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DEVELOPMENT OF FCC CATALYST MAGNETIC SEPARATION

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ABSTRACT

Magnetic separation has been historically active in several different industries, yet has not been utilized in petroleum refining until recently. Development of economical permanent magnets with high magnetic strength has led to a new process known as MagnaCat®. The MagnaCat® Process separates less active (high metals) particles catalyst from equilibrium Fluid Catalytic Cracking (FCC) catalyst, producing a higher activity/lower metals catalyst for recycle. Pilot FCC studies showed lower hydrogen, dry gas, and coke make with higher wet gas and octane from catalyst separated by MagnaCat®. With the use of a MagnaCat® Process unit, a refiner would produce an economic advantage of $0.20 to $0.40/Barrel of FCC charge and enhance unit operability.

INTRODUCTION

As the cost of operating a refinery increases due to environmental constraints plus increases in raw materials and maintenance costs, refiners look for processes which improve refining margins with the least amount of capital investment. Fluid catalytic cracking (FCC), in particular, has a significant bottom-line effect on both refining revenue generation and cost. FCC costs include virgin catalyst purchase as well as spent catalyst disposal, which can be significant at times. Both of these can be offset to a degree by utilization of a new process called MagnaCat®[1]. This process removes the older, higher metals content, less active fluid cracking catalyst from the equilibrium FCC inventory by dry magnetic separation techniques to produce a lower metals/higher activity and more selective catalyst.

Magnetic separation techniques[2] have been around for years in the mining, food and other industries. These techniques include the utilization of eddy currents, electromagnets, and permanent magnets for separation of magnetic from non-magnetic material on a wet or dry basis. We will not discuss eddy currents in this paper, but only mention the technology exists. Electromagnets use electricity to induce a magnetic field in a metallic object by flowing electrons through a wire-wound core to induce a magnetic field in a metal object in the center of the core. These types of magnets are relatively expensive and operating costs are usually high due to the consumption of electricity. Permanent magnets are generally used in operations where the material being removed exhibits strong ferromagnetic and/or paramagnetic properties.

Ashland and Nippon Oil independently applied High Gradient Magnetic Separation (HGMS) technology to cracking catalysts in the late 70's and early 80's and were granted patents, and Nippon Oil operated an HGMS carousel separator on their FCC unit in Japan for about one year. Due to high capital, power, and land costs, this unit was shut down. In the late 80's and early 90's, advancements in permanent magnet technology have enabled magnetic separation techniques to be applied to processes in the Petroleum Industry. Ashland demonstrated the applicability of this less expensive rare earth magnet roller separation technology to cracking catalysts in the late 80's. We expect future developments to rare earth roller magnets to produce magnetic field strengths above 20,000 gauss that would improve the MagnaCat® Process even further.

A typical refinery FCC catalyst balance is illustrated in Figure 1[3], demonstrating the large amount of catalyst used in an FCC process. The ability to recover a significant amount of good catalyst from that withdrawn from the regenerator provides an advantage that other refiners may not possess.

PROCESS

Fluid catalytic cracking converts crude oil fractions heavier than gasoline and diesel fuels into consumer usable products. A silica-alumina zeolite heterogeneous

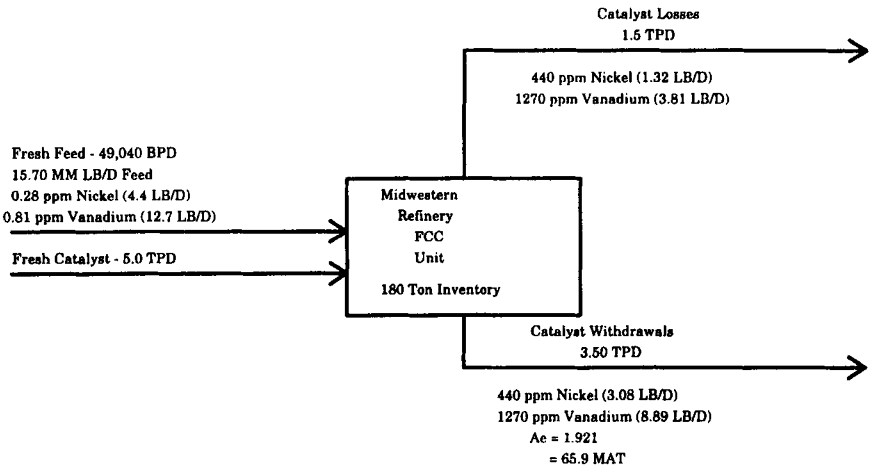

FIGURE 1.
Typical FCC Catalyst Balance

catalyst is used to promote an acid initiated carbonium ion cracking mechanism between 900°F and 1300°F to produce a wide range of products such as propane, gasoline, kerosene, diesel, and various petrochemicals. These crude oil fractions contain metals such as nickel and vanadium that collect on and deactivate the cracking catalyst. Iron is also present in these fractions, but nickel and vanadium contribute the most to deactivation of the catalyst acidity and subsequently the activity.

