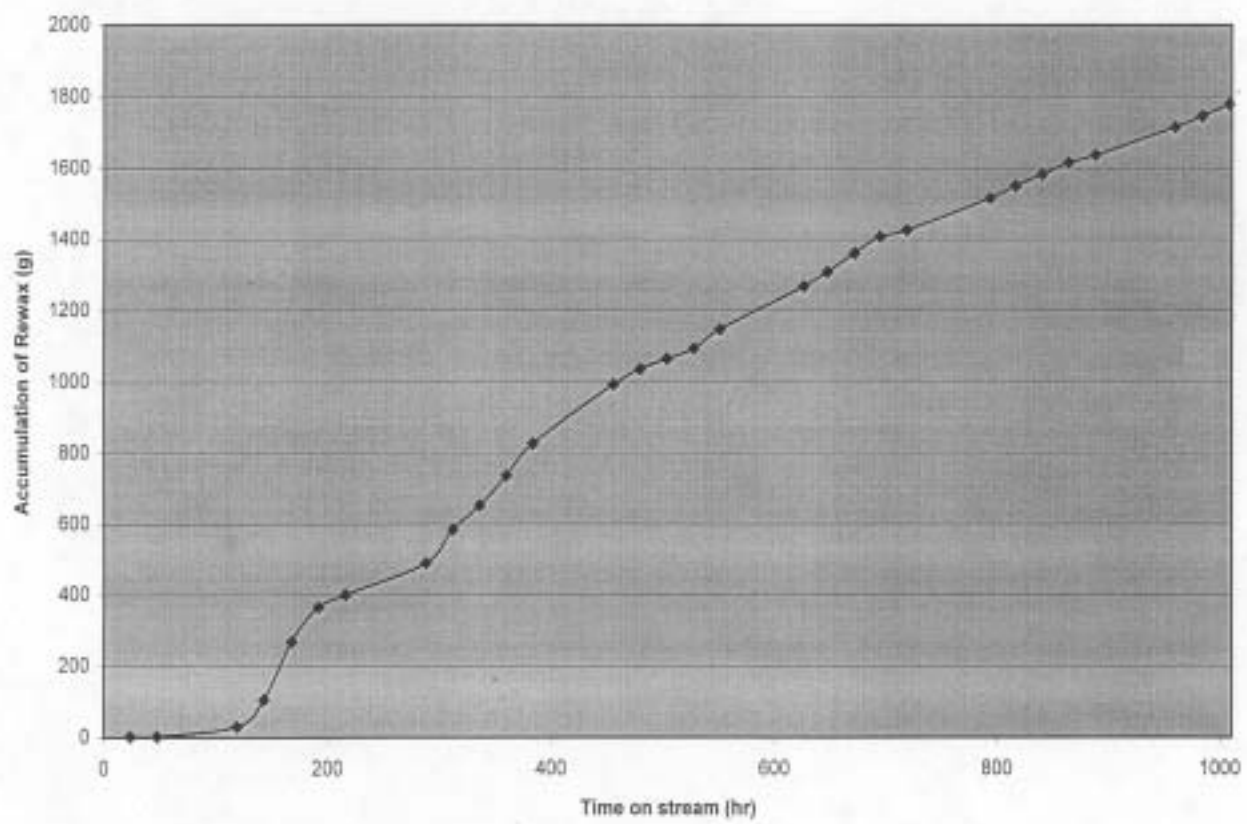
Figure 4.	Accumulation of rewax vs. time on stream for filter A.
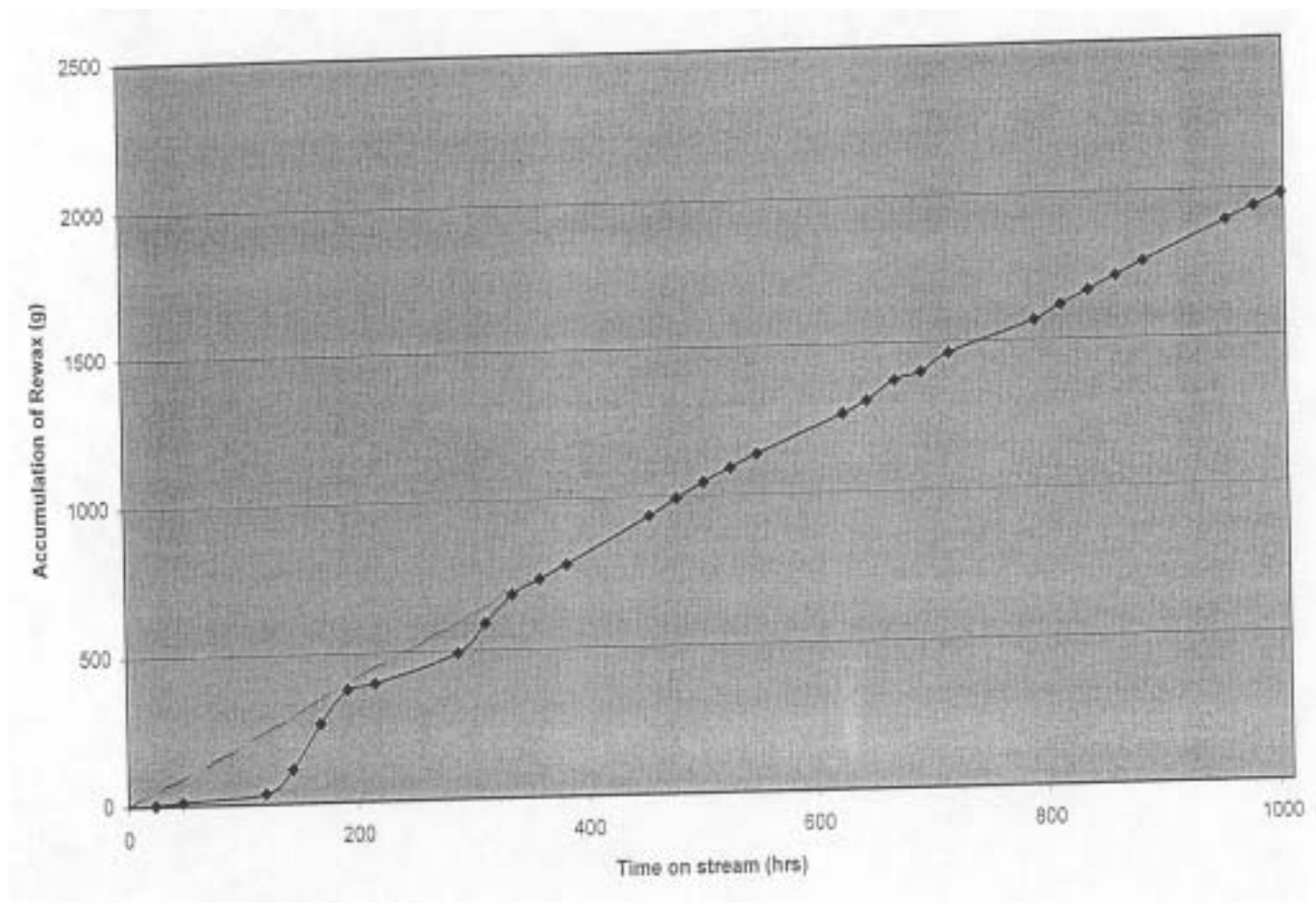
Figure 5.   Accumulation of rewax vs. time on stream.
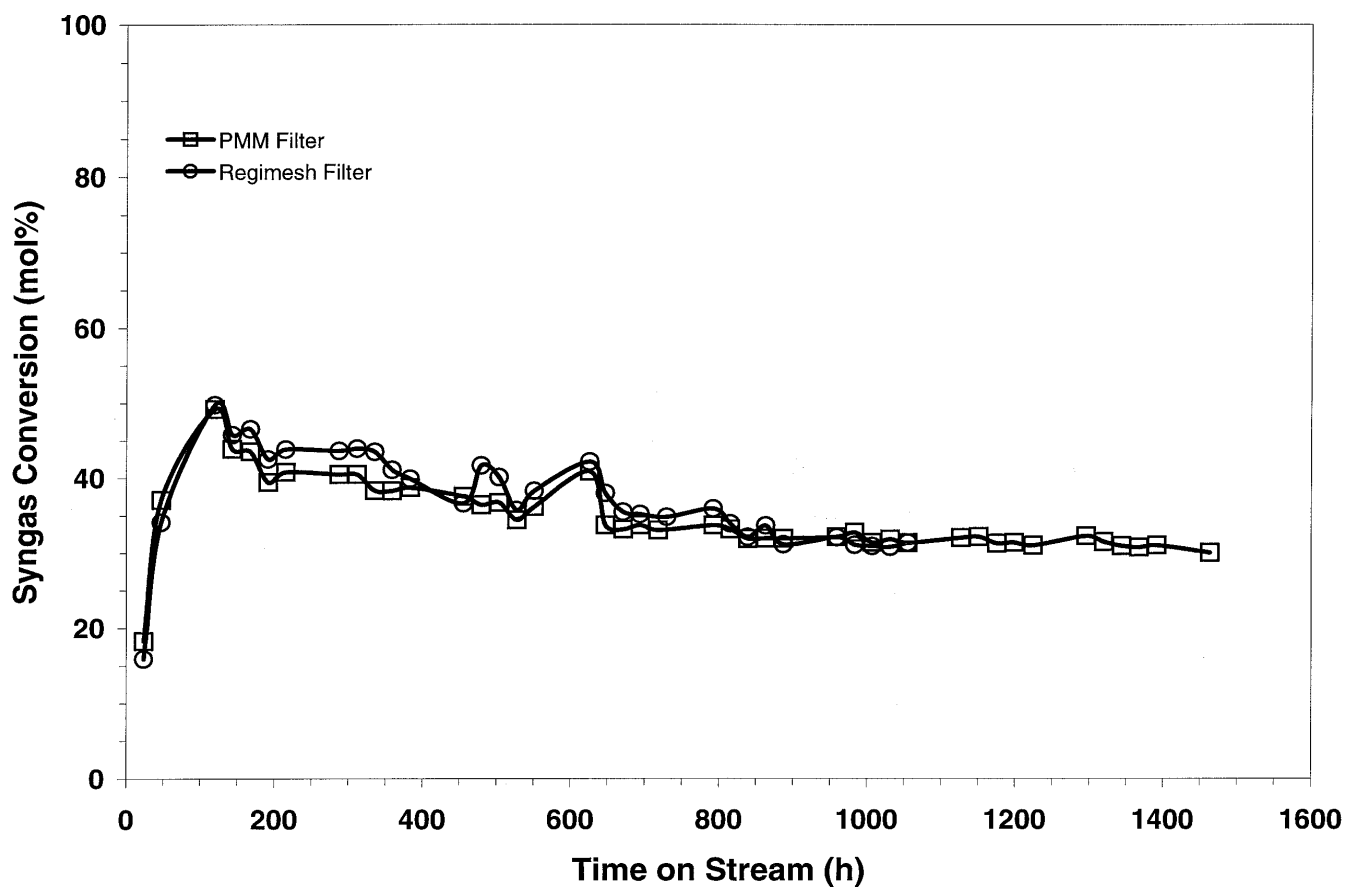
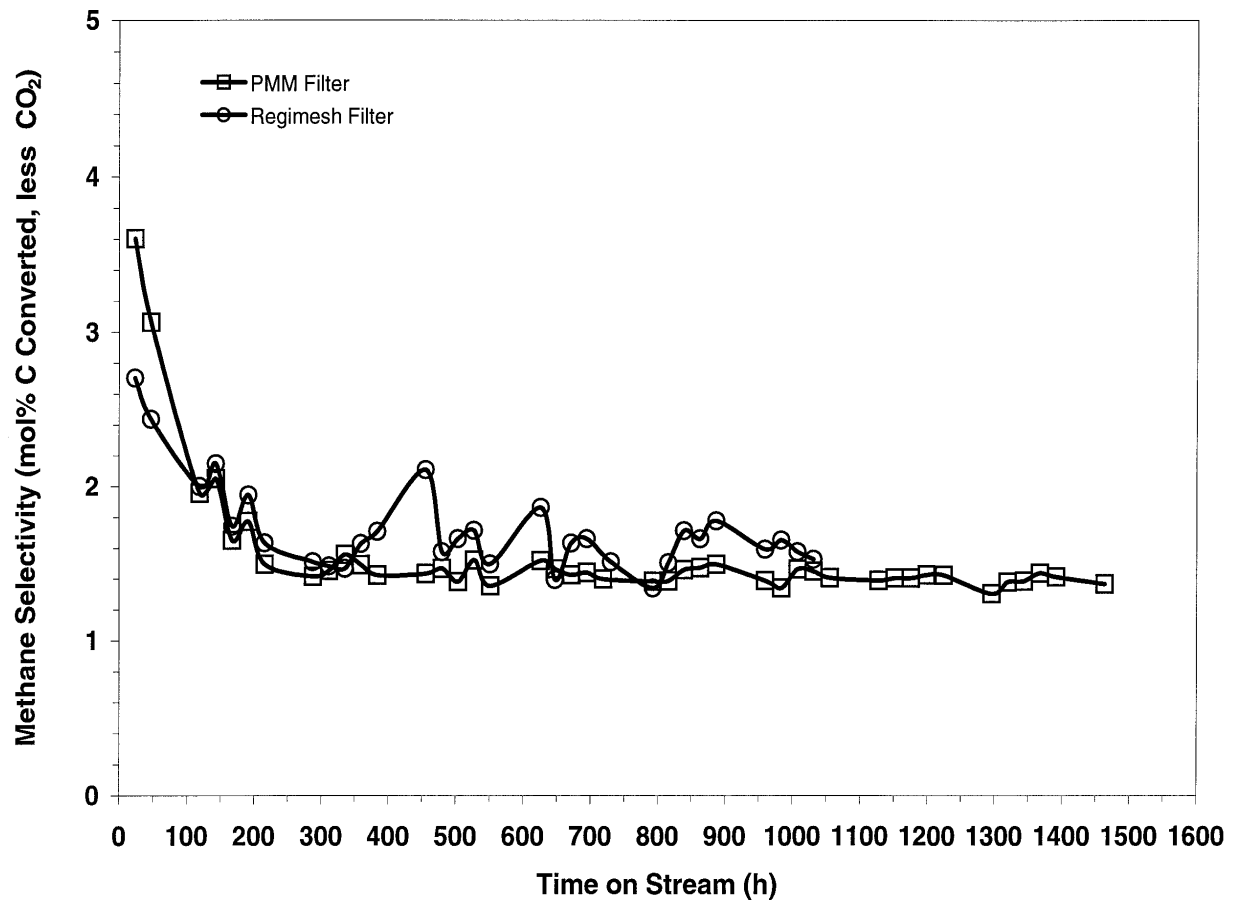Figure 6.   Syngas conversion as a function of time-on-stream.

