

Novel Magnetic Method for Separation of Iron Catalysts from Fischer-Tropsch Wax

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ABSTRACT

We describe a novel continuous magnetic method for separation of nano-meter size iron catalysts from Fischer-Tropsch wax (patent pending). The method has been scaled up from the bench scale to prepare clean wax containing 0.1 to 0.5 wt.% catalyst from slurries containing 20-25 wt.% catalyst at the rate of 50 barrels per day (BPD) feed wax at 500°F.¹ We will discuss the operating mechanism of the separator which is housed between the poles of an electromagnet producing magnetic fields in the range of 0.2 to 0.5 Tesla throughout the working volume. The method achieves high levels of catalyst separation from the wax by promoting magnetic agglomeration throughout the volume of the vertically oriented elongate cylindrical separation vessel. Downwardly-directed high velocity jet flows located adjacent to the inside walls of the separation vessel nearest the magnet poles are used to sweep the catalyst agglomerates from the magnetized volume of the separator. The jets are controlled to promote movement of the agglomerates without causing turbulent mixing. Clean wax with a low concentration of catalyst is continuously issued from the top of the separator while wax slurry with a high concentration of catalyst is issued from the bottom of the vessel. Use of a supplemental separation method such as batch operated high gradient magnetic separation to treat the product of the first stage continuous magnetic separator has produced clean wax containing 0.01 wt.% catalyst.

INTRODUCTION

Fischer-Tropsch synthesis (F-TS) is a well established technology for production of high quality synfuels.² The technology employs catalysts generally based on either iron (Sasol) or cobalt (Shell). Tubular fixed bed reactors originally employed at Sasol in 1955 and currently employed by Shell at its Bintulu, Indonesia plant have developed into slurry bed reactors

¹R. R. Oder, R. E. Jamison, and C. A. Znati, "Separation of iron catalysts from Fischer-Tropsch wax," *Proc., 20th Annual Pittsburgh Coal Conference: Coal, Energy and the Environment*, Pittsburgh, PA (September 15-19, 2003); R. R. Oder, "Magnetic separation of iron catalysts from Fischer-Tropsch wax," *Proc., Petroleum Chemistry Division, American Chemical Society Annual Meeting*, Anaheim, CA (March 28-April 1, 2004); R. R. Oder, "Magnetic separation of nm iron catalysts from Fischer-Tropsch wax," *Proc., Petroleum Chemistry Division, American Chemical Society Annual Meeting*, San Diego, CA (March 13-17, 2005); R. R. Oder, "Magnetic separation of nanometer size iron catalyst from Fischer-Tropsch wax," to be published in *Fischer-Tropsch Synthesis*, Elsevier (2006).

² R. B. Anderson, *The Fischer-Tropsch Synthesis*, Academic Press, New York (1984).

primarily for coping with the high heat release from the exothermic F-TS reactions.³ The catalyst is removed from the slurry bed reactor along with the wax products.

Currently, cobalt catalysts are of great interest because of the potential of cobalt-based F-TS for monetizing stranded natural gas. Iron catalysts are attractive, however, because of the highly olefinic nature of their products and because of the activity for the water-gas shift reaction that permits use of low H₂/CO syngas derived from the gasification of coal and other disadvantaged hydrocarbons.⁴ Unsupported iron catalysts have been developed which are micron size agglomerates of nanometer magnetite particles. In the F-TS reactor, the magnetite particles react with carbon monoxide to produce iron carbides which are the actual source of catalytic activity. The carbide particles differ in crystal structure from the oxide and as such are prone to break away from the surface of the agglomerate in the reactor due to attrition.⁵ More stable supported iron catalysts have not yet been developed for commercial application.

It is apparent that one of the major operational problems associated with the use of the iron catalyst for F-TS is separation of the catalyst from the product wax. Conventional methods of separation have proven to be ineffective. ExxonMobil has a patented magnetic method⁶ using High Gradient Magnetic Separation technology. This is a batch technology used commercially to separate micron sized discolorant particles from slurries of kaolin clay.⁷ Even though HGMS is capable of separating micron sized particles, it is expected to be limited to separation of low concentration catalyst from F-TS wax because of the nature of the magnetic filter employed. The need in the F-TS application, however, is for continuous separation of nominal 20 wt% catalyst streams making HGMS appear to be a better candidate for solids polishing than for primary separation.

