

## **SEPARATION OF IRON CATALYSTS FROM FISCHER-TROPSCH WAX**

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### **ABSTRACT**

We disclose a new concept (patent pending) for continuous magnetic separation of magnetic particles from viscous flows. It was adapted from a novel method for breaking tight emulsions (US Patent 5,868,939, February 9, 1999) and developed in room temperature separation of CO-activated iron catalysts from a fluid which simulates Fischer-Tropsch (FT) wax properties at 260 °C. The method was confirmed using a proprietary slurry of iron catalyst in molten FT wax. A high concentration catalyst-laden slurry is forced to flow through a chamber containing vertically erected magnetized rods. The catalyst particles are captured from flow around the rods by long range magnetic forces. The particles are forced down the rods by slurry flow and exit the chamber as a concentrated stream at the bottom. A continuous stream of molten wax with diminished catalyst concentration flows from the top of the separation chamber. The method is suitable for preparation of slurries of micron sized particles or aggregates of nm sized particles with concentration in the nominal 0.1 Wt.% range. Subsequent separation using HGMS has produced slurries in the 100-500 ppm range. Summary results are presented for a modification of this method operating at the rate of 50 barrels per day in continuous separation of concentrated slurries of nm iron catalyst in FT wax.

### **ETCi TECHNOLOGY**

EXPORTech Company, Inc. (ETCi) has developed a novel magnetic device to separate magnetic particles from viscous flows and tested it at the bench scale level (up to 2.3 L/min feed) in separation of iron-based catalyst from Fischer-Tropsch (FT) wax. The separator consists of a continuously operating flow-through device and has achieved reductions in the concentration of iron catalyst in FT product wax up to 99% in a single stage. The output concentration can be further reduced with a second stage such as High Gradient Magnetic Separation (HGMS) where catalyst concentrations of the order of 100-500 ppm have been achieved employing a proprietary slurry of iron catalyst in FT wax.

The continuous separator is illustrated schematically in Figure 1. The magnetic separator consists of vertically oriented permanent magnetic rods housed within a cylindrical vessel. The slurry is pumped into the vessel through an inlet located between the overflow and the underflow. Flow restrictors are employed to force the majority of the flow out the underflow. The rods may be permanent magnets or magnetic wires

which are magnetized by an external magnetic field. The catalyst particles in flow are magnetized by the magnetic field and thus agglomerate, forming large clusters chained along the lines of the magnetic field. The magnetized agglomerates are attracted to the magnetic rods by the horizontally directed fringing fields surrounding the rods. The particles collide with the rods and stick where they build a layer until the magnetic compressive force can no longer support additional weight. The particles are then forced down the rods by slurry flow and form a magnetic concentrate at the bottom of the rods. A high concentration catalyst/wax slurry is forced out the bottom of the separator (underflow) while a cleaned slurry of low concentration catalyst flows from the top port of the separator (overflow). This stream is low enough in catalyst concentration that it can be polished by subsequent filtration methods such as cross-flow filtration or magnetically assisted settling. HGMS was used in this work.

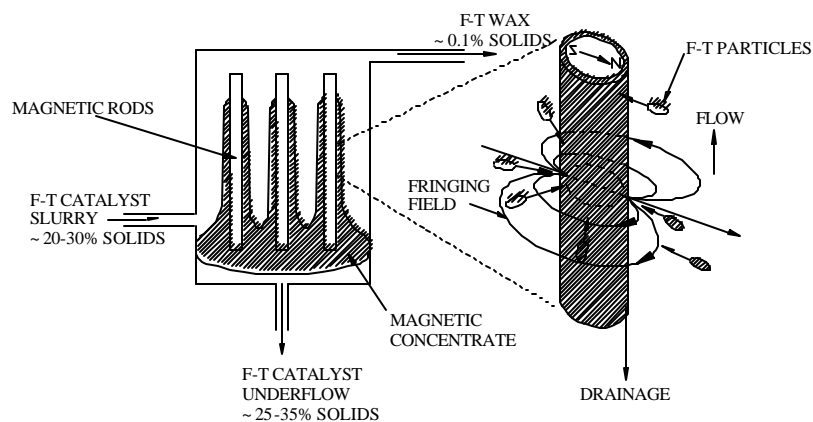


Figure 1. Fischer-Tropsch Catalyst Separator

The process is controlled by physical and magnetic properties of the particles, the spatial dependence of the magnetic field strength near the surfaces of the rods, the feed, underflow, and overflow rates, the direction of feed flow, and the effects of temperature and solids on slurry viscosity. When the magnetic forces are too high, bridging can develop between the rods. When this happens, the bridge will grow, and eventually the separator will plug. There is a balance between the variables (number of rods, surface magnetic force, flow rate, etc.) that will permit flow without plugging.