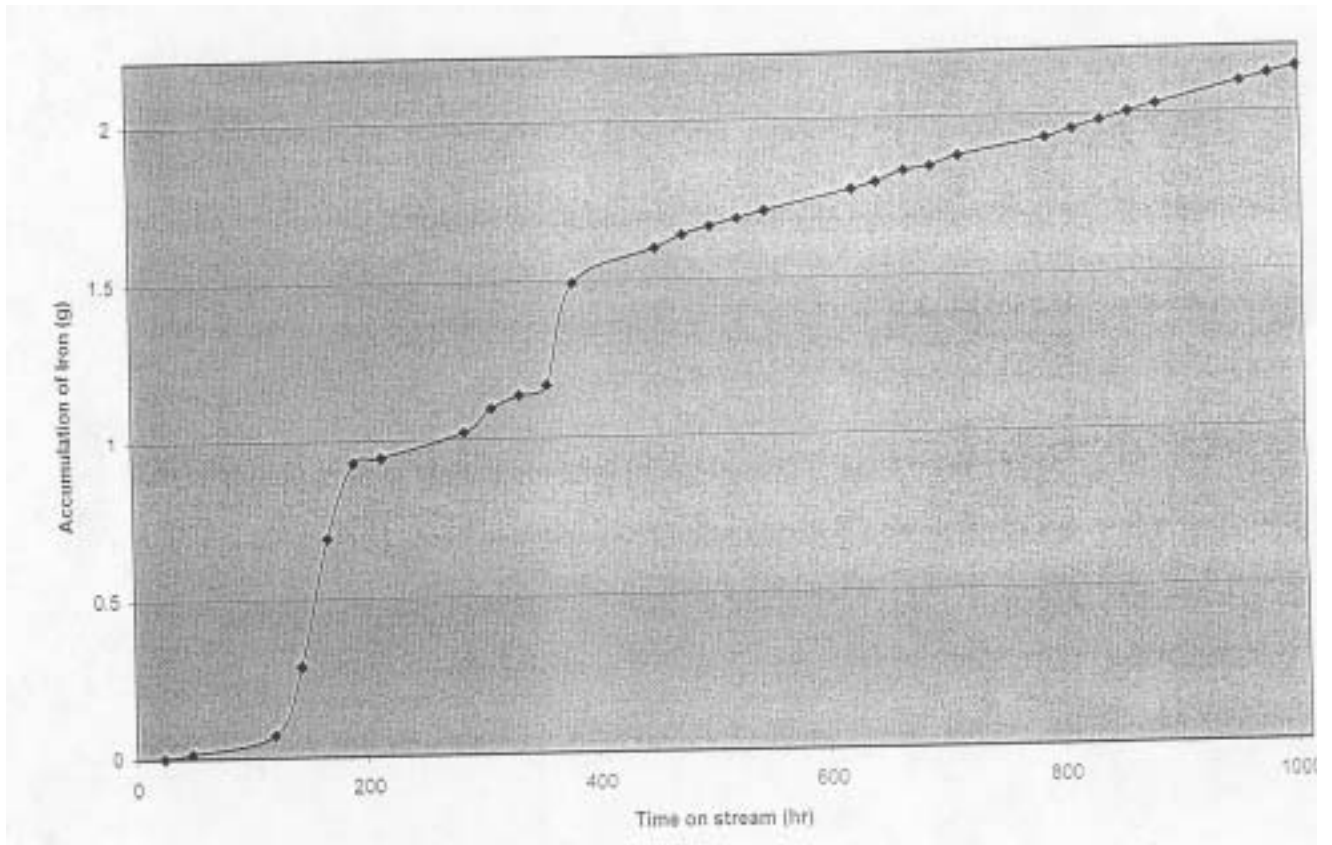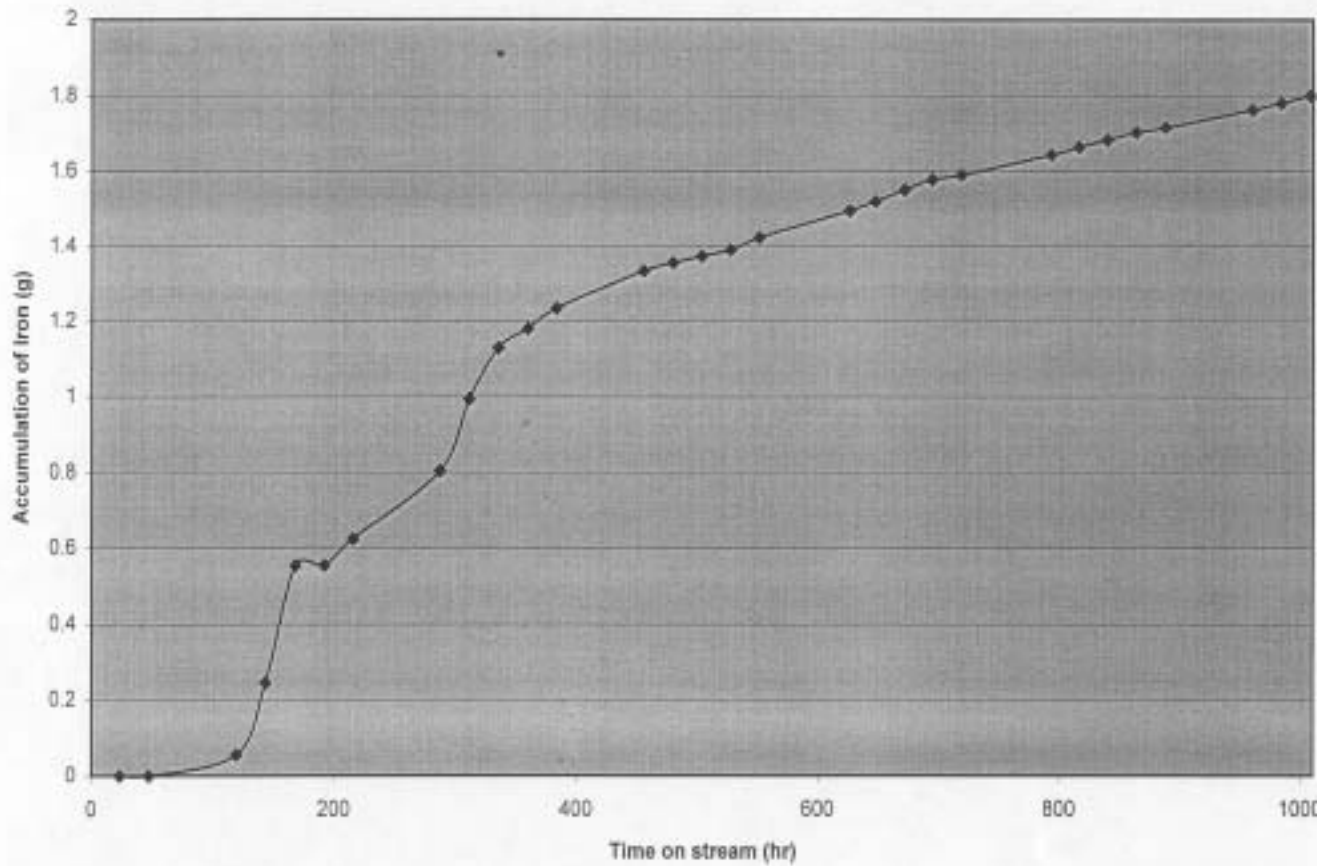Figure 7.   Methane selectivity as a function of time-on-stream.

