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MAGNETIC SEPARATION OF IRON CATALYSTS FROM FISCHER-TROPSCH WAX

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Abstract

This paper describes recent work in magnetic separation of precipitated iron catalyst particles from Fischer-Tropsch wax at 260 °C in fields up to 0.2 Tesla employing a novel **M**agnetic **M**icro-**P**article **S**eparator (MM-PS patent pending) adapted from an earlier **C**ontinuously **O**perating **M**agnetic **P**article separator (CO-MPS) described elsewhere.[1] The MM-PS is scaled up by a factor of 29 from the bench scale CO-MPS. In processing nominal 20-25 wt% catalyst slurries, it has operated at a product rate of 7950 liters per day (Lpd) while producing concentrations as low as 0.35 wt% solids with filtration rates up to 250 kg/min/m^2. The upper limit of the filtration rate is not known. The MM-PS is designed to achieve isobaric and isothermal separation of the bulk of the catalyst for immediate return to the Fischer-Tropsch reactor. Catalyst concentrations of 100 ppm were obtained employing a second stage batch operated HGMS. While the feed to the first stage exhibited strongly magnetic behavior, the product of HGMS was diamagnetic

Overview

In earlier work[2] a novel magnetic method employing flow past magnetized rods (the CO-MPS, patent pending) separated micron-sized iron catalyst particles from a Fischer-Tropsch wax simulant at 200°C. In the present work a Magnetic Micro-Particle Separator (MM-PS, patent pending) – a new concept for continuous magnetic separation of micron-sized particles from viscous flow – was investigated and successfully tested using a proprietary slurry of micron size iron catalyst agglomerates in Fischer-Tropsch wax at 260°C and ambient pressure.

Using a supply of 250 liters of Fischer-Tropsch wax slurry blended to 15-25 wt% iron catalyst concentration, slurries with catalyst concentration as low 0.35 wt% solids were produced at rates up to 7950 Lpd (50 gpd) in true continuous operation using the MM-PS. The upper limit of catalyst reduction seen in this work was imposed by the limited supply of slurry and by the experimental apparatus which had been designed for a lower throughput – not by the ability to separate catalyst particles from the slurry. High Gradient Magnetic Separation (HGMS) was tested to polish the MM-PS overflow. Catalyst concentrations in the 100-500 ppm range were obtained; similar to results obtained in earlier testing with the CO-MPS. The level of post-HGMS particle concentration may have been associated with contaminants in the slurry. About 71 % of the particles in the wax were rich in iron, the remaining particles were rich in Si/Al, Ca, Si, Ba, Cl, and Ca/S, in that order.

Apparatus

A test bed instrumented for temperature, pressure, and velocity measurement and control was built to contain the slurry, mix it, pump it to the separator, monitor it, and receive the product and return streams. A high pressure mixing tank and overflow and underflow tanks shown in Figure 1 were insulated to maintain the wax slurry at 260 °C. ETCi supplied a transverse access electromagnet capable of producing a uniform field up to 0.7 Tesla in the horizontal plane transverse to the flow. The entire apparatus was installed within an isolated air-swept enclosure which was continuously monitored for explosive gaseous build-up. The initial test runs employed a separation vessel of 1.8 by 3.5 cm cross-section. This was replaced by a cylindrical vessel of 5.1cm diameter which was later replaced by one of 15.2 cm diameter.

Figure 1. Test Bed

Characterization and Analytical Measurements

The magnetization of an 18 wt% solids slurry was hysteretic with a small high field paramagnetic component. The overflow from the separator exhibited weak hysteresis with a diamagnetic component. The overflow from HGMS was diamagnetic. Figure 2 is a TEM image of a cluster of particles which came through the first stage separator. The overall length of the agglomerate in the photograph is approximately 300 nm. Mössbauer measurements indicated 17% of the catalyst particles in the feed were superparamagnetic. Solids concentration of overflow and underflow samples were determined by a modified ASTM ashing procedure, D-482.

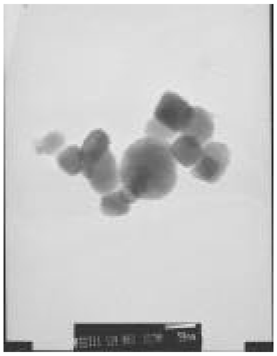

Figure 2. TEM image.

Results

A typical run of two hours duration consisted of feeding wax slurry containing 21.45 wt% catalyst into the separation vessel. The underflow contained 23.33 wt% ash and the overflow contained 0.35 wt% ash. The residence time in the apparatus was approximately 4 seconds. For the 15.2 cm diameter canister the total process flow during a two-hour run had a volume equal to 660 times that of the empty separation canister. No signs of plugging were observed.

