Task 3. Catalyst Characterization

The objective of this task is to obtain characterization data of the prepared catalysts using routine and selected techniques.

No scheduled or further activity to report.

Task 4. Wax/Catalyst Separation

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

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.

Table 1

Summary of Filtration with Iron and Cobalt Catalysts

Alpha	**Iron, Unsupported**	**Iron, Supported**	**Cobalt, Supported**
Low (< ≈ 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

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 200ºC). 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 *μ*m 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 (130ºC). 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 130ºC 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).

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 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).

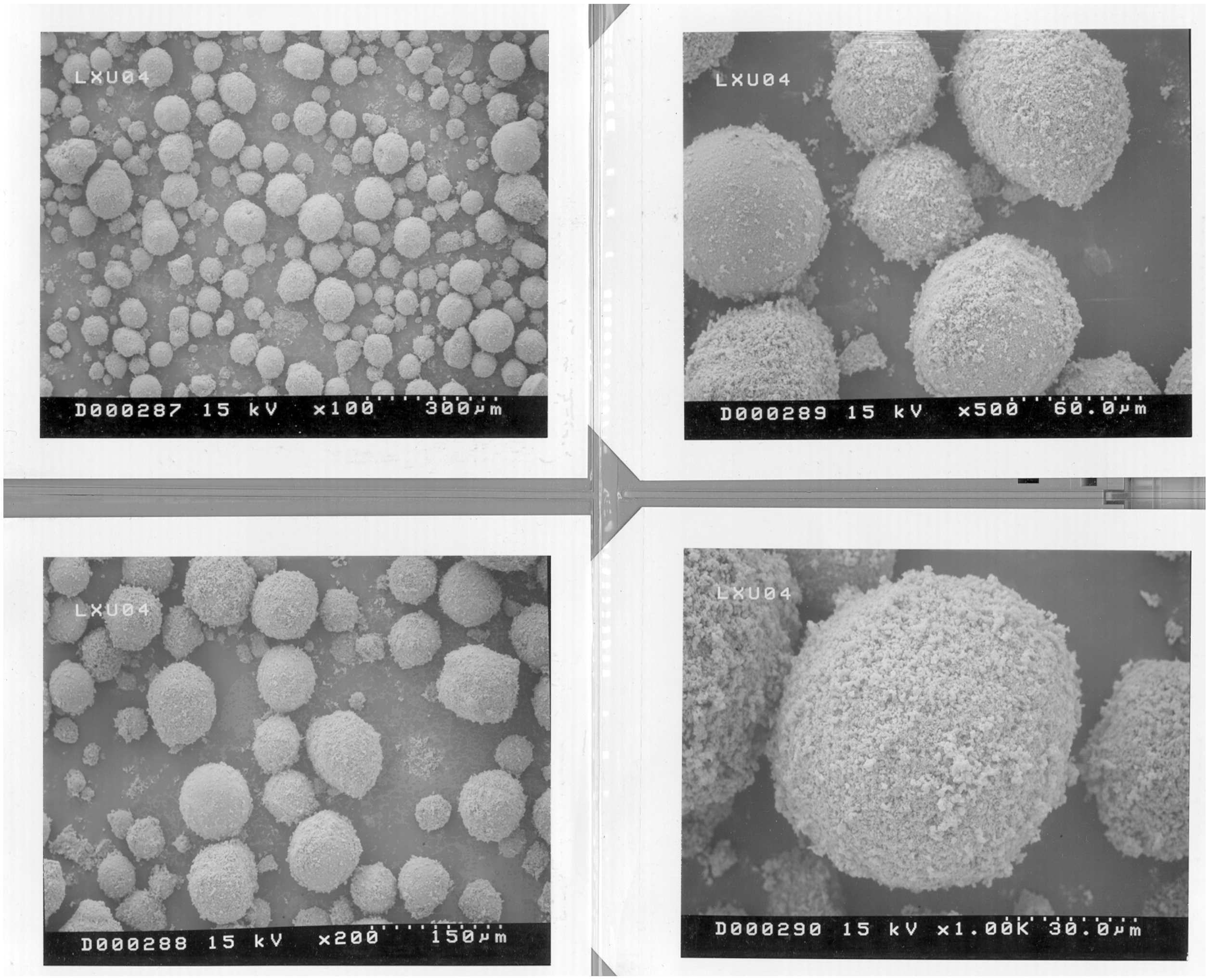


Figure 1. Scanning electron microscope pictures of spray-dried, precipitated, iron catalyst at four increasing magnifications (x100, 200, 500, 1,000; size scale indicated in picture).