Figure 8.   Accumulation of iron vs. tine on stream.

Figure 9.   Accumulation of iron vs. time on stream.
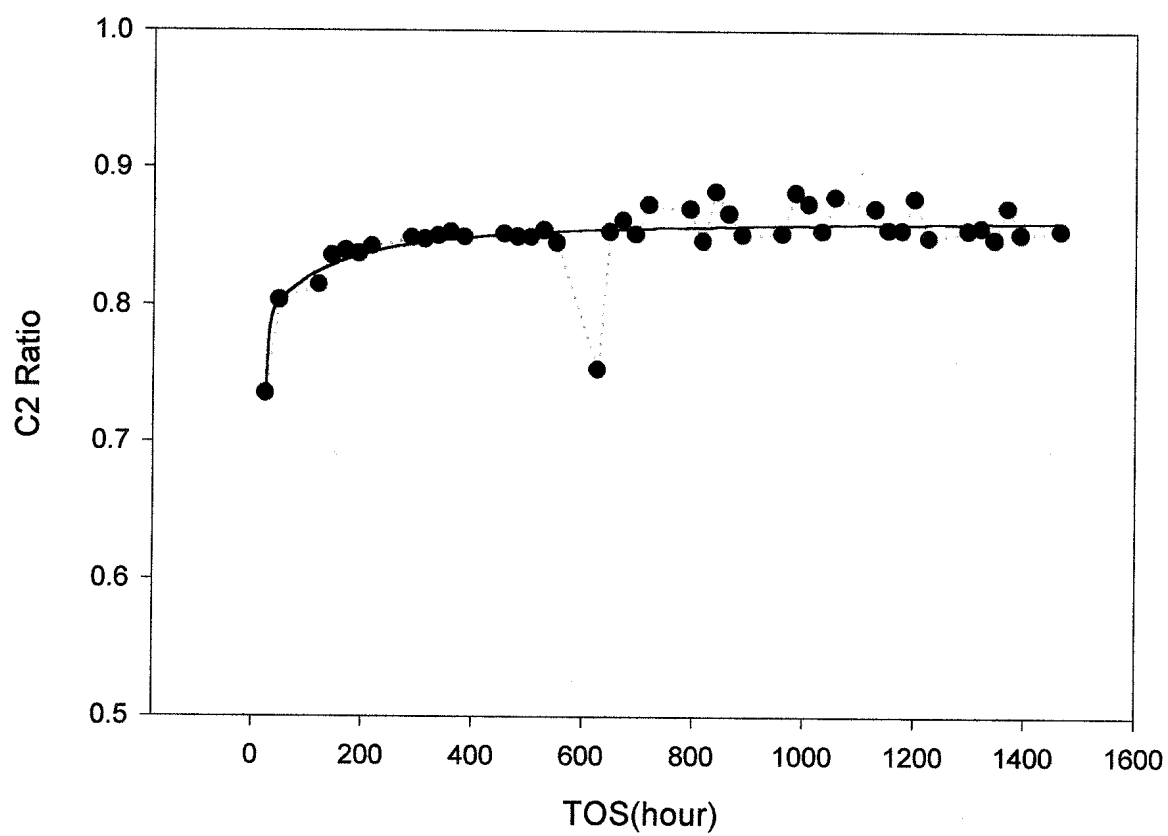
Figure 10.   C$_2$ ratio vs. time on stream.
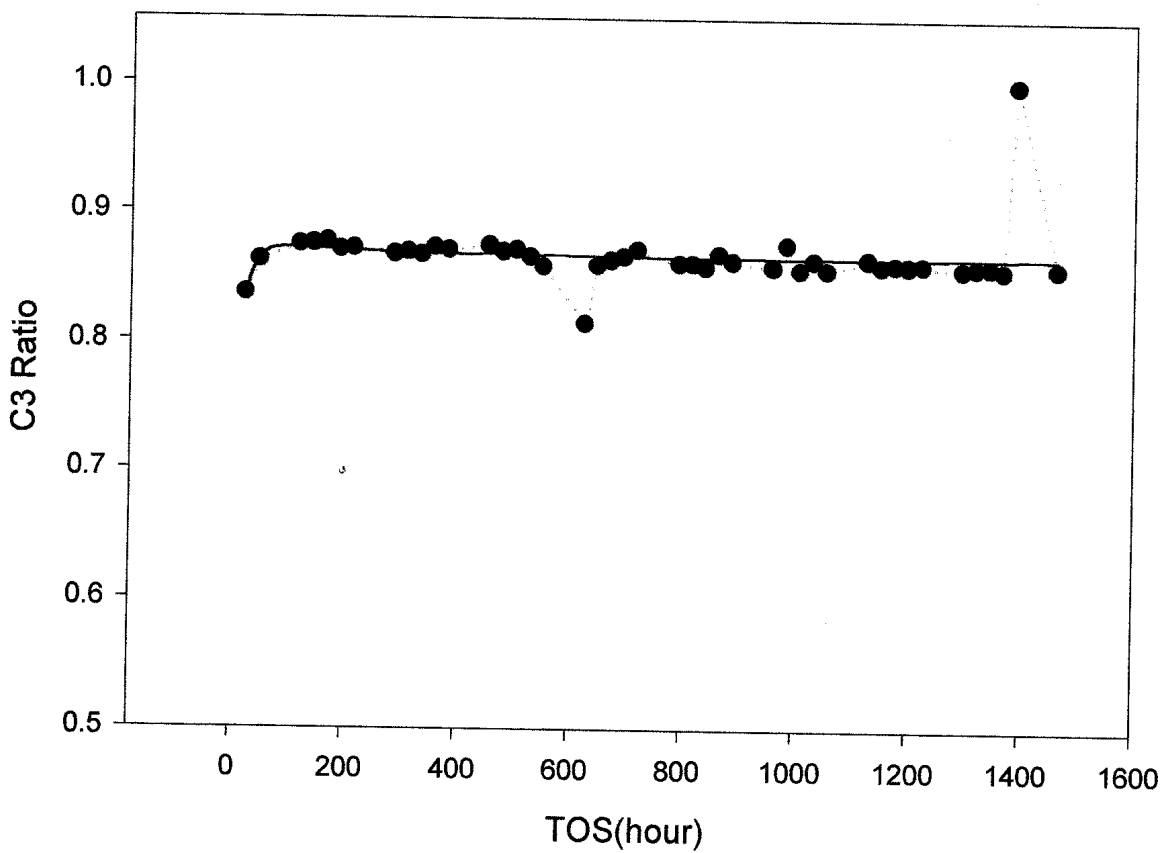
Figure 11. C_3 ratio vs. time on stream.
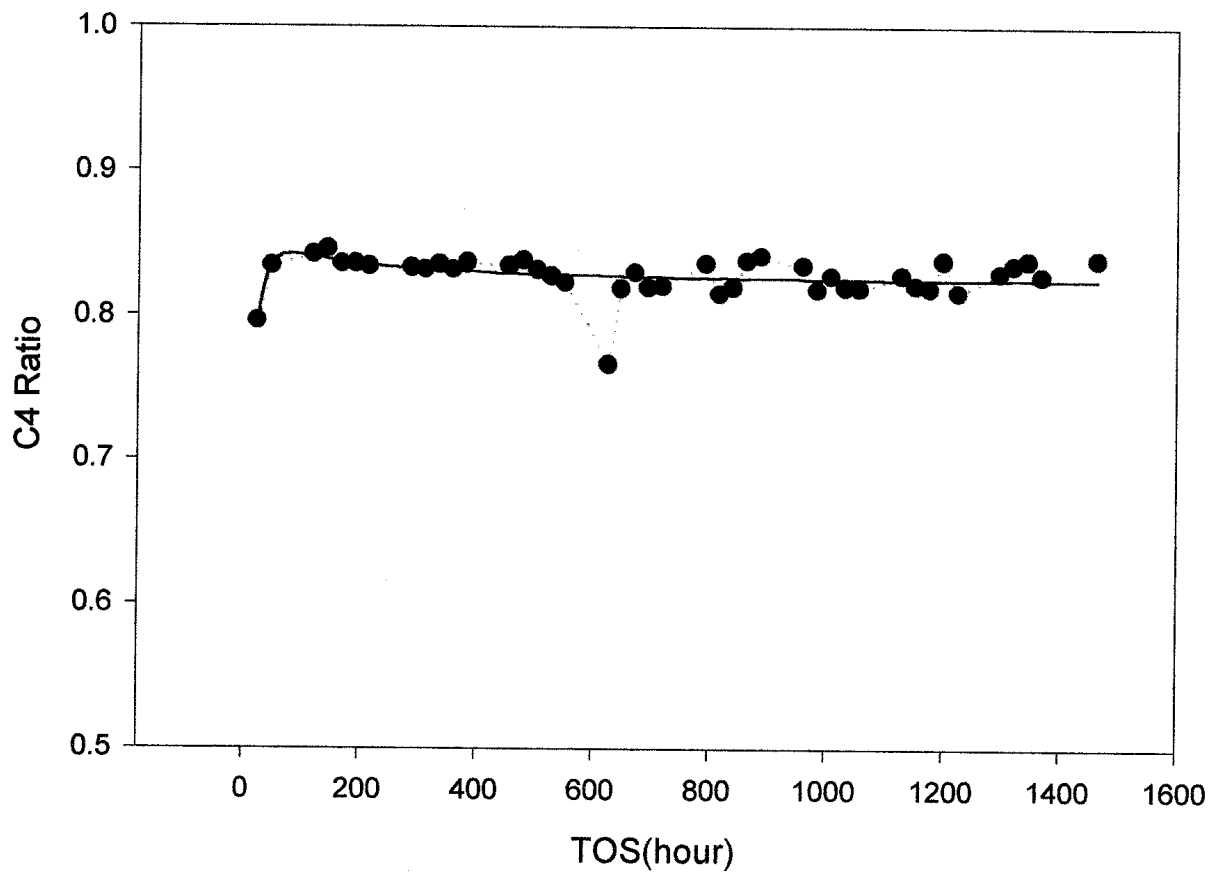
Figure 12. C_4 ratio vs. time on stream.