The effect of the magnetic field strength on separation of the catalyst particles is illustrated in Table 1. An applied magnetic field of 0.15 Tesla is sufficient to assure greater than 96% reduction in catalyst concentration for the MM-PS separator. Magnetic field strengths of this level are practical.

Table 1. Effect of Magnetic Field on Separation of Iron Catalyst Particles from Fischer-Tropsch Wax at 229 ^{o}C

Magnetic Field (Tesla)	**Feed Rate (Lpm)**	**Feed Ash (wt%)**	**Overflow Rate (Lpm)**	**Overflow Ash (wt%)**	**Ash Reduction (wt%)**
0	43.9	19.88	3.4	19.67	1.1
0.05	42.8	19.03	3.3	12.88	32.3
0.1	42.8	19.00	3.3	6.41	66.3
0.15	41.3	18.47	3.4	0.68	96.3
0.2	42.4	18.95	3.4	0.58	96.9

Application to Fischer-Tropsch Synthesis

Figure 3 is a flow diagram of one method of applying the technology to Fischer-Tropsch synthesis. The figure shows a Fischer-Tropsch reactor with a slurry zone containing a liquid comprising waxes and magnetic catalyst particles. Synthesis gas comprising hydrogen and carbon monoxide is added at the bottom of the reactor. Vapors are removed from the reactor overhead. Slurry is drawn from the slurry zone into the vapor liquid separator. Vapors are returned to the reactor and the slurry flows into the MM-PS.

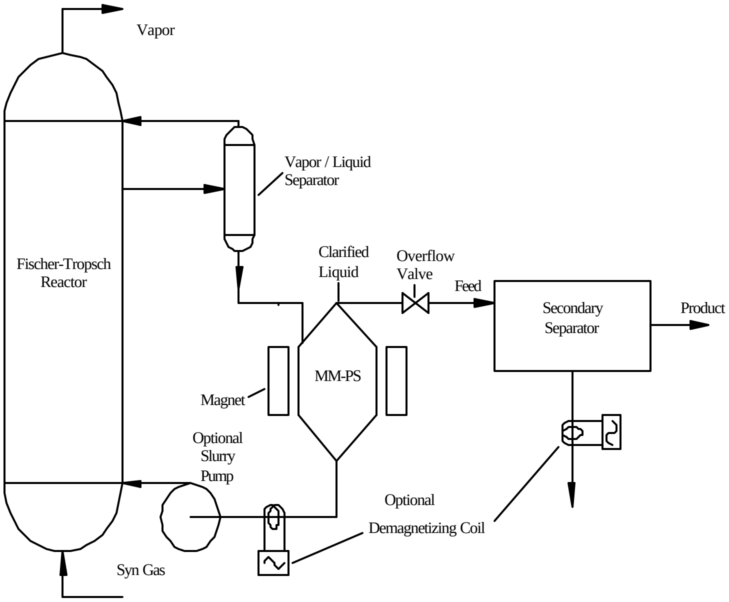

Figure 3. Flow diagram of F-T synthesis.

The magnetic particles exit the bottom of the separator and may be pumped back into the reactor to recycle the catalyst particles in the event that the pressure at the separator exit is not enough to force the flow into the bottom of the synthesis reactor. The underflow stream is shown passing through an optional demagnetizing coil.

The clarified liquid removed at the top of the continuous magnetic separator passes through a valve or other restrictor and is sent to a secondary separator for further processing. Any suitable micro separator such as High Gradient Magnetic Separation (HGMS) may be used as the second stage separator. It is not as important that this process step be continuous since it is not integrated into the synthesis process.

Cost Estimation

A conceptual level cost estimate to build an instrumented 56 Lpm (15 gallons per minute) MM-PS pilot test unit was prepared using the maximum filtration rate observed in this work. This makes a conservative projection of the 56 Lpm pilot unit since the experimental throughput was not maximized.. Using this cost estimate as a basis and employing a scaling factor of 0.8, capital and operating costs were approximated for 10,000 and 100,000 barrels per day (BPD) MM-PS commercial units. The capital costs are 30 and 19 $/BPD; operating costs, including capital amortized over 20 years, are 0.69 and 0.44 $/B, respectively. Multi-stage operation or post MM-PS polishing will be required to achieve a catalyst concentration in the 10 ppm range if required for downstream processing.

Conclusions

Micron size agglomerates of sub-micron size catalyst particles with an individual particle size ranging between 2 and 60 nm have been separated from Fischer-Tropsch wax at 260 ^{o}C by the MM-PS method at a rate of 50 barrels per day (7950 liters per day). These particles can be returned to the reactor or discarded as is required in the process application

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References

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(2) Ibid.