The ability to rapidly separate concentrated sub-micron size particles from viscous wax is of great importance because of the need to maintain temperature and pressure for efficient return of the catalyst particles to the reactor. This paper describes a novel magnetic method to do that. Testing was carried out at 500°F and ambient pressure. Justification for the technology derives from the fact that iron and cobalt are strongly magnetic. Magnetite is ferrimagnetic and carbides formed in F-TS are also magnetic.

MAGNETIC MICRO-PARTICLE SEPARATOR (MM-PS)

The MM-PS separates magnetic particles from non-magnetic particles in a non-magnetic fluid in which the particles are entrained. A slurry is passed through an empty chamber made from non-magnetic materials which is located between the poles of a magnet as shown in Figure 1. The separation chamber is empty except for the slurry contained therein, i.e., there are no magnetic elements built inside the separation chamber.

³ B. Jager, R. Espinoza, Advances in low temperature Fischer-Tropsch synthesis, *Catalyst Today* **23** (1955) 17-28.

⁴ L. Xu, S. Bao, R.J. O'Brien, A. Raje, and B.H. Davis, Don't rule out iron catalysts for Fischer-Tropsch synthesis, *Chemtech* (January 1998) 47-58.

⁵ Burtron Davis, Poster No. 6, Fischer-Tropsch Synthesis, <http://crtc.caer.uky.edu/fischt.htm>.

⁶ James A. Brennan, Arthur W. Chester, Yung-Feng Chu, Separation of catalyst from slurry bubble column wax and catalyst recycle, US Patent 4,605,678 (August 12, 1986).

⁷ R.R. Oder and C. R. Price, "Brightness beneficiation of kaolin clays by magnetic treatment," *TAPPI* **56** (1973) 75.

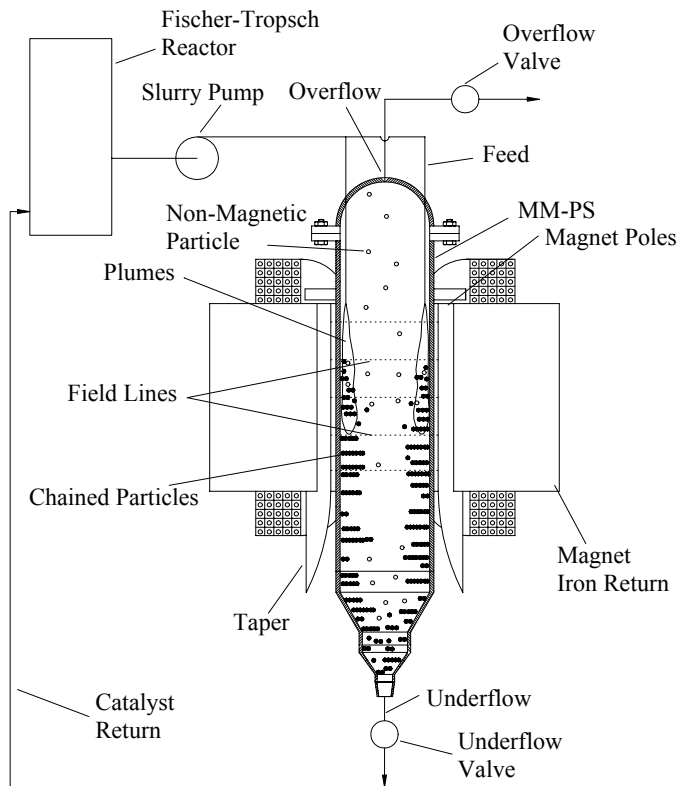


Fig. 1. MM-PS

chamber. The plumes of slurry emerging from the entrance ports bring particles into the separation chamber where they form chains which, in turn, provide a source of intense gradient magnetic fields for capture of additional particles. Simultaneously, the flushing action of the slurry plumes prevents the chains of magnetic particles from sticking to the inside walls of the separation chamber by sweeping the chained particles downward to the exit port at the bottom of the chamber. By this action, the unique apparatus is continuously creating new capture surfaces and retaining fresh particles from flow while simultaneously removing the captured particles. This creates a stream of fluid diminished in particle concentration which, by buoyancy, emerges from the top of the apparatus.