## EXPERIMENTAL

Initial testing was carried out at room temperature using CO-activated precipitated-iron catalysts suspended in Durasyn® 164 Polyalphaolefin oil and n-hexadecane. Measurements at elevated temperature employed both the in-house activated catalyst and a slurry of proprietary iron catalyst in FT wax.

### *Flow Sheet*

The test flow sheet is shown in Figure 2. The slurry was placed in a stainless steel beaker and stirred to keep the catalyst in suspension. A peristaltic pump was used to

pump the slurry into the separator. Samples of the product and underflow streams were withdrawn for analysis every 30 minutes. After analysis was completed (approximately 5-10 minutes), the samples were returned to the feed container. The flow split between underflow and overflow was adjusted by means of pinch clamps on the tubing for the product and underflow streams. The entire system could be heated to 200 °C.

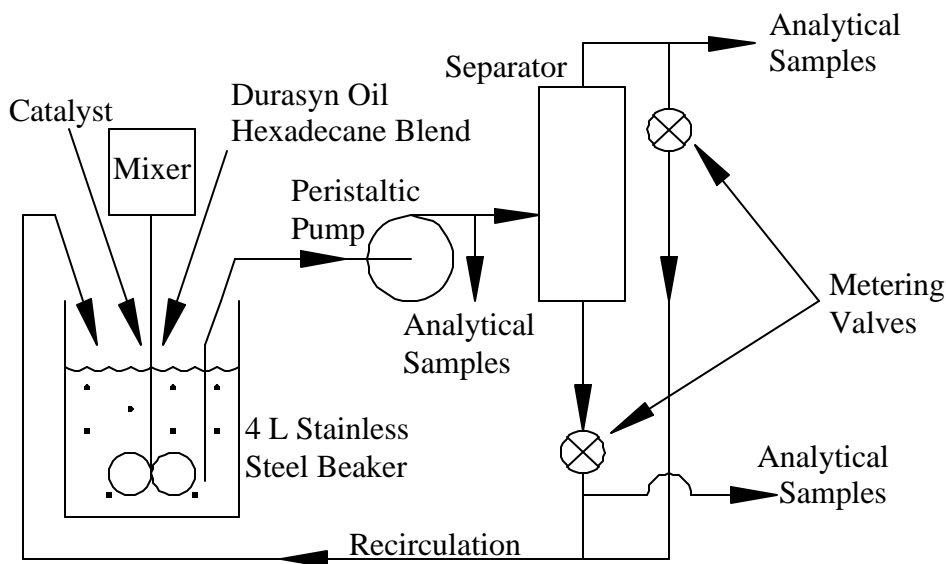


Fig. 2. Flow Sheet

### *Analysis*

Catalyst concentration measurements were made by a magnetic method. This method uses the diamagnetic susceptibility for the organic phase and an “apparent” magnetic susceptibility for the catalyst measured in very dilute concentration. The resultant concentration of the feed, underflow, and overflow streams are determined by mass balance. The method is rapid. It is believed to be accurate to within +/- 10% for concentrations greater than 0.5%. Lower concentrations are measured with considerably less accuracy.

The temperature and magnetic field dependences of the magnetization per gram of both the CO-activated catalysts and the proprietary catalyst employed here exhibit hysteresis with the proprietary catalyst being less magnetic than the CO-activated catalyst. The field dependences of both magnetizations above saturation were paramagnetic. In subsequent measurements the product of HGMS was diamagnetic. Fields up to 20,000 gauss and temperatures up to 300 °C were employed in the magnetization measurements.

