Abstract - The world-wide refinery industry is faced with increasingly difficult and challenging sulfur management needs, tougher emission reduction targets and progressively restrictive fuel specifications. These trends, which developed over time, have often been addressed as one-off problems within a refinery resulting in sub-optimized solutions. DuPont Clean Technologies provides customized sulfur & ammonia recovery, clean fuels (alkylation and hydroprocessing) and gas scrubbing environmental solutions to refiners which are designed to address in an integrated and sustainable form the above challenges. These integrated solutions are optimized to maximize synergies between technologies, minimizing cost to the refiner and offering the lowest environmental footprint.

Keywords: sulfur management, sulfur recovery, spent acid regeneration, nitrogen management, ammonia, ammonium sulfate, sulfuric acid, scrubbing, alkylation, hydrotreating, hydrotreating, hydrocracking, diesel, fuel switching, boiler, heater, steam, emission reduction.

1. INTRODUCTION

The world-wide refining industry is facing an increasing challenge to minimize and control refinery emissions while simultaneously addressing production of low sulfur-containing fuels. A catalyst for these transformations is the regulatory environment becoming increasingly stringent. At the same time, the high value of sulfur in today’s market demands the optimization of the refinery sulfur management scheme and the extension of the refinery sulfur conversion chain beyond typical elemental sulfur, to production of sulfur-derivatives for industrial and agricultural markets.

2. OVERVIEW OF DUPONT CLEAN TECHNOLOGIES

DuPont Clean Technologies provides integrated, customized environmental solutions for refiners’ sulfur management, nitrogen management, emission control and clean fuels.
needs. The building blocks for DuPont’s integrated environmental solutions include DuPont Sulfur Gas Recovery (SGR) and Spent Acid Regeneration (SAR) Technologies, DuPont™ Clean Fuel Technologies (STRATCO® alkylation and IsoTherming® hydroprocessing), and DuPont™ BELCO® Clean Air Technologies. DuPont’s science-based solutions to environmental problems are based on 200 years of experience in chemistry, process know-how, and on the effective integration of these recognized environmental building blocks. The end result is a customized, integrated environmental solution that optimizes synergies between technologies, offers the lowest environmental footprint and provides optimized savings in operating cost and capital investment to the refiner1,2,3.

3. INTEGRATED ENVIRONMENTAL SOLUTIONS

3.1 DuPont SAR-SGR Sulfuric Acid Technology

DuPont’s sulfur management takes place via conversion of sulfur gases (amine gas, SWS gas, gasifier gas, etc.) in an on-site spent acid regeneration and sulfur gas recovery unit (SAR-SGR) located on or adjacent to a refinery. This plant provides total or partial sulfur gas recovery (SGR) to the refinery at the lowest emission levels and cost compared to alternative technologies, producing sulfuric acid and high pressure steam as products. This sulfur management capability can be effectively integrated to alkylation, where the acid plant provides spent acid regeneration (SAR) to the refinery sulfuric acid alkylation units. Five SAR-SGR plants were successfully deployed by DuPont at three refinery facilities in the U.S. Figure 1 shows this acid plant-refinery integration concept.

The bar chart presented in Figure 2 shows the result of a case study for an on-site SAR-SGR acid plant. For this case study, a DuPont SAR-SGR plant was designed to improve control of refinery emissions, increase reliability and free up sulfur recovery capital from the refinery. The study shows that the DuPont SAR-SGR acid plant provided a lower cost for sulfur recovery (compared at constant NPV over 10 years) compared to a conventional Claus SRU approach.

3.2 DuPont™ STRATCO® Alkylation Technology Integrated to SAR-SGR Acid Plant

As one of DuPont’s strategies for clean fuels involves the production of alkylate, DuPont Clean Fuels Technologies deploys STRATCO® sulfuric acid alkylation technology, which is recognized as the safest and most mature alkylation technology. The effective integration of DuPont SAR-SGR sulfuric acid plant with STRATCO® alkylation technology yields a reduction in capital investment and optimization of operating cost and energy integration. Figure 3 shows this on-site acid plant – alkylation integrated solution.

Figure 1 – On-site DuPont SAR-SGR sulfuric acid plant.

Figure 2 – Cost comparison for sulfur recovery case study showing DuPont SAR-SGR plant providing improved benefits to the refinery compared to refiner’s best alternative.

Figure 3 – Integration of an on-site DuPont SAR-SGR sulfuric acid alkylation plant to a DuPont STRATCO® sulfuric acid alkylation plant.
3.3 DuPont IsoTherming® Hydroprocessing Technology

The second DuPont strategy for clean fuels involves hydroprocessing. DuPont IsoTherming® technology provides the petroleum refiner the most cost-effective means to meet conversion, product sulfur and product nitrogen specifications in an increasingly competitive and demanding environment. The DuPont IsoTherming® process technology is a commercially proven, flexible, breakthrough technology that allows a refiner to meet their increased hydroprocessing capacity needs at a significantly reduced capital and operating costs over conventional hydroprocessing technologies. This technology can be customized, including catalyst selection, to meet a particular refiner needs. In each case, reactor design and operating conditions are optimized around a catalyst system. IsoTherming® technology has been successfully practiced on a commercial scale in several ULSD units and has been licensed for several Mild Hydrocracking services.

Figure 4 shows a simplified diagram of the IsoTherming® process. For the case example of ULSD revamp, not only a significant capital savings can be realized with IsoTherming® vs. a conventional revamp but the net result is a unit that offers considerably more flexible operation.