D. Hi-alpha Catalyst and Special Filter

Today, the marketplace place a premium on FTS diesel but not gasoline; thus, the current view is that the most attractive option is to produce high molecular wight FTS products and then to hydrocrack them to produce high quality diesel fuel. High molecular weight FTS products are not volatile at the usual reaction temperatures and pressure. This requires that liquid products be separated from the catalyst.

The inability to operate the fixed-bed reactor isothermally makes it attractive to use a slurry bubble column reactor. With the slurry reactor, a wax-catalyst separation must be accomplished, either within or external to the reactor.

This report presents the preparation of three of high alpha iron catalysts that can produce large quantities of high molecular weigh FTS products and four filters to be used for wax-catalyst separation within the slurry reactor.

100Fe/4.6Si (Atomic ratio) is prepared by dissolving Fe $(NO_3)_3 \cdot 9H_2O$ (18907.29 g) and tetraethyl orthosilicate (448.76 g) in distilled water, then precipitated with concentrated ammonium hydroxide. The pH of the slurry was >9 . The slurry was filtered. The filter cake was dried at 110°C. The base catalyst was crushed to approximately 60μm and calcined in air at 350°C for 4hr.

The 100Fe/4.6Si bade catalyst was impregnated with the appropriate amount of K_2CO_3 and Cu $(NO_3)_2 \cdot 3H_2O$ to give an atomic composition of 100 Fe/4.6Si/2.0Cu/5K, 100Fe/4.6Si/2.0Cu/7.5K and 100Fe/4.6Si/2.0Cu/10k. The amount of K_2CO_3 and Cu $(NO_3)_2 \cdot 3H_2O$ added will depend on the iron content of base catalyst. Typically the base catalyst is about 68 wt% Fe. For an atomic composition of 100/Fe/4.6Si//2.0Cu/7.5K, 80.05g of 100 Fe/4.6Si was impregnated with 26.4 ml of an aqueous Cu $(NO_3)_2 \cdot 9H_2O$ (17.8289 g Cu $(NO_3)_2 \cdot 9H_2O$ Per 100ml solution). Following the impregnation the catalyst was dried at 110°C with

good mixing. The same procedure was used to add K. It was impregnated with 26.4ml of a K_2CO_3 solution (5.0484 g K_2CO_3 per 50ml solution). The catalyst was dried at 110˚C with good mixing.

Approximately 32.22g of catalyst (100Fe/4.6Si/2.0Cu/5K, 100Fe/4.6Si/2.0Cu/7.5K or 100Fe/4.6Si/2.0Cu/10K), respectively, and 310g Ethylflo 164 oil (C_{30}) were loaded into a 1-liter stirred autoclave reactor. The slurry was treated with carbon monoxide at 40 Lh^{-1} at 1.31MPa pressure; the temperature was then increased to 270ºC at 120ºCh^{-1} and held at this temperature for 24h. The temperature was reduced to 230ºC. CO flow was decreased and hydrogen flow gradually increased until the total flow was 3 SL/gFe/hr. The ratio of H_2 and CO is 0.7.

These catalysts (100Fe/4.6Si/2.0Cu/5K, 100Fe/4.6Si/2.0Cu/7.5K and 100Fe/4.6Si/2.0Cu/10K) have very low methane production and high alpha value (see Table 1). That means these catalyst produce a large amount of high molecular weight FTS products (reactor wax).

The main purpose for running these catalysts was to test whether these four filters possess sufficient ability to remove reactor wax from reactor, and whether these filter have enough ability to separate reactor wax from iron catalyst. Running conditions and filter specification are given in Table 2.

Carbon monoxide conversion for each high-alpha catalyst is shown in Figure 1. The 100Fe/4.6Si/2.0Cu/7.5K catalyst had the highest conversion. The catalysts went through an induction period in which the conversion increased from about 10 to 43 %. These high-alpha catalysts have sufficient activity at 230ºC for FTS.

The alkene selectivities, as a function of carbon number, are similar for the three high-alpha catalysts (Figures 2-4). These three high-alpha catalysts produce more alkene than the lower atomic K% catalysts.

During 1000 hrs. of run time, the amounts of reactor wax removed from the reactor are 1800g, 2000g, 1500g and 1200g for 100Fe/4.6Si/2.0Cu/5K, 100Fe/4.6Si/2.0Cu/7.5K, and 100Fe/4.6Si/2.0Cu/10K catalysts, respectively (Figures 5-8). The reactor wax removed from the reactor depend on potassium content of the catalyst, and during this time does not depend on the filter surface area and pore size. These filters, compared with the 2 micro sinter metal filters (used from 1991 until now for removing reactor wax) posses ability to remove reactor wax for high-alpha catalysts. For example, during a 100 hr run, using 100Fe/4.6Si/2.0Cu/10K high-alpha catalyst, we were able to remove only 5g of reactor wax form the CSTR but with these special filters we can remove about 120g.of reactor wax from CSTR each day. Filtration data for these filters are shown in Table 3.

For special filter, 1.8-2.1 g of iron (about 8–9.6 % of iron) is lost after 1000 hr running (Figures 9 and 10). Much of this iron (20-30%) is lost during the period of cake build-up and can be eliminated by engineering design.

In summary, these catalysts have sufficient activity to merit consideration for producing high molecular weight FTS products and the preliminary data using the filters suggest that they may have sufficient ability to remove reactor wax form CSTR.

