

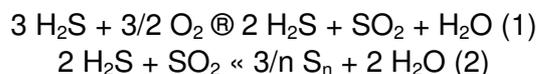
The Claus Process

Introduction

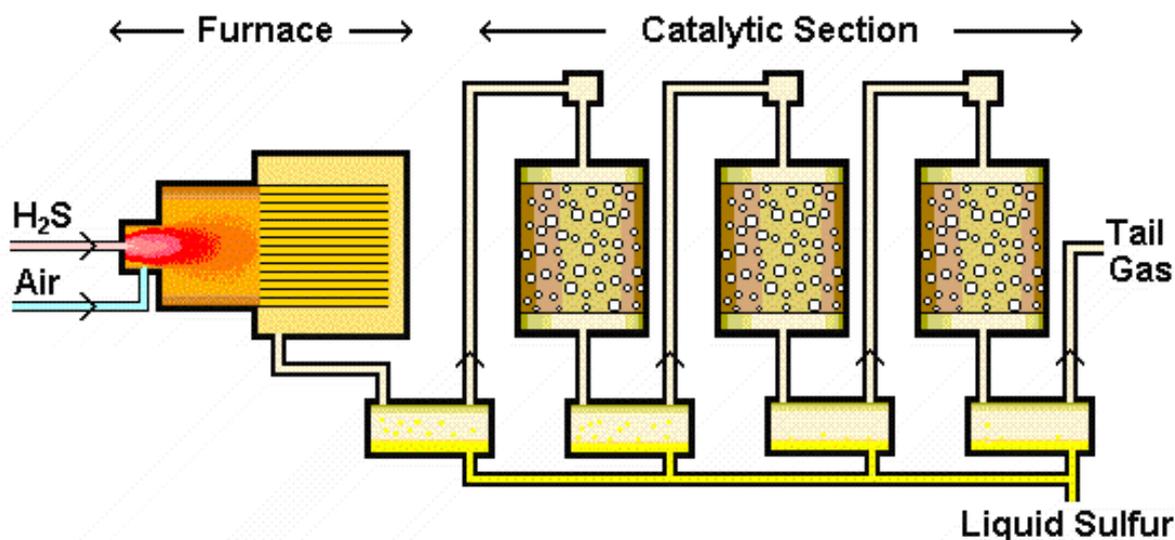
The modified Claus process, developed by London chemist Carl Friedrich Claus in 1883, is used to recover elementary sulfur from hydrogen sulfide (H₂S) in gases from oil refineries, natural gas, etc. Hydrogen sulfide is a smelly (with its signature "rotten egg" smell), corrosive, and toxic gas. In the U.S., OSHA guidelines set the maximum allowable exposure for prolonged periods at 10 ppm. Exposure to concentrations greater than 600 ppm for 30 minutes can be fatal. As a result, H₂S needs to be converted to non-toxic and useful elemental sulfur. In industry, this is usually done by the Claus process.

The Process

The Claus reaction consists of H₂S and sulfur dioxide (SO₂) reacting in the vapor phase to produce sulfur and water. The H₂S is first separated from the host gas stream using amine extraction. Then it is fed to the Claus unit, where it is converted in two steps. The first step is the thermal step, where one-third of the H₂S is oxidized, producing the H₂S and SO₂ in a 2:1 ratio. This is done in a reaction furnace at high temperatures (1000-1400 °C). Some sulfur is formed, but the remaining unreacted H₂S proceeds to the next step, the catalytic step. In the catalytic step, the remaining H₂S is reacted with the SO₂ formed in the thermal step at lower temperatures (200-350 °C) over a catalyst bed to make more sulfur. Two to four catalytic stages are needed to obtain 94% to 98% conversion. The reactions and a schematic drawing of the process are as follows:



Schematic of Claus Process



The liquid sulfur produced can be reused in the plant. The effluent tailgas contains SO₂ [by equation (1)], and carbon disulfide (CS₂) and carbonyl sulfide (COS), which are byproducts produced in the Claus reactors.