Particle size measurements made with transmission and scanning electron microscopy showed that the in-house-activated and the proprietary catalysts were made of micron-sized clusters of nm sized particles. X-ray diffraction of both slurries showed similar peaks for iron carbide and magnetite but the proprietary mixture, unlike the in-

house catalyst activated in Durasyn® 164 Polyalphaolefin oil and n-hexadecane, exhibited a paraffinic XRD background spectrum. No  $\text{Fe}_2\text{O}_3$  was detected in either catalyst. Catalyst particle size distributions measured with a MicroTrac are shown in Figure 3. There is a small difference in particle size between fresh and used CO-activated catalyst, the latter being finer. The first stage product for the CO-activated catalyst is significantly finer than the feed. For catalysts separated at  $200^\circ\text{C}$  the particle size is reduced significantly after a few heating cycles (heated to  $200^\circ\text{C}$  and cooled to room temperature twice), more than 600 passes through the separator, and extended mixing time (more than 3 hours). Even though attrition is undesirable, the method was effective in separating these fine catalyst particles (78 % of the particles below  $10\mu\text{m}$ ).

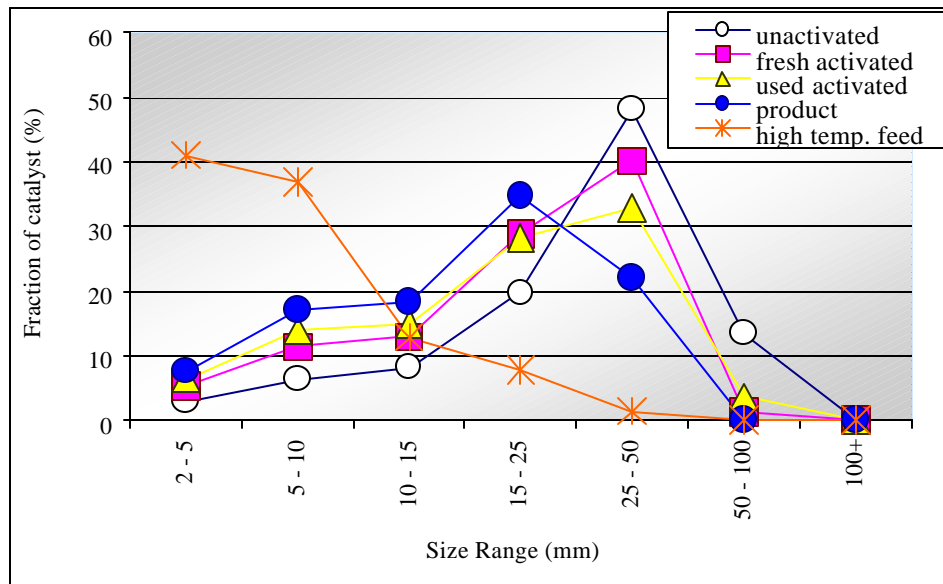


Fig. 3. Particle Size Distributions

### Apparatus

Carbons steel rods of 0.063 inch diameter and 23 cm length were used for all of the measurements reported here. A photograph of a test cell containing two wires is shown in the left portion of Figure 4. The right portion of the figure shows a two stage arrangement. The first stage continuous separator is mounted between the poles of the electromagnet. The second stage, on the right in the figure, is an HGMS unit. The canister for the HGMS unit, similar in size to that of the first stage, is packed to nominal 6% occupancy with fine grade ferritic stainless steel wool. The canister, made from non-magnetic material, was 23 cm long and had a square inner cross-section measuring  $1.8\text{ cm} \times 3.5\text{ cm}$ . A rope heater was wrapped around each cell and coated with a heat transfer putty for high temperature tests.

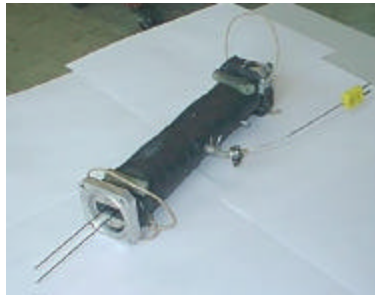


Figure 4. First Stage Cell and Continuous First Stage (left) and HGMS Polisher Apparatus (right)

## RESULTS OF MEASUREMENTS

### *First Stage Only*

**Field Strength:** Figure 5 shows the catalyst concentration in the overflow versus the amount of slurry processed at room temperature, expressed as cell volume exchanges. The number of cell exchanges is the number of cell volumes (1 cell volume ~ 160 ml) that have passed through the separator (overflow and underflow streams are recirculated). 600 cell exchanges are equivalent to over 100 L passing through the separator. The feed flow rate is 30 and the throughput is 3.3 GPM per square foot of separator cross section. The recycle ratio, which is the rate of underflow divided by the rate of overflow, is 8. Separation is not achieved without an applied field.