Table 1			
CH$_4$ Selectivity and Alpha Value			
Run No.	Average CH$_4$ Selectivity	α_1	α_2
Bao035	1.60	0.68997	0.91438
Bao036	1.50	0.73293	0.91468
Bao041	1.50	0.71138	0.92363
Bao043	1.70	0.76618	0.90876

		Table 2					
		General Information					
Run No.	Catalyst	Reactor Temp, °C	Reactor Pressure (psig)	Filter Length (inch)	Filter Diameter (inch)	Filter Surface Area (inch)^2	Pore Size
Bao035	100Fe/4.61Si /2.0Cu/5K	230	175	0.5	1	1.57	2μ
Bao036	100Fe/4.6Si/ 2.0Cu/5K	230	175	0.5	1	1.57	18μ
Bao041	100Fe/4.6Si/ 2.0Cu/7.5K	230	175	1.0	1	3.14	18μ
Bao043	100Fe/4.6Si/ 2.0Cu/10K	230	175	1.5	1	4.71	18μ

	Table 3	
Filtration of Bao041 (Filter L = 1"; reactor pressure = 175 psig; pressure of rewax trap set = 125 psig)		
Number	Time Sample Taken (min.)	Amount of Wax Removed (g/5 min)
1	5	2.5
2	5	4.32
3	5	2.99
4	5	5.35
5	5	2.77
6	5	1.69
7	5	2.70
8	5	2.25
9	5	3.60
10	5	1.64