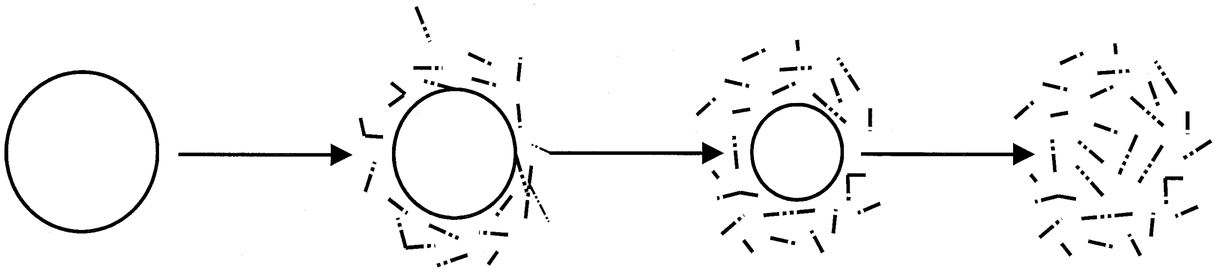


Figure 2. Schematic of attrition of spray-dried precipitated iron catalyst by a gradual decrease in size of the primary particle.

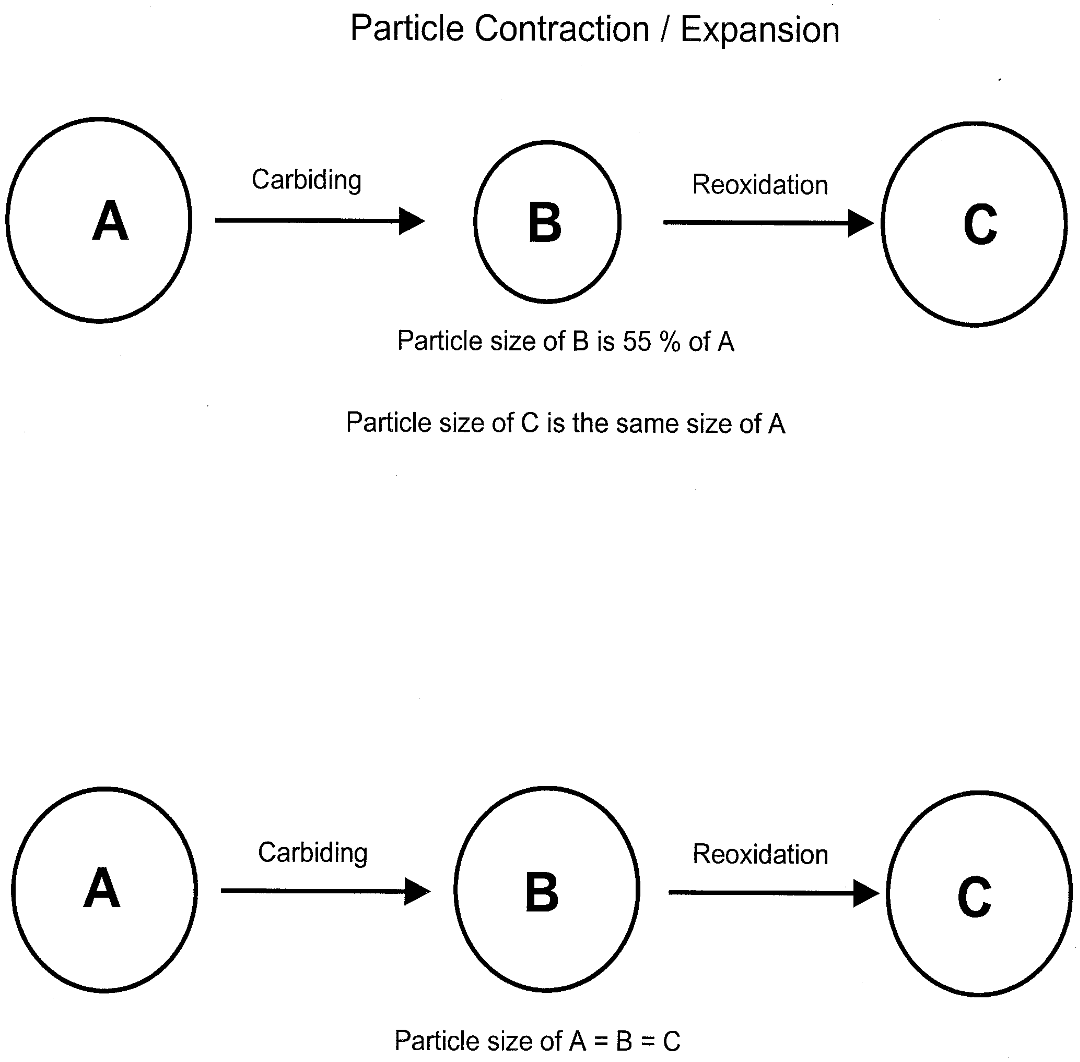


Figure 3. Schematics of size changes in activation of an iron catalyst and then reoxidation for: (top) whole particle charges size and (bottom) whole particle remains same size and individual units of particle changes size.

