More Economical Sulfur Removal for Fuel Processing Plants

Challenge

Sulfur is naturally present as an impurity in fossil fuels. When the fuels are burned, the sulfur is released as sulfur dioxide—an air pollutant responsible for respiratory problems and acid rain. Environmental regulations have increasingly restricted sulfur dioxide emissions, forcing fuel processors to remove the sulfur from both fuels and exhaust gases.

The cost of removing sulfur from natural gas and petroleum in the United States was about $1.25 billion in 2008*. In natural gas, sulfur is present mainly as hydrogen sulfide gas (H_2S), while in crude oil it is present in sulfur-containing organic compounds which are converted into hydrocarbons and H_2S during the removal process (hydrodesulfurization). In both cases, corrosive, highly-toxic H_2S gas must be converted into elemental sulfur and removed for sale or safe disposal.

At large scales, the most economical technology for converting hydrogen sulfide into sulfur is the Claus process. This well-established process uses partial combustion and catalytic oxidation to convert about 97% of the H_2S to elemental sulfur. In a typical application, an amine treatment unit concentrates the H_2S before it enters the Claus unit, and a tail gas treatment unit removes the remaining 3% of the H_2S after it exits the Claus unit.

This multi-step process has low operating costs but high capital costs—too expensive for plants recovering less than about 20 tons of sulfur per day. These plants were using liquid-phase reduction-oxidation (redox) processes to remove sulfur. While these processes removed essentially all of the sulfur and offered a lower capital cost, they also imposed high chemical and operating costs ($300 to $600 per ton of sulfur), too costly for many small fuel processing plants.

Innovating Solutions

TDA Research became aware of the need for improved sulfur treatment processes while working with the Gas Technology Institute. Building on their experience with catalytic processes, they began research on H_2S oxidation with internal research and development (R&D) funding in 1995. In 1996, TDA was awarded DOE EERE SBIR funding to advance their research to the bench scale during Phase I and II SBIR projects. This funding supported proof-of-concept and scale-up of both the catalyst synthesis and the process. The R&D project continued until 1999, when TDA obtained funding from the National Petroleum Technology Office (now the Strategic Center for Natural Gas and Oil) to perform a full-scale field test at a gas plant in Texas. Additional cost-shared funding from the Gas Technology Institute was used to design and fabricate the field test unit.

TDA collaborated with Saint-Gobain NorPro (NorPro), a global leader in ceramics and catalysts that scaled up the catalyst formulation to 1 ton for the field test. Butcher's Welding of Houston, Texas, built and installed the test unit at a Whiting oil and gas facility in Plains, Texas. By 2002, 1,200 hours of field testing had been successfully completed, processing 300,000 cubic feet of sour (high sulfur) gas per day.

As a result of these efforts, TDA developed a new, simple, low-capital cost process that sweetens "sour gas" streams (those containing H_2S) by oxidizing the H_2S into elemental sulfur and water without requiring upstream H_2S separation. This process removes the bulk of the sulfur (about 90%), leaving about 10% of the original H_2S in the product gas. The remaining H_2S can be removed by a second stage of direct oxidation and/or a tail gas treatment process, such as a scavenger or small liquid redox unit.

* Ober, J.A. (2009) "Sulfur" USGS commodity minerals data sheet; Leppin, D. (1997) GRI Program in Small Scale Sulfur Removal and Recovery, 1997 Update (production costs adjusted to 2008 dollars).

DOE Small Business Innovation Research (SBIR) support enabled TDA to develop and commercialize its direct oxidation process—a simple, catalyst-based system for removing sulfur from natural gas and petroleum—that was convenient and economical enough for smaller fuel processing plants to use.

TDA Research, Inc. (TDA) of Wheat Ridge, CO, formed in 1987, is a privately-held R&D company that brings products to market either by forming internal business units or by partnering with larger Global 2000 manufacturing companies. TDA has primarily been a research company but is increasingly generating revenue through sales of products and technology. TDA's R&D focus areas include new materials, catalytic and sorbent-based chemical processes, and military and aerospace components.

www.tda.com

A case study from the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy SBIR program, providing competitive grants for scientific excellence and technological innovation to advance critical American priorities and build a strong national economy – one small business at a time.

Sulfur Removal for Fuel Processing Plants

In 2000, TDA received a patent covering its catalyst formulations and process for oxidizing H_2S to sulfur, and in 2004, the firm licensed the direct oxidation technology to SulfaTreat, a business unit of M-I, LLC (a joint venture between Smith International and Schlumberger). They now market the technology to small- and medium-sized gas and petroleum processing plants.

The first two direct oxidation plants, commissioned in 2006, are located in Southern California and are designed to treat gas associated with steam-driven heavy oil recovery.

SBIR Impacts

Benefits of the SulfaTreat Direct Oxidation Process vs. Conventional Liquid Redox Plants[1]

The TDA/SulfaTreat direct oxidation process provides a convenient and economical alternative for desulfurizing natural gas and gas associated with petroleum recovery, especially for small-scale applications (1-20 tons of sulfur per day). By enabling smaller producers to remove sulfur economically, the process can:

- Reduce energy consumption by about 30% compared to conventional liquid redox plants
- Reduce capital and operating costs by over 30% compared to conventional liquid redox plants
- Produce marketable, bright yellow sulfur
- Replace liquid chemicals with a long-lasting, non-toxic, dry catalyst—eliminating hazardous waste disposal
- Reduce system complexity and maintenance requirements

Innovation

The TDA/SulfaTreat direct oxidation process catalytically converts toxic hydrogen sulfide in natural gas and petroleum into safe elemental sulfur which can then be sold or stored away. Key features are:

- Process Type: Dry catalytic oxidation
- Capacity: Up to 30,000 ppm per stage and 25 tons of sulfur per day
- Conversion Efficiency: Greater than 80% per stage
- Sulfur Selectivity: 99%
- Catalyst Life: Minimum of 2–3 years

Company Success

Since the start of this SBIR project in 1995, TDA has grown from a staff of 30 with annual revenue of $3.5 to a staff of 80 and annual revenue of $12 million.

SBIR funding was vital to TDA in performing the initial proof-of-concept work for its direct oxidation process. Other factors in successful commercialization of the technology were the availability of follow-on funding and the numerous successful teaming relationships that were initiated and nurtured during the project. Funding provided by DOE and the Gas Technology Institute supported the field testing that was crucial to successful licensing of the technology.

TDA's choice of Saint-Gobain NorPro as catalyst manufacturer for the project built on a successful relationship that began in the early 1990s. NorPro successfully scaled up TDA's catalyst formulation for the field test and manufactured the catalyst for SulfaTreat's first two commercial plants. Westfield Engineering constructed these plants, and TDA supported SulfaTreat on technical issues during and after commissioning.

TDA chose to commercialize the technology through licensing, and recognized the importance of selecting the right firm. By exhibiting the technology at gas processing conferences, TDA was able to identify and build relationships with several potential license partners. TDA spent about a year screening potential licensees and then negotiating a license with SulfaTreat. SulfaTreat participated enthusiastically after seeing TDA's field test results, attractive economic analysis, and support from DOE and the Gas Technology Institute.

[1] Information provided by TDA based on experimental and operational experience.

For additional information, please contact:

DOE

Charles Russomanno
EERE SBIR-STTR Portfolio Manager
(202) 586-7543
charles.russomanno@ee.doe.gov

TDA

Girish Srinivas, PhD
Program Manager
(303) 940-2321
gsrinivas@tda.com

Sulfa-Treat

Bill Brundick
Business Development Manager
(800) 726-7687
bbrundick@miswaco.com