As these metals accumulate, the catalyst becomes deactivated over a period of time and fresh FCC catalyst is added in order to maintain unit activity. Catalyst is also withdrawn to maintain a constant amount of catalyst in the unit inventory. The withdrawn catalyst contains a dynamic mixture of catalyst particles from inactive very old/high metals to relatively fresh low metals/high activity, as illustrated in Figure 2.[4] In order to produce a separation using magnetic separation techniques, the catalyst must exhibit magnetic properties, with a distribution of magnetic susceptibility being the most important. Figure 3 shows that as metals are deposited onto the catalyst over a period of time, the magnetic susceptibility of the catalyst particles increases, and magnetic separation can be achieved with the MagnaCat® Process.

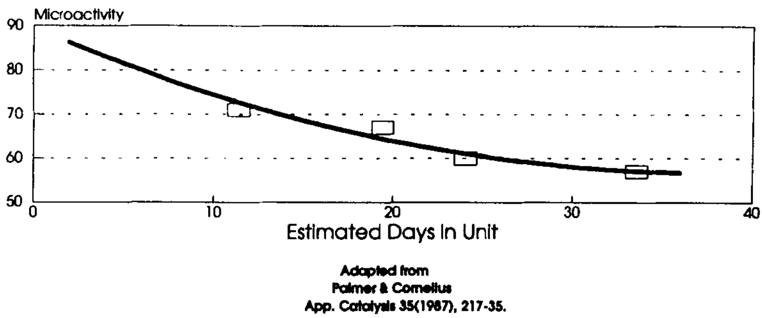

FIGURE 2.
Distribution of Catalyst Activity as a Function of Age

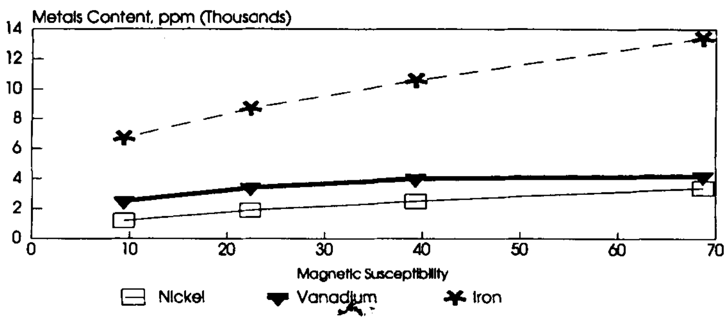

FIGURE 3.
Metals Distribution Correlates with Magnetic Susceptibility

The MagnaCat® Process illustrated in Figure 4 shows a commercial application of this process. Spent catalyst from the regenerator is cooled and fed onto the belt of the magnetic separation unit. The catalyst passes over a permanent magnet where the highest magnetic catalyst is bound on the belt by magnetic forces. As the roller rotates, the least magnetic catalyst is thrown away from the belt and the magnetic catalyst follows around until it passes the magnet. At that point, the magnetic forces diminish and the high metals/low activity catalyst falls into a collection hopper. The least magnetic (lower metals/higher activity) catalyst is recycled back to the FCC unit and the highest magnetic catalyst is typically discarded.