The plume length and the elevation at which the slurry flow is released into the separation chamber are adjusted so as not to stir up magnetic particles which have concentrated in the bottom of the separation chamber. The bottom of the chamber extends below the bottom edge of the magnet return frame and is sloped to a narrower exit diameter outside of the magnetic field region. This slope is introduced to minimize effects such as frictional drag which would tend to hold the magnetic particles inside the separation cell. An overflow outlet port is located at the top of the chamber where non-magnetic fluid and some particles flow from the separator. Non-magnetic particles and fluid follow the lines of flow and exit at the top and the bottom of the apparatus. The upper surfaces of the magnet poles terminate abruptly at a distance below the top of the separation chamber for the purpose of creating a field gradient which serves to keep magnetic particles from exiting the top of the separator.

The slurry of fluid containing the magnetic particles is released into the chamber from above through downwardly-directed inlet ports located against the inside walls of the separation chamber adjacent to the magnet pole faces at an elevation below the top of the chamber and above the bottom. Exit ports are located at the top and the bottom of the chamber.

The magnetic particles, which themselves may be clusters of particles, become magnetized by the externally applied magnetic field as they enter the separation chamber and attract one another to form chains of particles joined end to end strung out along the lines of the magnetic field. In this device the magnetic field is applied transverse to the direction of flow which is along the axis of the separation

The lower edges of the magnet poles extend from the bottom of the straight section of the separation chamber below the bottom of the magnet and are tapered outward. The elongated poles serve to lengthen the flow path through the magnetic field which in turn permits higher rates of feed to the separation chamber without the plumes of slurry disturbing the concentrated magnetic particles located at the bottom of the chamber. Additionally, the outward slope of the poles minimizes the upward directed magnetic force which would hold magnetic particles in the lower regions of the separator and cause plugging.

A pump or gravity is employed to force the fluid through the separation canister. Valves are employed with the pump to control the rates of high solids underflow and diminished solids overflow respectively. Depending on the length of the separation chamber, flow recycle ratios (underflow rate divided by the overflow rate) generally greater than 5 provide flows strong enough to sweep the chained particles downward without disrupting the magnetic particles in the bottom of the separation chamber. Flow ratios greater than or equal to 10 are preferred. The magnetic fields employed need to be large enough to saturate the magnetism of the particles when strongly magnetic particles exhibiting ferromagnetism or other forms of collective magnetism are to be separated.

The configuration of pump and valves is redundant. The pump and the underflow valve can be interchanged. To assure separation it is necessary that flow be forced through the device, that the applied magnetic field be strong enough to saturate the magnetization of the particles, and that the ratio of flows be controlled to assure the greater flow exits the bottom of the separator.

As shown in Figure 1 above, the high solids slurry exiting the bottom of the separation chamber through the exit valve could be returned to the slurry source if appropriate. Likewise, the low solids slurry exiting the top of the separation chamber through the overflow valve could be subjected to additional separation employing this or other methods such as cross flow filtration, sedimentation, centrifugation, high gradient magnetic separation, etc.

The apparatus is effective in separating micron size particles and especially agglomerates of nm size iron catalyst particles from Fischer-Tropsch wax at elevated temperatures. Magnetic fields of 1500-2000 gauss are sufficient to separate micron size precipitated iron catalyst particles from Fischer-Tropsch wax at 500°F. This experimental apparatus is capable of separating 20 ~ 25 wt.% concentration sub-micron size iron catalyst to produce a Fischer-Tropsch wax concentrate with catalyst concentration in the 0.1 – 0.5 wt.% range on a continuous basis at throughputs 20 to 50 times greater than can be achieved by sedimentation. Diamagnetic wax slurries with particle concentrations in the 0.01 to 0.05 wt.% range were prepared when high gradient magnetic separation was employed as a second stage of separation.

CONCLUSIONS

The MM-PS is a novel new technology for separation of magnetic particles from viscous flow including non-magnetic particles. The benefit of this technology is that flows containing a high concentration of magnetic particles of a very broad size range can be efficiently separated in a true continuous mode of operation. Further, the throughputs achievable with this method are

much higher than possible with conventional sedimentation or filtration so that the separation apparatus can be kept small by comparison. This is advantageous where high temperature and high pressure are involved as is the case in commercial separation of magnetic catalysts from Fischer-Tropsch wax.

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