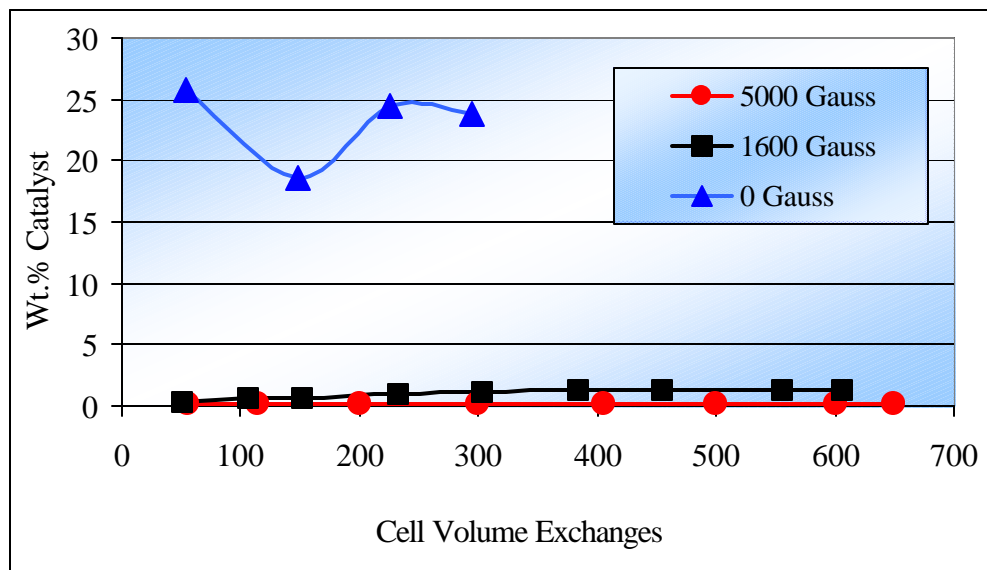


Fig. 5. Cell Volume Exchanges

Figure 6 shows the product concentration for room temperature separations where the field strength is 1600 and 5000 gauss. Flow rate and recycle ratio are the same as in Figure 5. The rate of particle separation from the slurry appears to be constant for 5000 gauss operation while the rate decreases for the lower field strength as the separation proceeds reaching a steady value after 300 cell exchanges such that the overflow concentration is several times greater than for operation at 5000 gauss. It is conjectured that the agglomerates are loosely bound at 1600 gauss compared to 5000 gauss where the particles are magnetized to 90% of saturation. Additionally, the demagnetizing factor for the elongate cylinders reduces the effective magnetization of the rods. The fringing fields, proportional to the magnetization, are weakened and the forces drawing the particles to the surface of the rods are significantly less than for an applied field of 5000 gauss.