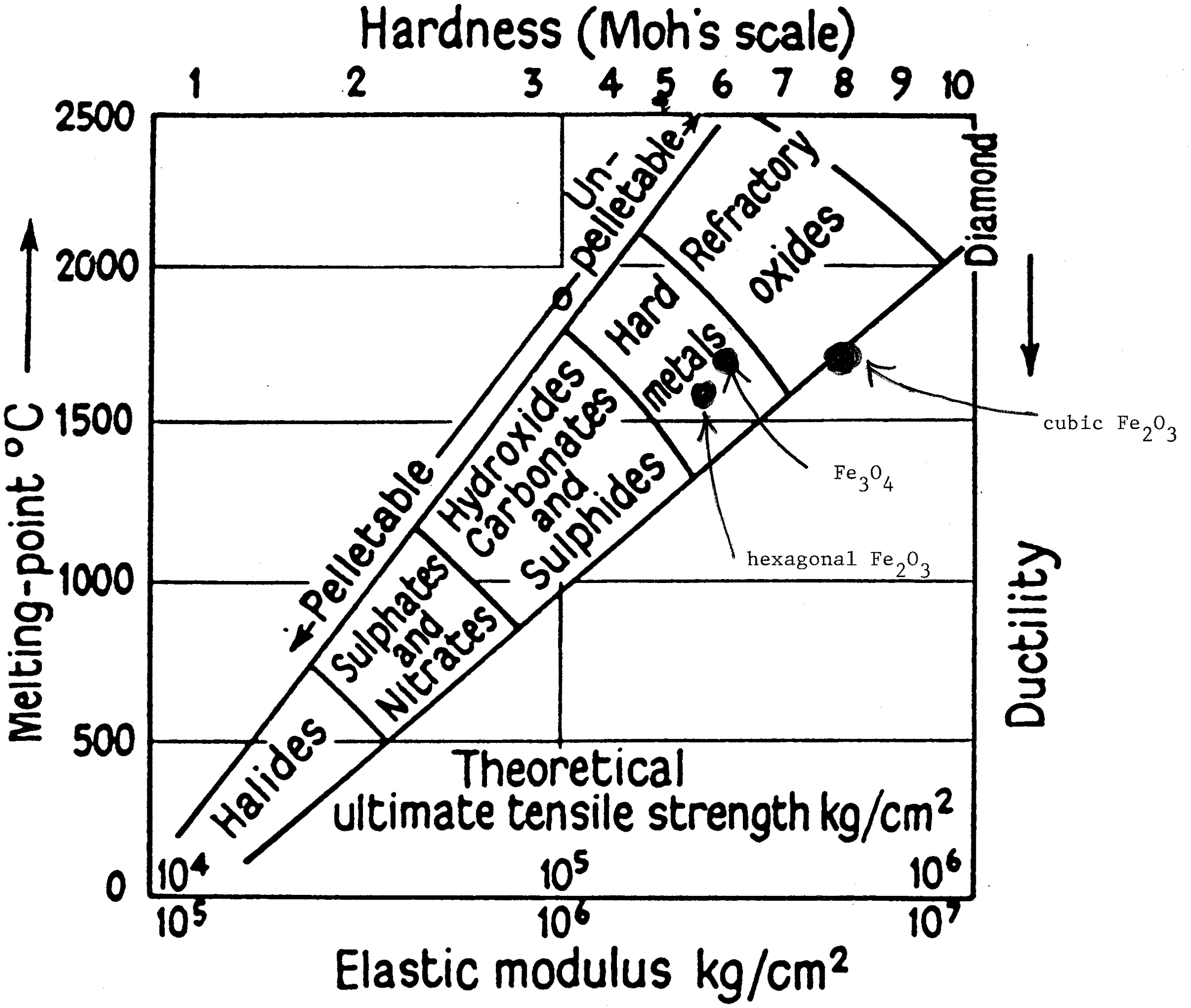
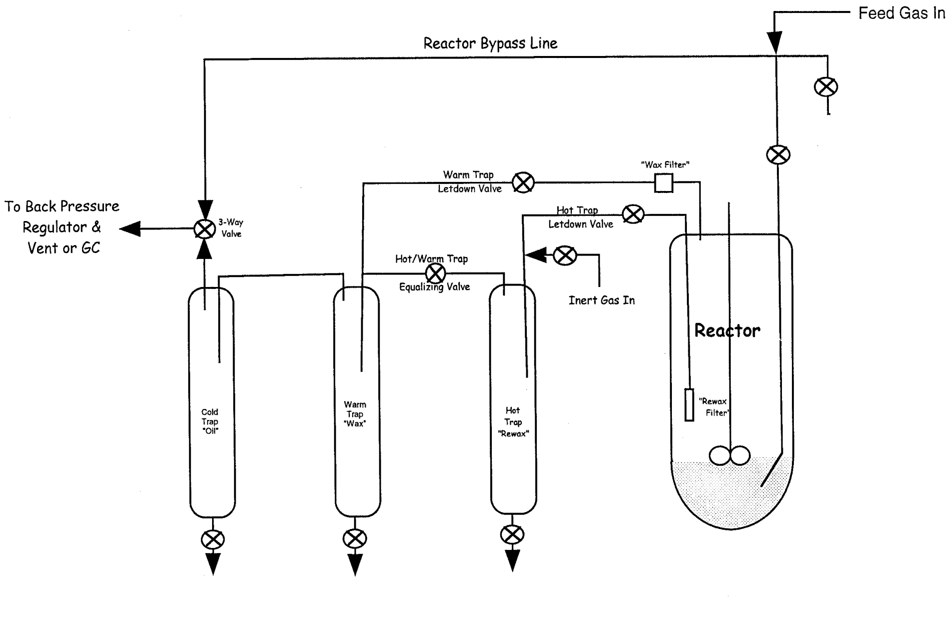
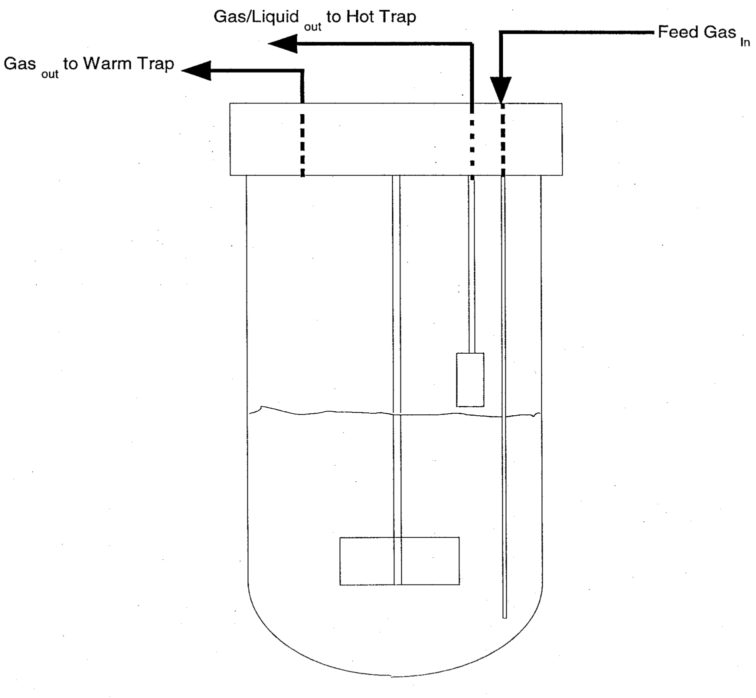


Figure 4. Relationship of physical properties and pelletability of compound classes.



FTS Reactor System



FTS Reactor

Figure 5. Schematic of CAER reactor system (top) and CSTR (bottom).