Figure 1. CO conversion Vs TOS at 230 ^{0}C
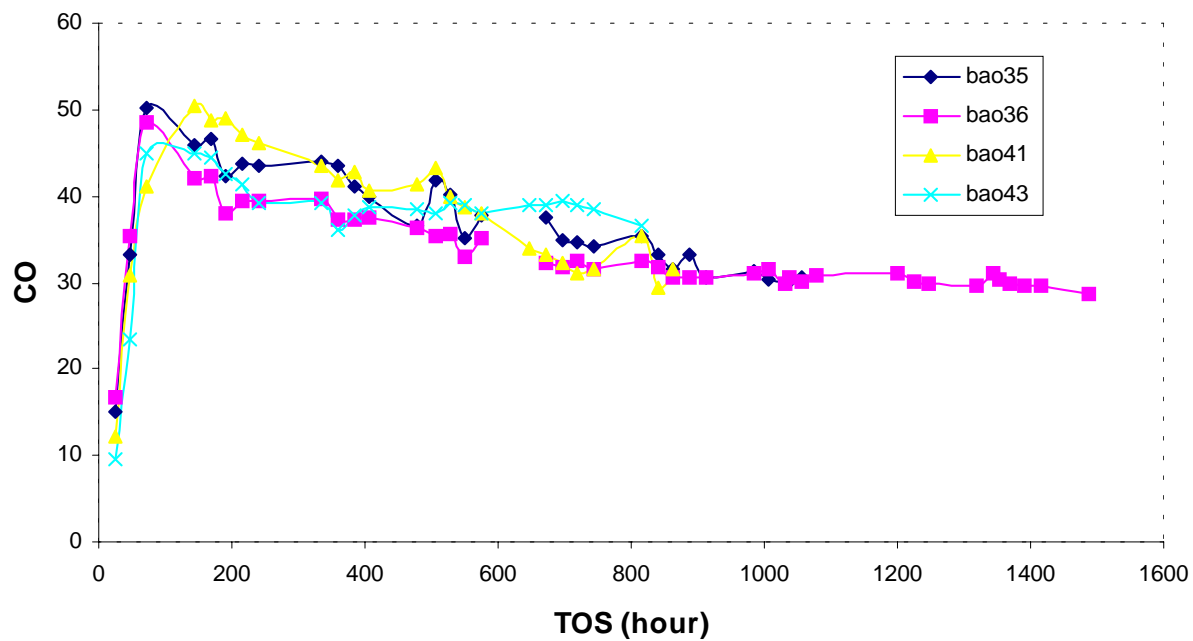
Figure 2. olefin/(olefin+paraffin) Vs.carbon number for the catalyst containg 5%K(Bao035
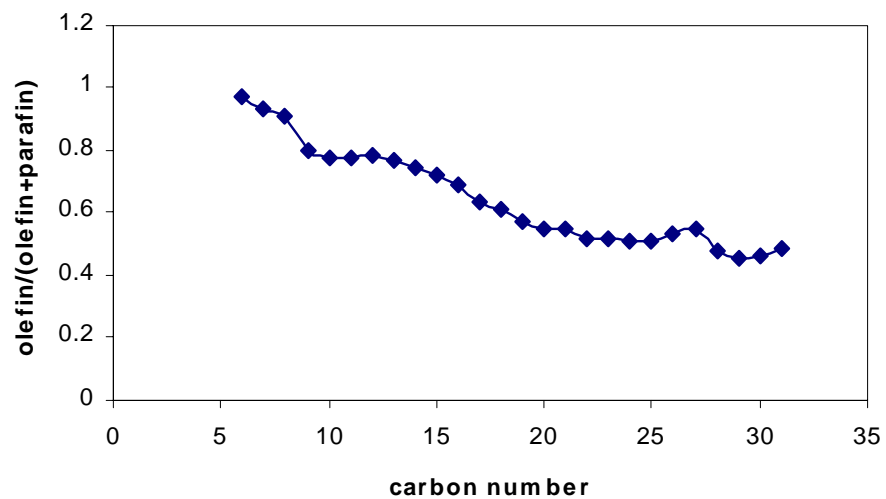
Figure 3. olefin/(olefin+paraffin) Vs. carbon number for the catalyst containg 7.5%K (Bao041)
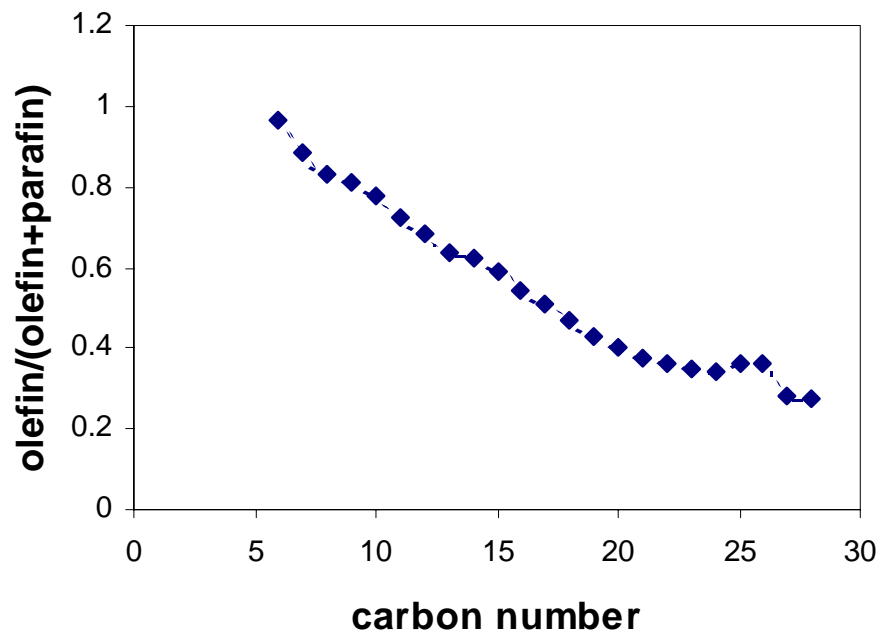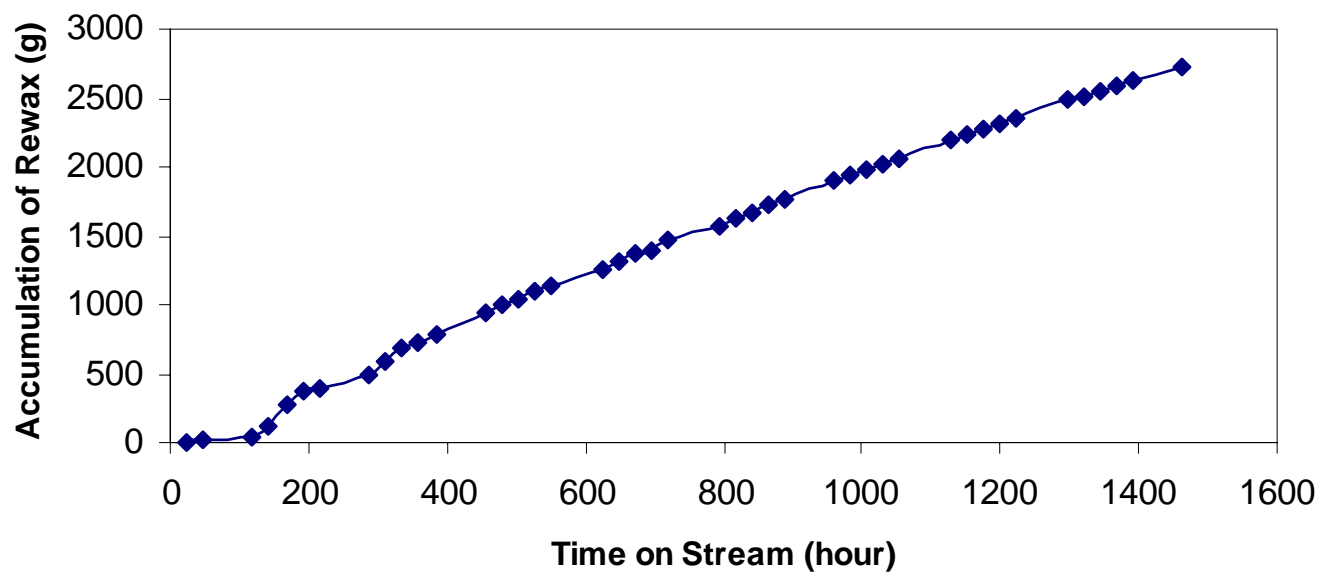