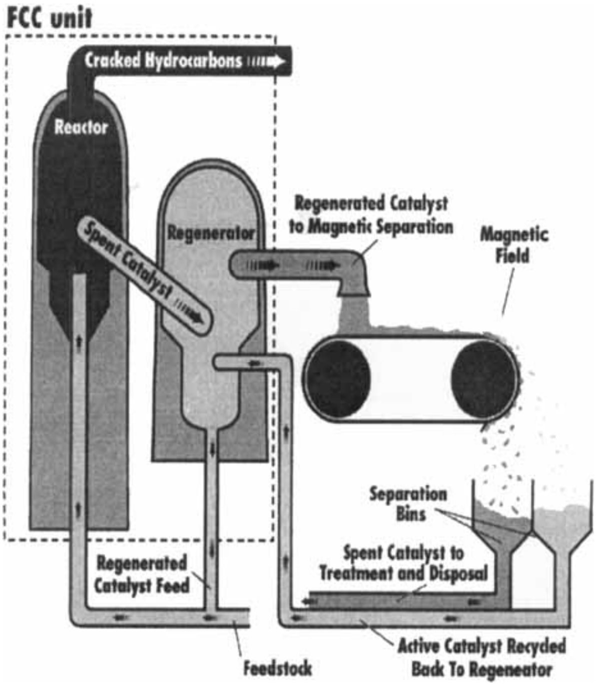

FIGURE 4.
The MagnaCat™ Process

We began investigating commercial applications of this new magnetic separation technology to Ashland's FCC units in 1991. The MagnaCat® Process is the first commercial Petroleum application of magnetic separation of its kind, which is based on a dry processing of equilibrium FCC catalyst. Separation of the equilibrium FCC catalyst is accomplished by the combination of magnetic, gravitational and centrifugal forces (momentum). The amount of magnetic force acting upon the catalyst particle results from a relationship between the magnetic field from the rare earth magnet roll and the thickness of the belt. The gravitational force pulls the catalyst particle downward and the centrifugal force is produced by the speed of the belt and the size of the roller acting upon the weight and/or size of the particle to give the particle momentum to overcome the magnetic field. To achieve a separation at a specific percentage, the magnet strength, roller size, belt speed, belt type, belt thickness, material feed rate onto the belt,

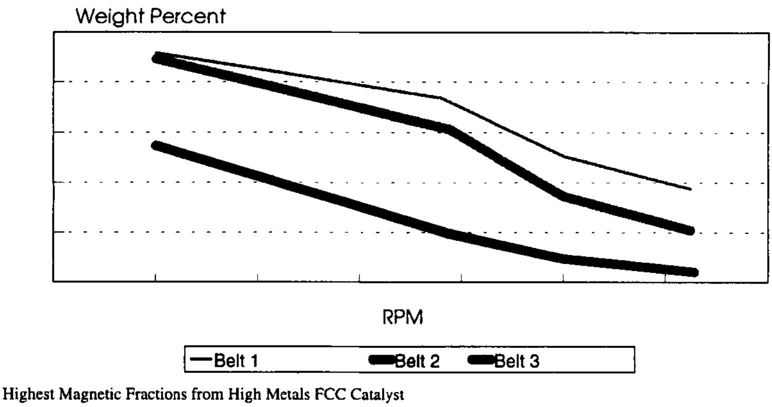

FIGURE 5.
Effect of Belt Types and Thickness Upon Magnetic Separation

and the magnetic susceptibility of the material being separated must be considered, as shown in Figure 5.

The different belt types used in magnetic separation provide one means to effectively separate materials with different magnetic susceptibilities. The higher the magnetic susceptibility, the thicker the belt needed to produce the desired split or separation as illustrated in Figure 6. This also illustrates there is some overlap between the belt thickness used in the separations and the magnetic properties of the catalysts being separated.

The magnetic separation rate of an FCC catalyst is a combination of these magnetic separator variables. Again, these variables are belt speed, belt type, belt thickness, magnet strength, roller size, material feed rate, and magnetic susceptibility.

Magnetic separation results vary from one commercial FCC unit to the next as illustrated in Figure 7 for high and low magnetic catalysts. Some refiners operate their FCC units at low nickel plus vanadium levels and others at a higher metals level. Yet one can achieve fractionation of the dynamic catalyst mixture with mass magnetic susceptibilities ranging from 1.5×10^{-6} emu/g to over 1.0×10^{-4} emu/g.

One property of an FCC catalyst is fluidization, which is related to the particle size distribution of the catalyst. The question can be asked, "What effect does magnetic separation have upon the catalyst particle size distribution?" The particle size