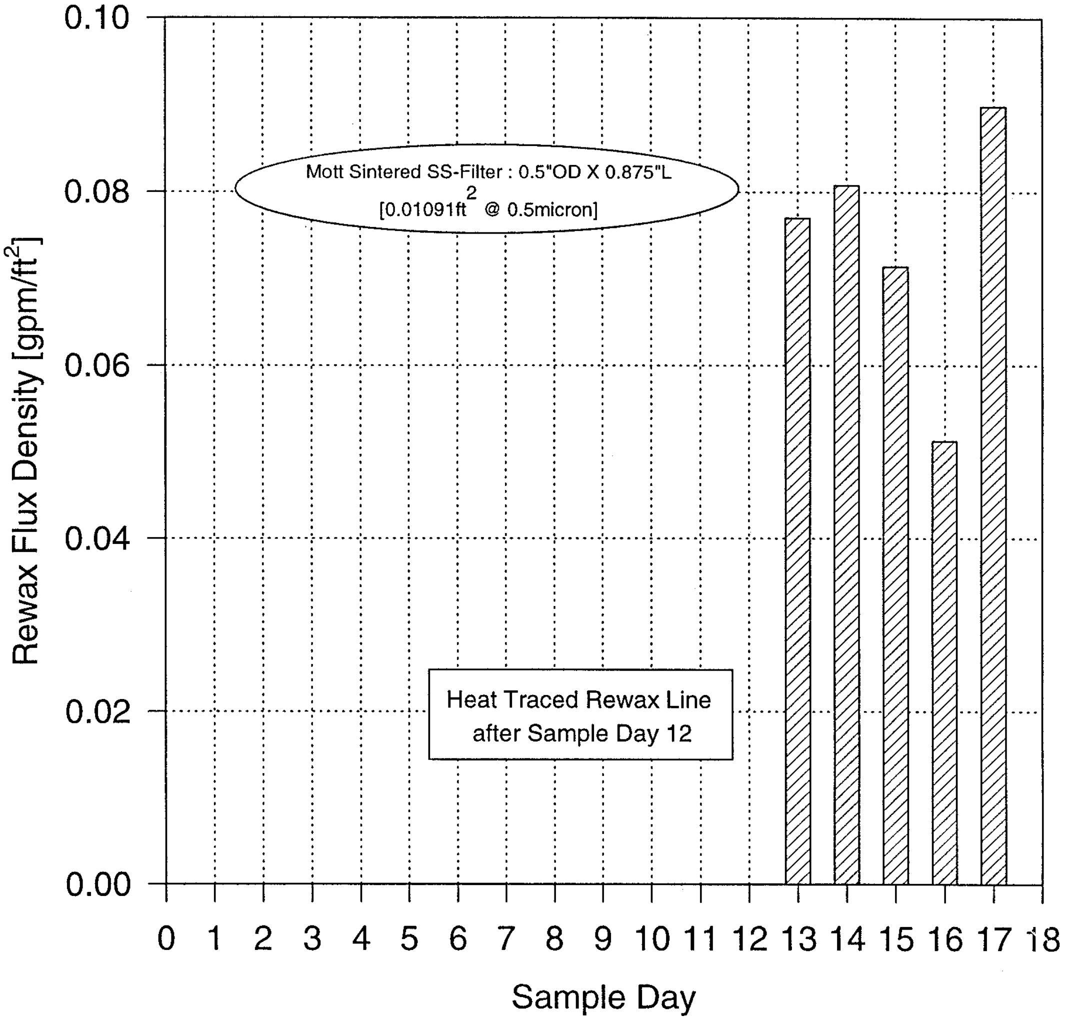


Figure 6. Rewax flux density vs. sample day for run LGX263$_{R7}$ (100Fe:4.60Al/2.72Cu/0.00K).