The relative costs of IsoTherming® process technology in mild hydrocracking service will vary depending on the refiner need and the existing infrastructure capability. For a 30,000 BPD 2,000 psi application the capital cost for IsoTherming® is substantially lower as compared to the conventional trickle bed process. Fuel gas and power requirements are slightly lower and steam generation is higher.

Table 1 presents a capital cost comparison between IsoTherming® and conventional hydrotreating. DuPont IsoTherming® hydrotreating technology offers the lowest cost per barrel for severe gas oil hydrotreating, mild hydrocracking, and diesel (revamp and grassroots) applications.

Table 1 – Capital cost comparison in $/bbl (30,000 bbl/day – 4,750 m³/d basis) between DuPont IsoTherming® technology and conventional hydrotreating for various applications.

3.4 DuPont NH₃ SWS Gas Scrubbing / Ammonium Sulfate Technology and Its Integration with a DuPont SAR-SGR Sulfuric Acid Plant

This technology comprises the separation (reactive scrubbing) of ammonia from sour water stripper (SWS) gas and its conversion, using sulfuric acid, to ammonium sulfate solution. The resulting ammonia-free, dry, SWS-scrubbed gas can be fed into a Claus unit freeing additional sulfur recovery capacity and improving downstream SRU operation. It is expected that up to 3.75 tons of additional sulfur capacity per ton of ammonia can be obtained by scrubbing ammonia from the SWS gas feed. The resulting ammonium sulfate liquor product can be used as liquid N, S-containing fertilizer feedstock or further crystallized for solid bulk use. This technology is very suitable for refineries that process crudes with a high level of nitrogen-bound species and/or larger amounts of sour water.

This SWS gas NH₃ scrubbing / ammonium sulfate process can be readily integrated to an on-site SGR sulfuric acid plant. As the SGR plant converts sulfur gases providing incremental or total sulfur recovery capacity and/or SRU backup to the refinery, it produces non-fuming sulfuric acid and steam which become feedstock for the ammonium sulfate plant. Figure 5 depicts the integration of these technologies.
DuPont™ BELCO® scrubbing technologies are well known in the refining industry for their use as emission control units on fluid catalytic cracking units to abate the PM, NO\textsubscript{x} and SO\textsubscript{x} emissions. BELCO® systems are also used for other applications such as emission control on fired heaters and boilers to allow for the use of high sulfur fuels in these units.

One challenge for the refining industry today is the management of the bottom of the barrel components. Traditionally these streams were blended and sold, at a large discount to crude oil, as bunker fuels. An alternative use for these materials is to use them as fuel sources for steam production and to fire process heaters. Significant economic advantages can be derived through this approach: reduced use of expensive natural gas, on-site value for distressed stocks, and the economic value derived by redirecting the diluents needed to blend with bottoms materials to produce marketable bunker fuels.

Given the increased level of sulfur in bottoms materials, a robust emission abatement system must be included to reduce PM and SO\textsubscript{x} emissions. The long experience of BELCO® scrubbers lends itself well to these applications and depending on the local environmental regulations, the scrubbing system could be a once through caustic scrubber or regenerative in nature using either a dual alkali approach or an SO\textsubscript{2}-capture buffer. DuPont Clean Technologies will work with the refinery to provide a customized service offering to regenerate the scrubbing solution and market the resulting products (sulfuric acid or gypsum). In this way the refinery can focus on core activities and capture value from distressed refinery stocks.

Figure 6 shows how a DuPont™ BELCO® LABSORB™ regenerative scrubber can be integrated to a Claus unit and to a DuPont SAR-SGR sulfuric acid plant or Dual Alkali Scrubber to replace a SRU tail gas unit and enable the use of high sulfur fuels on site. Effective sulfur management is provided while minimizing emissions and producing valuable chemicals such as sulfuric acid or gypsum for market sales.

In a comparison case study conducted by DuPont Clean Technologies on alternative SO\textsubscript{2} scrubbing options for refineries implementing “fuel switching” (e.g., use of cheaper high sulfur fuels instead of natural gas to fire heaters and boilers) it was found that larger flue gas conversions favor regenerative scrubbing systems (e.g., LABSORB™). Furthermore, it was found economically favorable to convert both unit heaters and facility level boilers to high sulfur fuel feeds using the appropriate SO\textsubscript{2} scrubbing and sulfur gas conversion integrated sulfur management configuration. Figure 7 shows the results of the study, depicting the comparison of scrubbing options and its impact on investment NPV and fuel savings.

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**Figure 6 – Integration of a DuPont™ BELCO® LABSORB™ regenerative scrubber with a DuPont SAR-SGR sulfuric acid plant and Claus unit for emission control and sulfur management on refineries using high sulfur fuels for heaters and boilers.**

**Figure 7 – Comparison of scrubbing options depicting its impact to NPV and fuel savings for a refinery fuel switching case.**
4. CONCLUSIONS

The effective integration of sulfur management, nitrogen management, emission control and clean fuels technologies allows the design and implementation of customized environmental solutions that take full advantage of technology synergies and offers the lowest environmental footprint while maximizing benefit to the refiner.

DuPont offers extensive know-how on diverse and innovative environmental and clean fuels technologies and processes as well as a demonstrated broad operations expertise and environmental stewardship track record. DuPont environmental solutions include diverse capital and operations options, offering customized, flexible and cost effective sulfur & nitrogen recovery, scrubbing and clean fuels solutions to the refining community.

REFERENCES

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