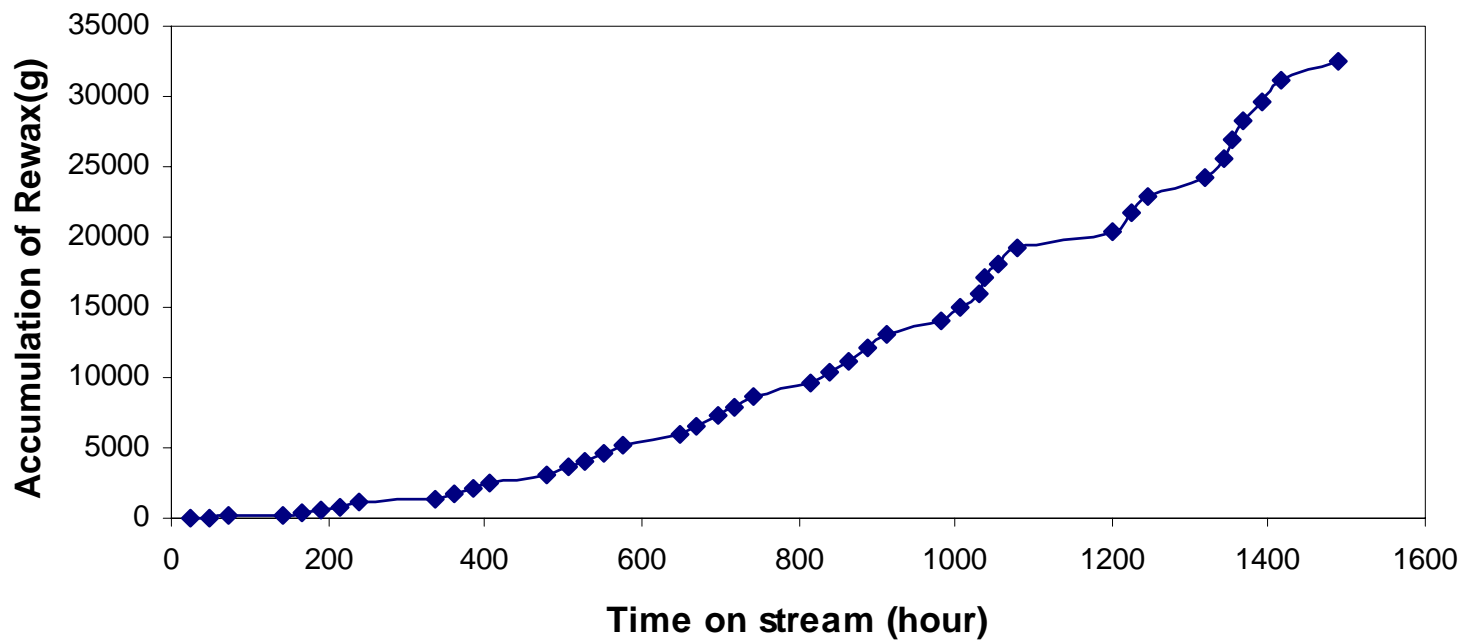**Figure 4. olefin/(olefin+paraffin) Vs. carbon number for catalyst containg 10%K (Bao043)**
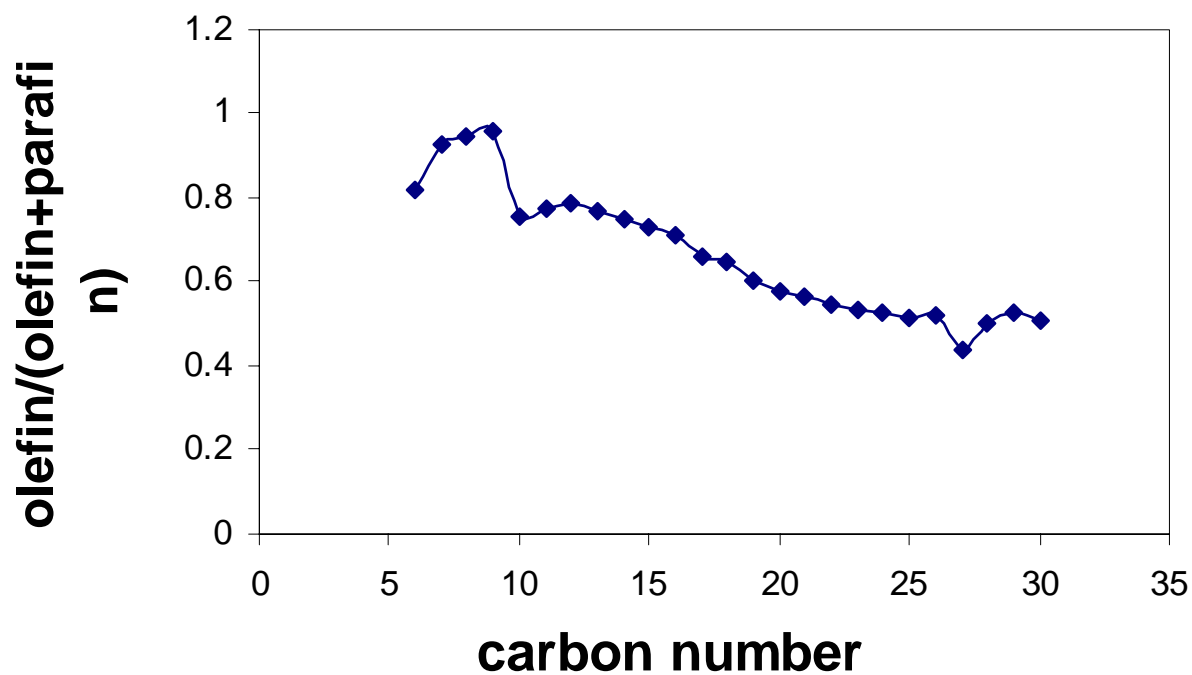
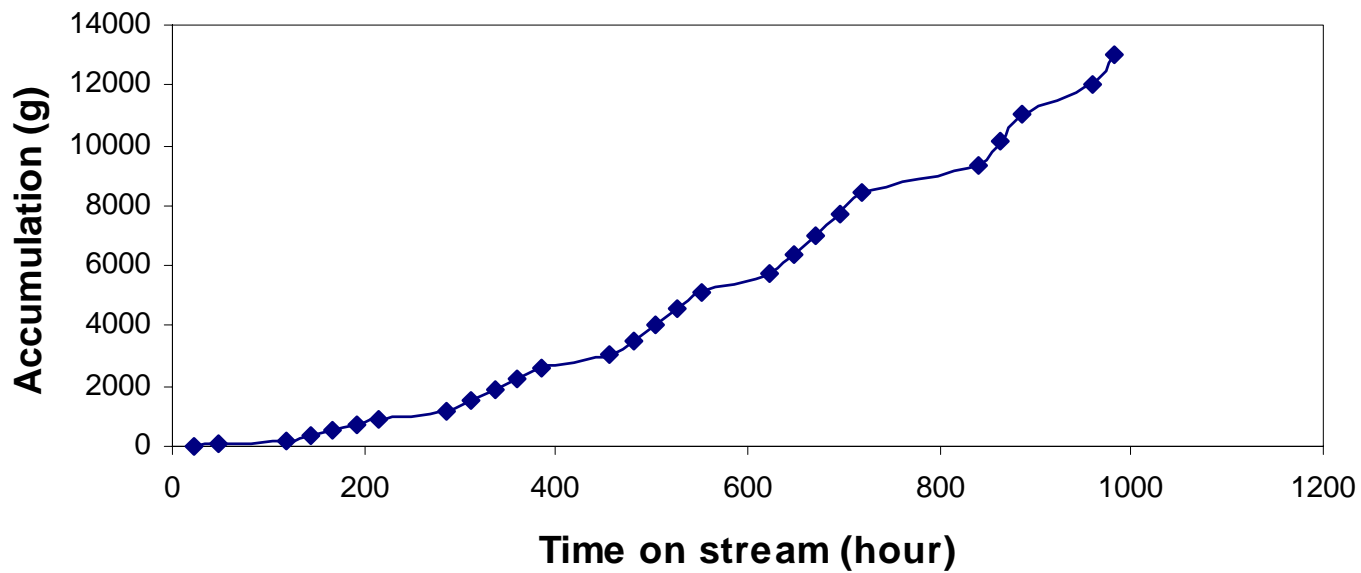**Figure 5 Cumulation Rewax Removal Vs. Time on stream for 100Fe/4.6Si/2.0Cu/5K Catalyst**
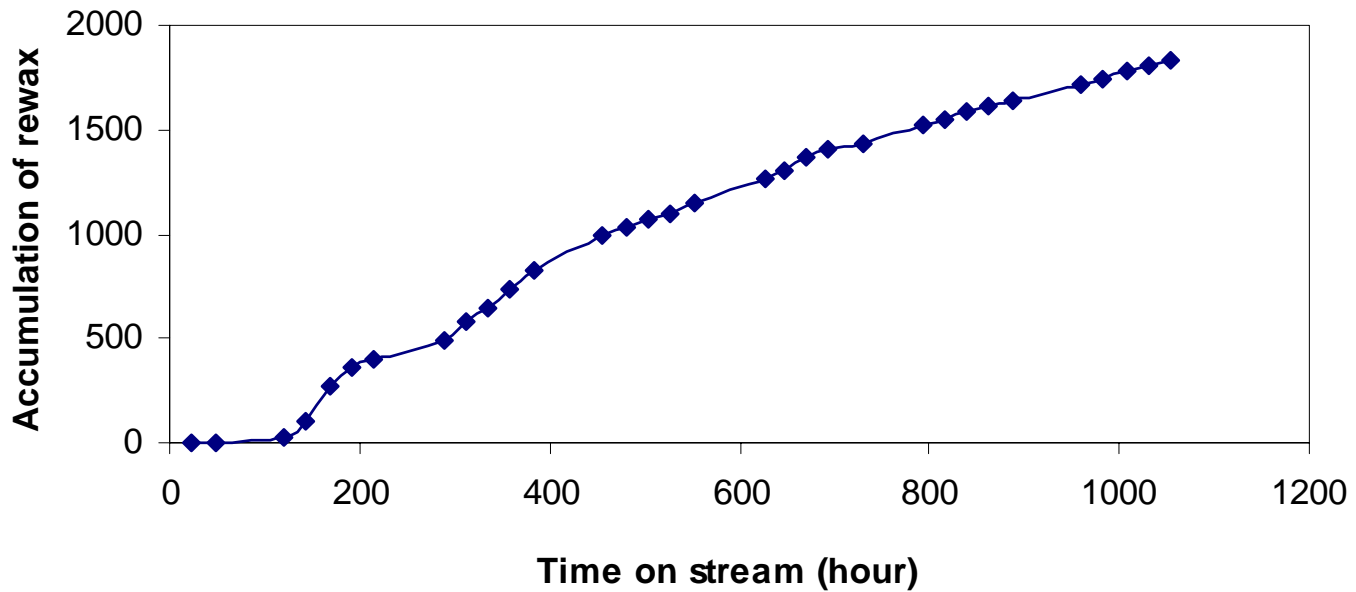
Figure 6 Cumulation Rewax Removal Vs. Time on stream for 100Fe/4.6Si/2.0Cu/5k Catalyst