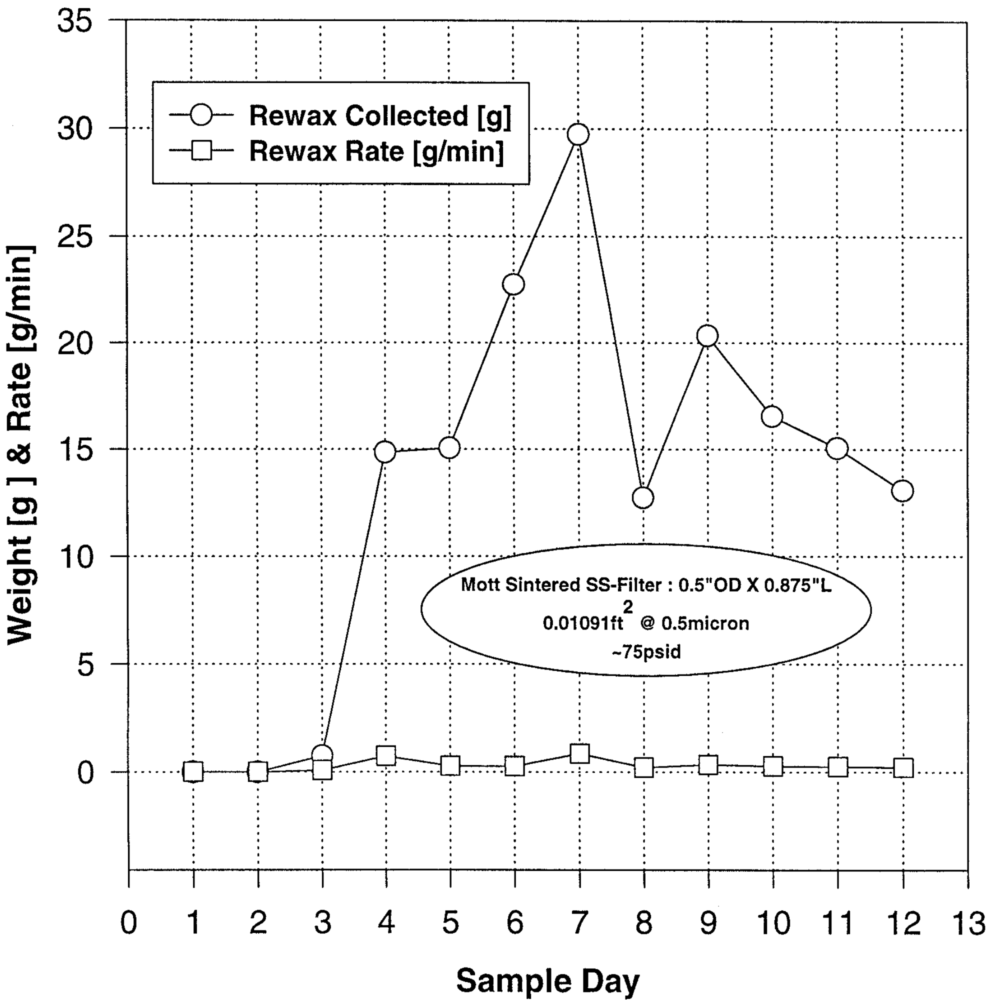


Figure 7. Rewax withdrawal weight and rate vs. sample day for run LGX266$_{R7}$ (3.0wt.% Cu, 5.0 wt.% K, T_{syn} = 230°C).