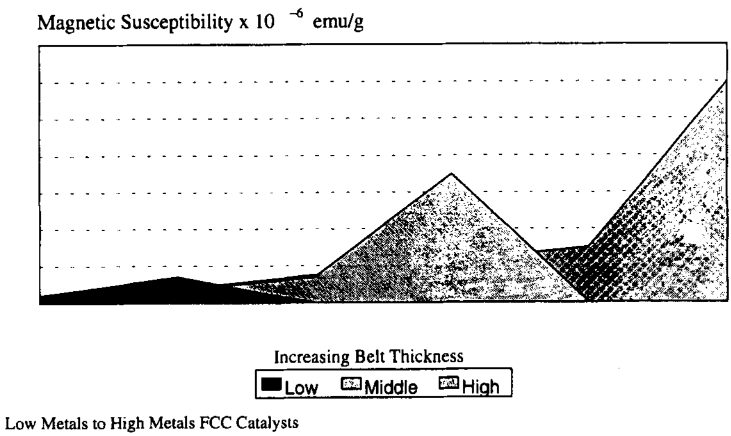

FIGURE 6.
Relationship of Magnetic Susceptibility and Belt Type

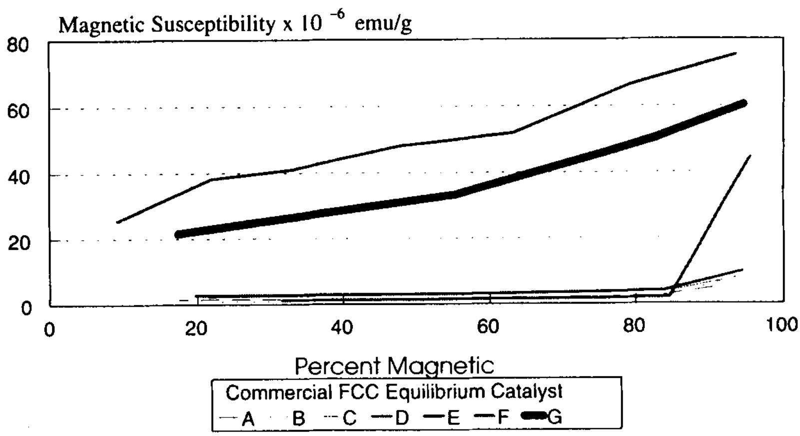

FIGURE 7.
Magnetic Susceptibility versus Percent Magnetic

distribution for an FCC base catalyst and magnetic separation fractions (magnetic reject and recycle) indicate a slight increase in average particle size for the least magnetic fraction which the graph shows to be distributed throughout the particle size range. The highest magnetic fraction particle size is slightly smaller than the full-range catalyst. Offsetting this is the ability to reject very large particles of catalyst inerts and refractory. With these results, we expect a commercial FCC unit would not encounter any adverse fluidization effects from use of the MagnaCat® Process. Some users may actually observe improvements in the fluidization properties of the equilibrium catalyst due to the removal of the largest particles.

MagnaCat® Process Pilot Studies

Magnetic separation of a high metals fluid cracking catalyst was followed by FCC process studies. A commercial FCC sweet crude charge feedstock with 10% vacuum bottoms was used in these studies. Tables I and II present the properties of the equilibrium catalyst and the feedstock used for these studies. The catalyst was magnetically separated into two fractions, a 70 percent least magnetic or recycle and 30 percent high metals magnetic reject using a laboratory scale rare earth roller magnetic separator. The base catalyst compared with the recycle and magnetic reject showed a decrease in metals for the recycle fraction. Figure 8 shows that the reject nickel, vanadium and iron results are 35 percent, 9 percent, and 61 percent, respectively, higher than the recycle. The impact of removal of this reject sample can be seen by comparing the micro activity (MAT) of the base, recycle, and reject catalysts, shown in Figure 9.

The recycle MAT has increased by two volume percent conversion over the equilibrium base case catalyst. The reject on the other hand has a MAT of 50 volume percent conversion, 10 volume percent lower than the base catalyst and almost 13 volume percent lower than the recycle fraction.

Note these results indicate a significant amount of this commercial FCC catalyst inventory (30% based on this magnetic separation) has an average MAT activity of 50. This causes product selectivities to diminish due to thermal cracking and metal dehydrogenation reactions from this high metals/low activity catalyst fraction.