**Figure 7. Cumulation Rewax Removal Vs.Time on stream
for 100Fe/4.6Si/2.0Cu/7.5K**

Figure 8. Cumulation Rewax Removal Vs.time on stream for 100Fe/4.6Si/2.0Cu/10K

Figure 9 Cumulatial of iron Vs. time on stream for 100Fe/4.6Si/2.0Cu/5K Catalyst
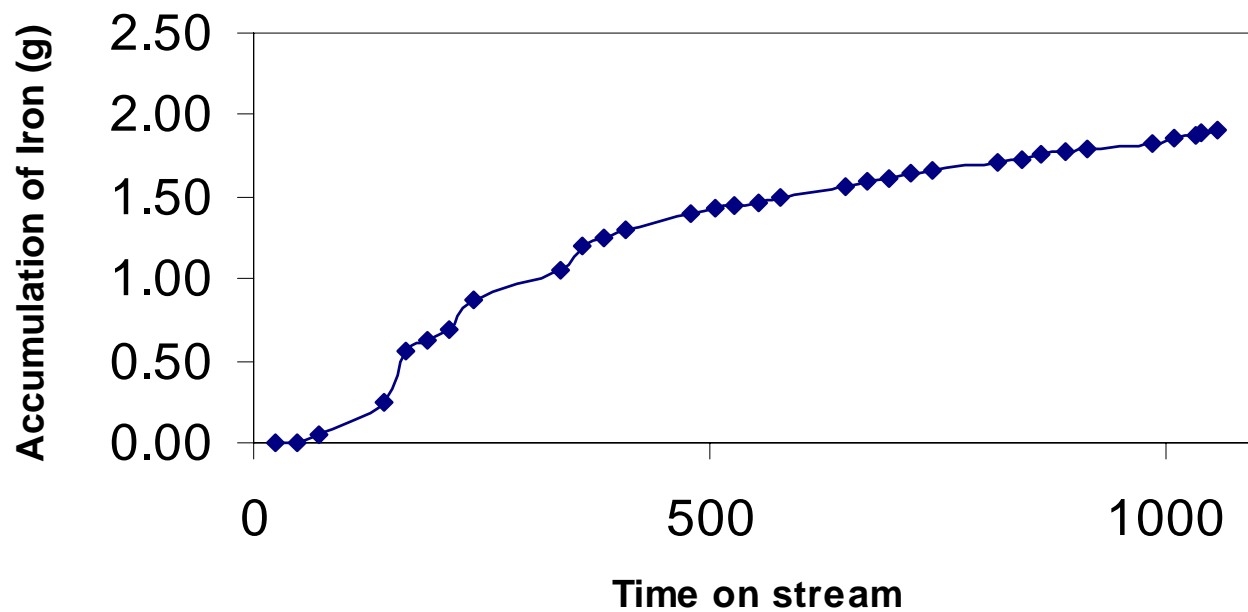
Figure 10 Cumulation of Iron Removal vs. time on stream for 100Fe/4.6Si/2.0Cu/5K Catalyst