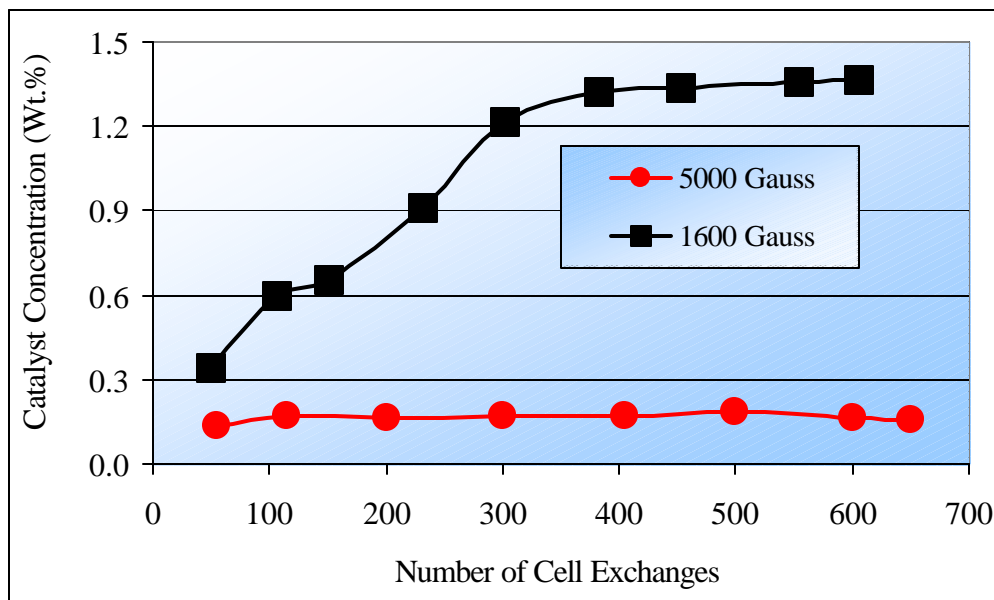


Fig. 6. Number of Cell Exchanges

Temperature: Results of testing at room temperature and 200 °C are shown in Figure 7. These tests indicate that the separations were better for four rods than for two and that the catalyst concentrations in the product streams at 200 °C are substantially the same for separations run with recycle ratios ranging from 4 to 9.

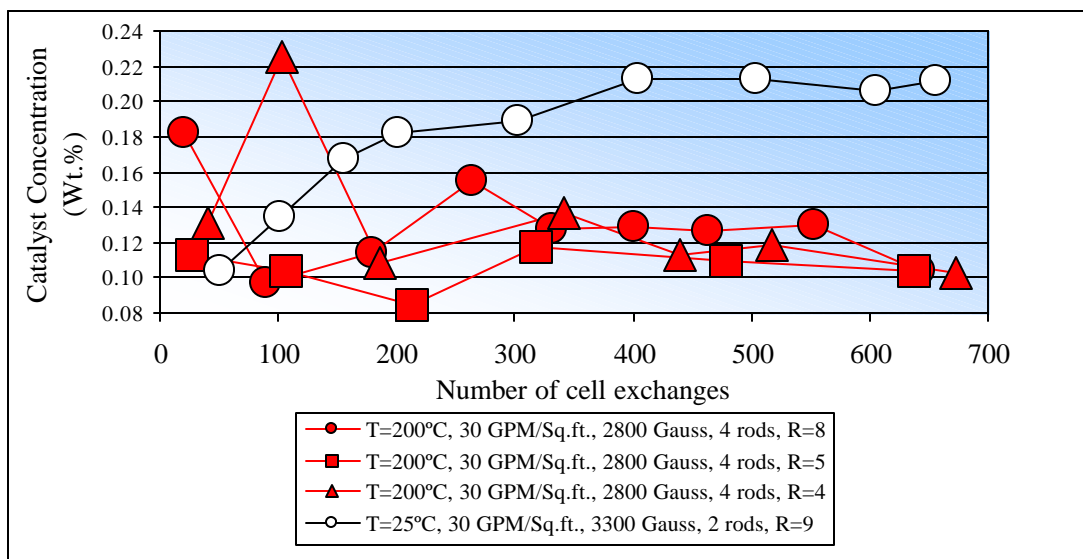


Fig. 7. Product Stream Concentrations for Room Temperature and 200°C Runs

**Recycle Ratio:** Figure 8 shows the effect of recycle ratio. All measurements are at a feed rate of 30 GPM/Sq.Ft. and 1600 gauss. Increasing recycle ratio, R, greatly improves performance.  $R/(1+R)$  is equal to the ratio of underflow to feed flow rates. Since  $R/(1+R)$  is a monotonically increasing function of R, this suggests that low field values require high values of underflow relative to the feed.