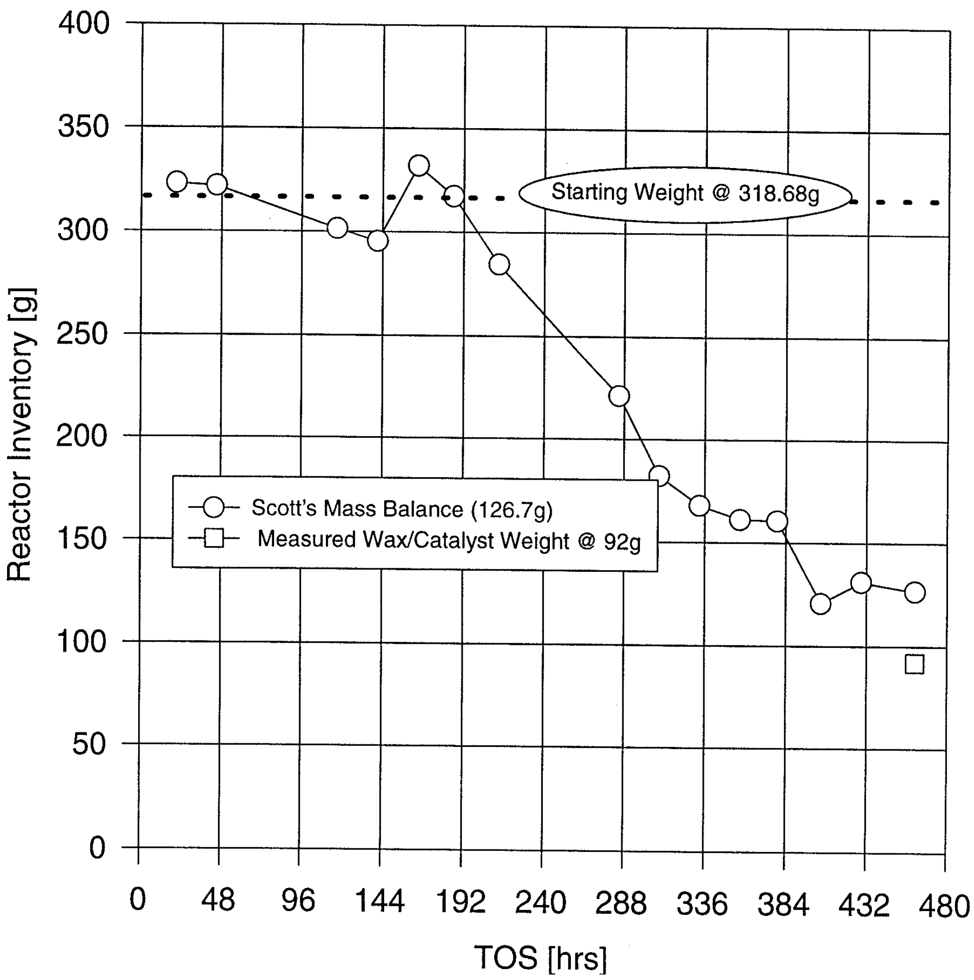


Figure 8. Predicted reactor inventory vs. time-on-stream for run LGX267$_{R1}$.

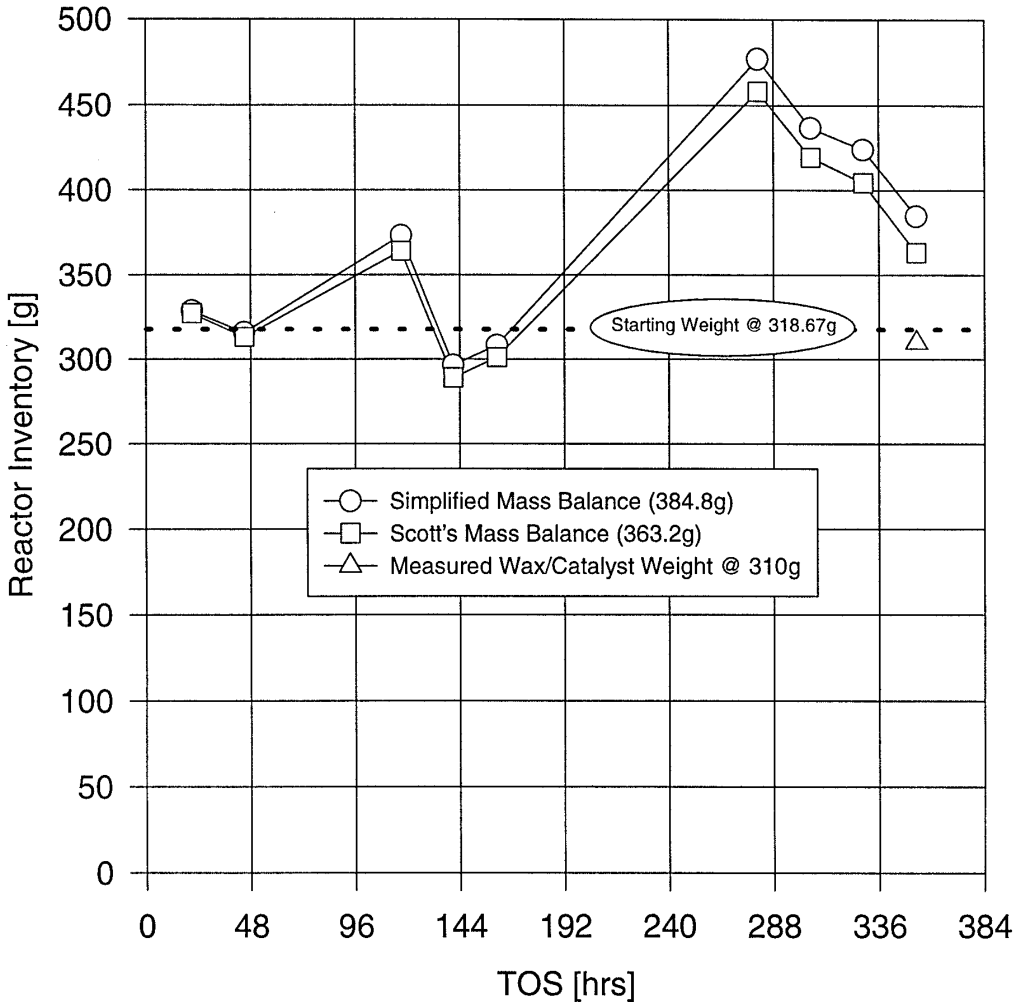


Figure 9. Predicted reactor inventory vs. time-on-stream for run $LGX270_{R4}$.