To evaluate the above assumptions, the base, recycle, and magnetic reject were tested using Ashland Petroleum Research and Development's catalyst evaluation procedure.[5] The FCC Process Pilot scale unit is a circulating isothermal unit with the capability of processing one-half of a barrel per day of FCC crude feedstock. This unit

TABLE I. EQUILIBRIUM CATALYST PROPERTIES		TABLE II. FEEDSTOCK PROPERTIES	
PHYSICAL PROPERTIES		FEED CHARACTERIZATION	
Surface Area, sq. m/g	98.5	Gravity, API	27.0
Water Pore Volume, cc/g	0.36	Viscosity @ 210°F, CST	6.82
Average Particle Size, Microns	83	Ramsbottom Carbon, Wt.%	1.74
Zeolite Intensity, %	5.1	Pour Point, °F	+70.0
		Heptane Insolubles	0.37
CHEMICAL PROPERTIES			
Composition, % By X-ray		Distillation - D1160, °F	
Al_2O_3	47.6	5% vol.	580
SiO_2	48.2	50	792
REO	1.41	Cracked @ 94%	1050
Metals, ppm by AA			
Nickel	2300	ELEMENTAL ANALYSIS	
Vanadium	5500	Sulfur, Wt.%	0.16
Iron	8900		
Sodium	6300	Metals, WPPM	
		Nickel	2
MICROACTIVITY			
Conversion, Vol.%	60.2	Vanadium	1
Coke Factor	1.3	Sodium	1
Hydrogen Factor	9.5	Iron	7
		HPLC, Wt. %	
		Saturates	67.9
		Mono-Aromatics	17.2
		Di-Aromatics	3.0
		>Di-Aromatics	8.8
		Polars	3.2
		Asphaltenes	0.0

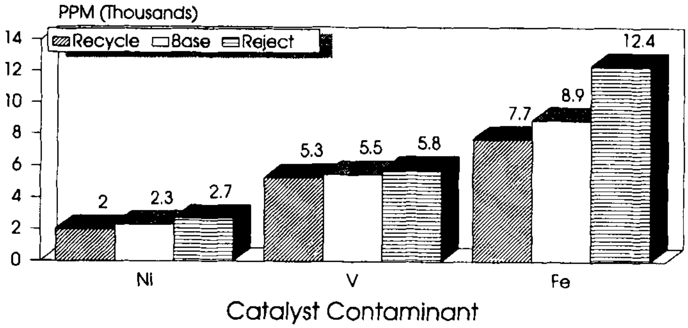

FIGURE 8.
MagnaCat Process
Metal Separation Comparison

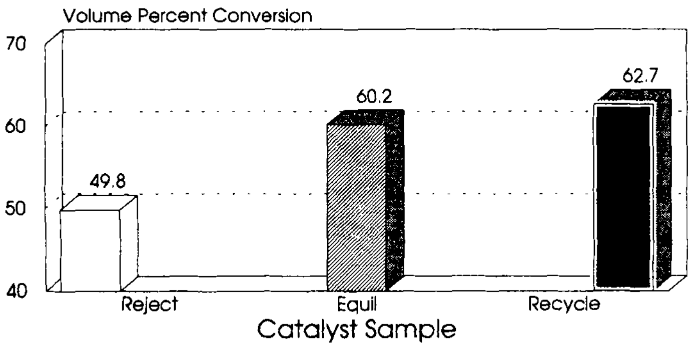

FIGURE 9.
MagnaCat Process
Separation Comparison – MAT

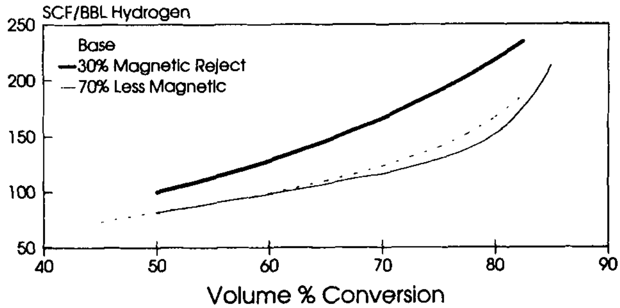

FIGURE 10.
Magnetic Separation Pilot Plant Study
Effect Upon Hydrogen

is capable of processing FCC feedstocks at riser temperatures ranging from 900°F to 1010°F. Figure 10 shows that the magnetically separated recycle catalyst makes less hydrogen (SCF/BBL) relative to the base case without magnetic separation.

The magnetic reject fraction produces a much higher hydrogen yield. This is caused by two factors: (1) the magnetic reject contains a higher level of nickel and (2) this fraction has a much lower catalyst activity requiring more severe reaction conditions to obtain equivalent conversions for comparison with the base case and least magnetic fraction. This is particularly obvious in the hydrogen to methane results shown in Figure 11.

Figure 12 shows that at constant conversion, magnetic separation results in slightly higher gasoline plus alkylate yields, with most of the benefit of higher conversion levels. Again, the magnetic reject produced inferior yields compared with the base case and least magnetic fraction.