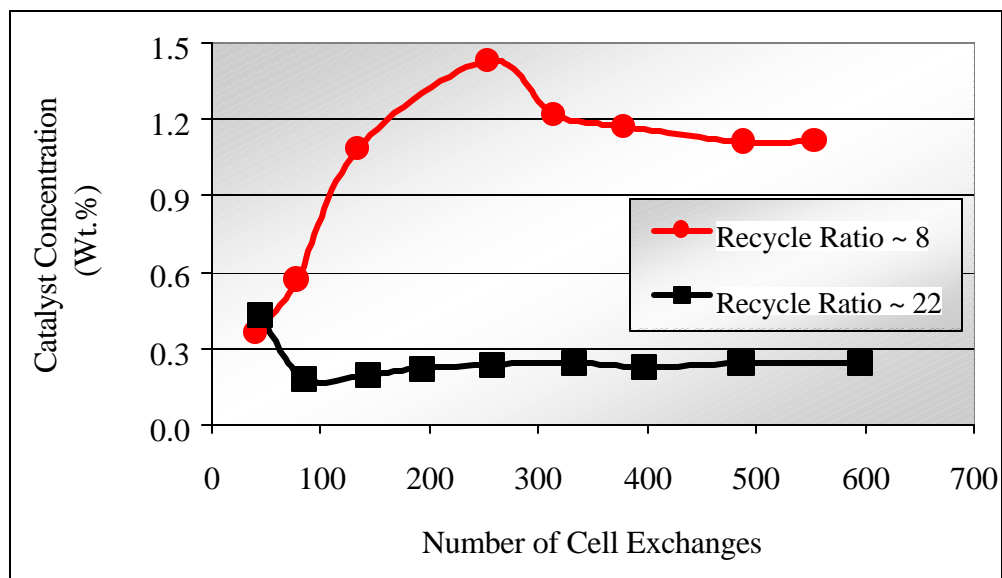


Fig. 8. Effects of Recycle Ratio

**Feed Flow Rate:** Figure 9 shows measurements of the effect of feed flow rate on catalyst concentration in the overflow. Note that the values at 90 GPM/SqFt were taken at a higher recycle ratio than were the other two data sets. The data generally indicate a modest degradation of performance with feed flow velocity.

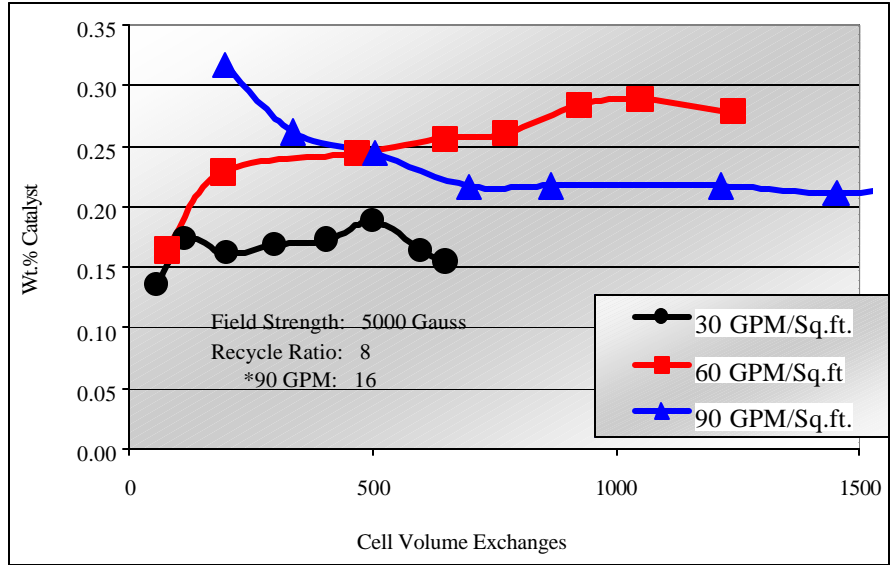


Fig. 9. Flow Rate

*Two Stage Operation:*

The first stage continuous separator was operated in tandem with the second stage batch operated HGMS as shown in Figure 4 above. CO-activated precipitated-iron catalysts suspended in Durasyn® 164 Polyalphaolefin oil and n-hexadecane was used. The feed flow rate was 10 GPM/SqFt. The results shown in Figure 10 were obtained at 200 °C. The catalyst concentration was measured by the magnetic method and may range from 100 –500 ppm.