Task 5. Oxygenates

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalsyts.

An HP G-2350A gas chromatograph with an Atomic Emission Detector (AED) has been purchased in April 1999 at no cost to this project. This instrument has an oxygen channel which will detect only compounds which contain oxygen. This channel in combination with the carbon channel will allow oil samples to be screened for small concentrations of oxygenates.

Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

No scheduled or further activity to report.

Task 7. Co Catalyst Preparation

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

No scheduled or further activity to report.

Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

A. Ru, K, Pt, Re promoted cobalt silica catalysts

Davisil silica gel 644 produced by W R Grace was used as support material. Particle size of silica gel is 100-200 mesh, surface area is $300m^2/g$ and pore volume is $1.15cm^3/g$. Incipient wetness impregnation technique was used to prepare the catalyst. 2kg of silica gel was impregnated by cobalt nitrate solution and then dried by air in a fludized vessel. Three steps of impregnation was carried out to get 15% cobalt loading.

Ruthenium, potassium, platinum and rhenium promoted cobalt silica catalyst was prepared by incipient wetness impregnation also and precursor used were: ruthenium nitrosylnitrate, potassium carbonate, tetramineplatinum nitrate and rhenium oxide respectively. For each promoter, four catalysts with different metal loadings were prepared. Ruthenium loadings are 0.2%, 0.5%, 1.0%, 2.0% (weight percent). To platinum and rhenium prompted catalysts, Pt:Co and Re:Co atomic ratios are the same as Ru:Co atomic ratios in ruthenium promoted catalysts. Potassium loadings of Co-K/SiO_2 catalysts are: 0.5%, 1.5%, 3.0% and 5.0% (weight percent) respectively. All promoted catalysts were dried in a rotary evaporator and then calcined at 400^0C for 4hrs.

B. Cobalt silica catalysts with different cobalt loading

Davisil 952 silica gel by W R Grace was used as support material, particle size 60-80 mesh, surface area 309m^2/g and pore volume 1.61cm^3/g. Five catalysts with different cobalt loadings(weight percent 5%, 10%, 15%, 20% and 25%) were prepared by incipient wetness technique using cobalt nitrate as precursor, multiple impregnation steps were used to prepare high cobalt loading catalysts. All the catalysts were dried in a rotary evaporator and followed by calcination at 400^{0}C for 4hrs.

C. Preparation of boron-modified Co/TiO_2 catalysts

A series of boron-modified TiO_2 carriers (0.05, 0.10, 0.50 and 1.00 wt% boron) were prepared by pore volume impregnation of Degussa P-25 TiO_2 (72% anatase, 45 m^2/g, calcined at 673 K for 6 h) with solutions containing various amounts of boric acid (Aldrich). Samples containing 1.00 wt% boron was prepared by double impregnation of the TiO_2 using one-half the required amount of boron for each impregnation step. Samples were dried at 393 K for 4 h between impregnation steps. All samples in the series were finally dried at 393 K for 16 h and then calcined in air for 6 h at 693 K.

Cobalt (10 wt%) was deposited on the boron-modified (or boron-free) TiO_2 carrier by pore volume impregnation with cobalt nitrate (Alfa) solution. Samples were dried at 393 K for 16 h and calcined at various temperatures before they were used.

D. Preparation of Ru-modified Co/TiO_2 catalysts

Co-Ru/TiO_2 catalysts were prepared by impregnating pretreated (10 wt%) Co/TiO_2 with solutions containing different amounts of ruthenium nitrosylnitrate (Alfa). The samples were dried at 393 K for 16 h and calcined at various temperatures before they were used. The ruthenium contents were 0.05, 0.10, 0.20 and 0.40 wt%, respectively, corresponding to an atomic Ru/Co ratio of 0.00292, 0.00583, 0.0117 and 0.0233.

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

No scheduled for further activity to report.

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

No scheduled or further activity to report.

Task 11. University of California, Berkeley (Subcontract)

The objective of this task is the characterization of the structure and function of active sites involved in the synthesis of high molecular weight hydrocarbons from CO and H_2 on multi-component catalysts based on Fe as the active component.