One of the most significant advantages with the MagnaCat® Process can be seen by a decrease in coke, Figure 13. The least magnetic fraction produces a lower coke yield than both the base and magnetic reject. A large amount of the coke produced in an FCC unit can be attributed to the high metals/low activity catalyst. Relating this to a commercial FCC operation, the refiner could either increase feed throughput or increase incremental vacuum bottoms to the cracking process unit by use of magnetic separation of his equilibrium cracking catalyst.

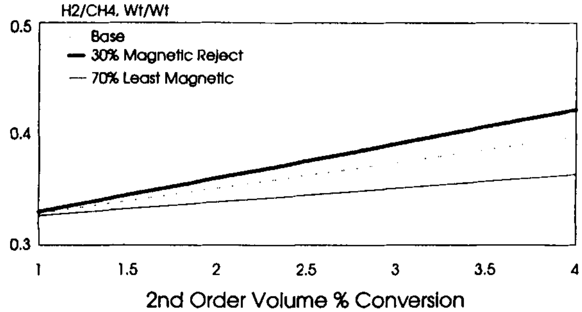

FIGURE 11.
Magnetic Separation Pilot Plant Study
Effect Upon Hydrogen to Methane Ratio

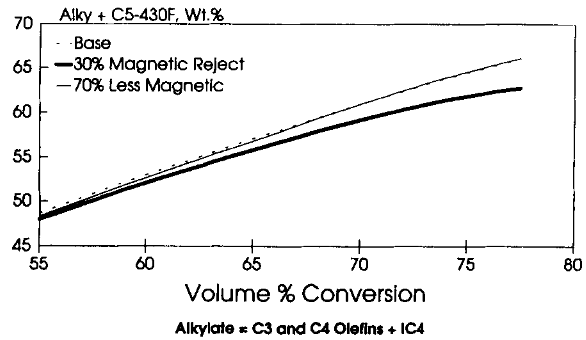

FIGURE 12.
Magnetic Separation Pilot Plant Study
Effect Upon Gasoline + Alkylate Yield

Most refiners ask, "What can this process do for me and how much money will it generate?" Based on these pilot data, the MagnaCat® Process produces an economic advantage ranging $0.20-0.45/barrel of feed processed in the FCC unit, depending on the specific separation rate and process/economic assumptions used. Operating costs for the process are less than $0.01 for FCC per barrel, and investment costs for a typical size unit are between $1-2 million. The process is also very safe and environmentally benign. Refining Process Services[6] offers the MagnaCat® Process for license to the refining industry.

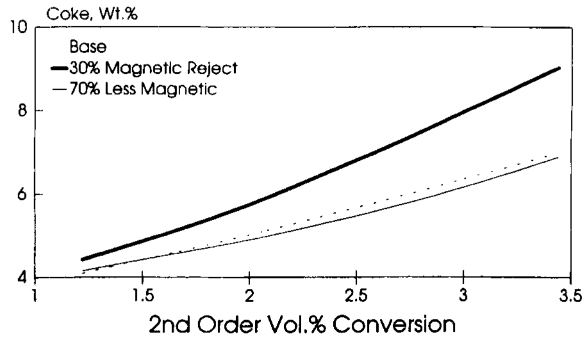

FIGURE 13.
Magnetic Separation Pilot Plant Study
Effect Upon Coke

CONCLUSIONS

Magnetic separation of FCC equilibrium catalysts is a relatively new process to the petroleum industry. Rigorous testing of this process has resulted in the following conclusions:

- The strength of the magnetic roll, the belt thickness, belt speed, and the magnetic susceptibility and distribution of the catalyst are the key factors in magnetic separation.
- Equilibrium catalyst activity is raised about 2 MAT numbers at constant addition/withdrawal rates.
- Significant reductions in hydrogen yields and H_2/CH_4 ratios are consistently obtained.
- Reduction in Delta coke will allow either an increase in FCC feed throughput or in incremental vacuum bottoms processing.
- Improved catalyst fluidization characteristics may result from the use of MagnaCat® Process.
- The process can be operated in different modes, or a combination:
  - increase equilibrium activity/selectivity at constant catalyst addition.
  - reduce fresh catalyst addition and spent catalyst disposal costs at constant equilibrium activity.

- A $0.20-0.45/barrel economic advantage was estimated for use of the MagnaCat® Process for FCC applications.

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