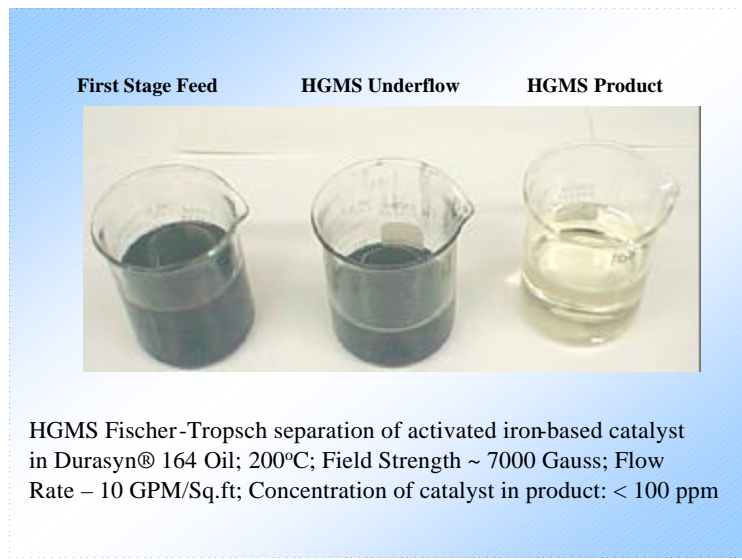


Fig. 10. HGMS Fischer-Tropsch Separation

## CONCLUSIONS

The objective of the continuous stage of separation is to obtain a concentration of catalyst less than nominally 0.5 wt.% at the highest throughput possible. The separated catalyst is to be recycled to the FT reactor. The subsequent stages will be used to lower the catalyst concentration to levels necessary for downstream processing. With this objective in mind, the results obtained with the first stage of separation are strongly affected by the product of the magnetic field strength and the ratio of the underflow to feed rates as shown in Figure 11.

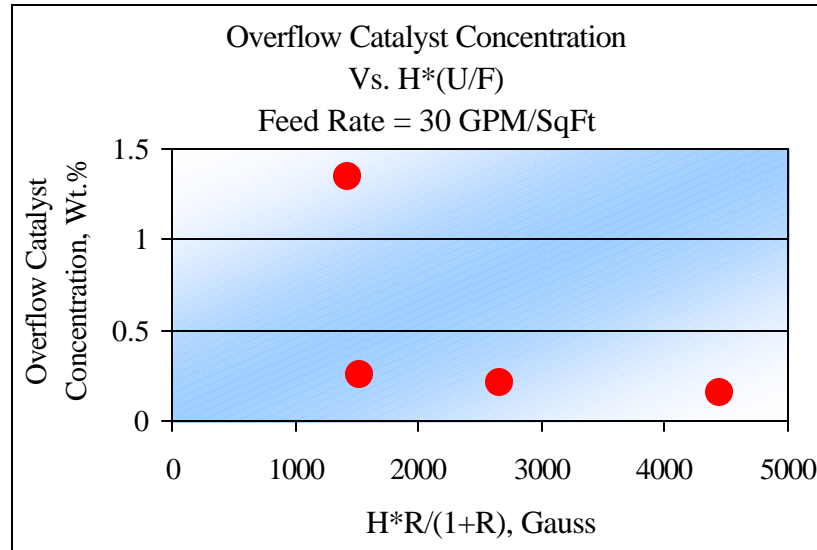


Fig. 11. Overflow Catalyst Concentration vs. Field

The field strength must be great enough to magnetize the particles and the rods and the underflow rate must be sufficient to carry away the concentrated catalysts to prevent solids buildup to the point where the slurry cannot be pumped.

## STATUS OF THE TECHNOLOGY

The above measurements were made at the bench scale of operation with the rod-separator described above. We have now changed the method of magnetic agglomeration and separation to permit higher feed rates and throughputs without sacrifice of separation performance and scaled to a throughput of 50 barrels per day of proprietary nm sized iron catalyst in FT wax. The feed, underflow, and product tanks for the new apparatus are shown in the photograph of Figure 12 which is to be compared with Figure 4 above. A description of the new method will be published elsewhere.



Fig. 12. 50 Barrels Per Day Apparatus

## **ACKNOWLEDGEMENTS**

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