Catalysts

The most widely used Claus catalyst in sulfur recovery units is non-promoted spherical activated alumina. Properties associated with optimum non-promoted Claus catalyst include high surface area, appropriate pore size distribution, and enhanced physical properties. Catalysts with areas over 300 m²/g, macroporosities over 0.15 ml/g, and macropore radii as high as allowed by pellet density should have good performance. Alumina has a surface area of 325 m²/g, a macroporosity of 0.14 ml/g, and a macropore radius of 5,226 Angstroms. Other catalysts sometimes used in the Claus process include activated bauxite (surface area of 184 m²/g), cobalt-molybdenum hydrogenation catalyst (surface area of 270 m²/g), and Kaiser S-201 active alumina (surface area of 270 m²/g).

Alumina catalysts may be deactivated generally by sulfation, but also by carbon deposition, surface adsorption, or capillary condensation of sulfur. This deactivation will lower the conversions, with the consequence of higher sulfur content in the tailgas and correspondingly increased tailgas cleanup costs. The effectiveness factor of the catalyst particle may be improved by increasing either its external area or its pore sizes.

Process Improvements

As stated earlier, the basic Claus process is about 94% to 98% efficient in removing H₂S. Many improvements have been developed to allow the process to obtain 99+% conversion, as emission limits have tightened. A tail gas clean-up process is often used. An example is the amine-based tailgas clean-up process, which reduces all of the sulfur compounds in the tailgas leaving the front-end Claus sulfur plant back to H₂S, then uses selective amine absorption to remove the H₂S while allowing most of the carbon dioxide to slip by. The H₂S and carbon dioxide removed by the amine are stripped from the amine and recycled back to the Claus plant, allowing an overall sulfur recovery in excess of 99.5%. Another improvement to the Claus process is the Superclaus process. The Superclaus process offers an overall sulfur recovery of up to 99.5% without any tail gas treatment, application in new as well as existing Claus plants, low investment and utility costs, and a continuous gas phase catalytic process without water condensation or waste streams. In the Superclaus process, the Claus reaction [reaction (2) above], which limits sulfur conversion because it is in equilibrium, is replaced by the reaction of H₂S with O₂, which is thermodynamically complete.

The Superclaus catalyst is designed to give complete and highly selective conversion of H₂S to elemental sulfur, low formation of SO₂, and low sensitivity to water concentrations in the process gas so it has no Claus reaction reactivity. The catalyst consists of active metal oxides on a carrier. Its properties include the following: H₂S conversion to sulfur higher than 85%, not sensitive to excess air, not sensitive to high water concentrations, no Claus reaction, no CO/H₂ oxidation, no formation of COS/CS₂, and chemically and thermally stable with good mechanical strength and long effective life. Two options for the Superclaus process are the Superclaus 99 and the Superclaus 99.5 processes. Superclaus 99 consists of a thermal stage followed by three or four catalytic reactor stages, much like the Claus process. The first two or three catalytic stages are loaded with the standard Claus catalyst while the final stage is loaded with the new selective oxidation catalyst. In the Superclaus 99.5 process, a hydrogenation stage (using a cobalt/molybdenum catalyst) between the last Claus reactor and the selective oxidation reactor is added. Sulfur recovery in the Superclaus 99 process with 2 Claus stages

is in the range of 98.9% - 99.4% and in the range of 99.3% - 99.6% with 3 Claus stages. Sulfur recovery in the Superclaus 99.5 process is in the range of 99.2% - 99.6% with 2 Claus stages and 99.4% - 99.7% with 3 Claus stages.

Possible Future Improvements

Some potential improvements that could be made in the Claus reaction include CS₂ destruction. It is formed as a byproduct in the furnace and some laboratory work has found that some catalysts can destroy the CS₂ before it gets into the catalytic reactors. Also some optimization work for temperatures in the final reactors can be done. The conversion of H₂S increases at higher temperatures, but a more favorable equilibrium is found at lower temperatures. It is not yet known for sure whether higher or lower temperatures are needed.