Small Capacity Sulfur Removal Units for Coal Gasification

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Introduction

Over the past decade, production/consumption gaps for both power and petrochemical products have encouraged the development of projects aimed at the gasification of anything organic-based such as: coal, petroleum coke, biomass, wood-based materials, agricultural wastes, tars, coke oven gas and asphalt. Additionally this search for clean, flexible alternative fuel and chemical feedstock sources continues to become more and more economically attractive as the prices of natural gas and crude oil continue to increase as a result of both logistics and demand.

While sulfur removal from gas streams has been an issue since the first use of sour gas, it continues to receive ever-increasing attention as an environmental issue. In addition to the desirable syngas components (CO, H2 and CO_2) that are generated in a gasification process, a feedstock such as coal has many more constituents, which produce undesirable byproducts (H_2S, HCN, COS, CS_2, CO_2, Cl_2, and ash or slag).

The recovery of sulfur from syngas must be accomplished to complete the process of converting coal into clean, environmentally friendly fuels and petrochemical feedstocks. Traditionally Claus Technology has been the standard route to recovery of elemental sulfur in quantities greater than 25 tons/day and LO CAT® Technology has been the standard for sulfur removal capacities less than 25 tons/day. However, the high capital costs and operating complexity associated with operating Claus units on extremely dilute sulfur concentration (requiring acid gas enrichment) and variable flowrates (requiring complicated process control methods) has forced gasification developers to search for alternative technologies. Whenever the hydrogen sulfide contained in a sour gas stream is less than 25 vol% and/or the volumetric sour gas flowrate varies on a frequent basis; LO CAT® Technology is a valid option for treating sour gas streams with sulfur removal capacities as high as 40 tons/day.

A number of gasification projects have relied on LO CAT® Technology from the Merichem Company to cost-effectively remove hydrogen sulfide and provide clean syngas for a variety of applications. Successful implementation of LO CAT Technology in gasification began in 2001 with treating syngas derived from the gasification of industrial waste products. These waste gasification applications provided the technical basis for extending the technology into other gasification markets in Europe, China, and the United States. Merichem Company was first approached by a Chinese client who desired to produce acetic acid from a coal-derived syngas by first producing methanol followed by methanol conversion to acetic acid; in 2007. Additionally, LO CAT units that are currently being constructed and commissioned for two other coal gasification projects in China; an IGCC application (coal-to-SNG) in Tainjin and a coal-to-chemicals application (first producing Hydrogen followed by Ammonia synthesis) in Nanjing.

Background

Hydrogen sulfide is an extremely toxic, corrosive and odorous gas, causing safety and material of construction issues in its unaltered form. High levels of H_2S in many raw natural gas streams have long required processing to reduce the contained acid gases before transport and distribution of the fuel to market. The H_2S remaining in the fuel is oxidized to sulfur dioxide (SO_2) through combustion, and becomes a major contributor to acid rain. Hydrogen Sulfide is also extremely detrimental to the downstream synthesis catalysts on two fronts: first is a revenue loss – the synthesis catalyst losses conversion efficiency in the presence of H_2S as a result of limiting chemical product production; and second is the cost (tens to hundreds of millions of dollars) replacing the synthesis catalyst – continued exposure to sulfur and cyanide compounds will result in premature failure of the synthesis catalyst.

Early on, scientists recognized iron as an excellent oxidizing agent for the conversion of H_2S to elemental sulfur. However, due to the very low solubility of iron in water, the iron had to be utilized in a dry state, such as the case is with Iron Sponge Technology; or in suspensions as was the case for Ferrox Technology; or compounded with toxic materials such as cyanide or arsenic as was the case with Thylox Technology. In the 1960's development work was begun in England to increase the solubility of elemental iron in aqueous solutions. This work led to the introduction of CIP process, CIP being an acronym for "Chelated Iron Process." However, it wasn't until the late 1970s that a system of chelates was developed by Merichem (known as ARI Technologies at the time) that had sufficient oxidative resistance to be technically stable and commercially successful. This development work led to the introduction of LO CAT® Technology; which has proven to be a extremely versatile.

For more than thirty years, this technology has been adopted by a number of industries. Starting with oil and gas production (upstream and midstream), and oil refining (downstream), the basic process has been continually improved and modified to allow for expanded use in other markets and industrial segments. There are more than 200 process installations around the world that depend on LO CAT Technology to remove H_2S from their sour gas streams. On a combined basis, these installations remove over 600,000 kilograms of sulfur per day. From petrochemicals to metals (coke oven gas and direct reduced iron off gas), from water and waste water treatment (municipal and industrial) to carbon dioxide products (food and beverage), this simple robust technology has found many niches. More recently unconventional and alternative energy resources such as: shale gas, stranded offshore requiring FPSO, geothermal, landfill gas, biogases, and gasification have been added to the portfolio of applications successfully utilizing LO CAT Technology for sulfur recovery. The first commercial installation of LO CAT Technology took place in 1980. Currently there are 10 companies that have been continuously operating their LO CAT units for more than 25 years. As was the case with most new adopters of LO CAT Technology; oil and gas producers and refiners were the first in China to adopt LO CAT Technology more than 10 years ago.

Table 1: LO CAT China Installations

LO CATion	Date	Industry	LO CAT Type	Application	Flow rate Nm^3/hr	Inlet H2S ppmv	Outlet H2S ppmv	Sulfur ton/day
Shaanxi, Chongqing	2010	Oil & Gas	Autocirculation	Amine Acid Gas			<10	3
Jiangsu, Jinling	2010	Petrochem	Autocirculation	Coal-to-Chem	7,100	6 vol%	<5	15
Tianjin	2009	Power	Autocirculation	IGCC	4,700	4,000	<10	25
Shaanxi, Yulin	2008	Refining	Conventional	Fuel Gas Amine Acid Gas SWS Gas	15,425	2%	<5	10
Shaanxi, Yonping	2008	Refining	Autocirculation	Amine Acid Gas SWS Gas	855	34%	<0.1	10
Xinjiang, Kuele	2008	Oil & Gas	Autocirculation	Amine Acid Gas	250	23%	<10	6
Yunnan, Qujing	2007	Petrochem	Conventional	Coal-to-Chem	31,000	4000	<0.1	5
Shaanxi, Yangzhuanhe	2006	Refining	Autocirculation	Amine Acid Gas SWS Gas	800	48 vol%	<5	12
Shaanxi, Yan'an	2006	Refining	Autocirculation	Amine Acid Gas SWS Gas	1,700	27 vol%	<5	16
Sichuan, Longchang	2000	Oil & Gas	Autocirculation	Amine Acid Gas	150	23 vol%	<10	1
Beijing	1998	Food & Beverage	Conventional	Carbon Dioxide	2,500	1,200	<1	<1

LO CAT in Gasification

The first application of LO CAT Technology in a gasification type application was started up in the USA in the early 1990s to treat coke oven gas. In 2001 the high cost of waste disposal in Japan encouraged the development of solid waste gasification projects. The successful implementation of LO CAT Technology in these gasification projects quickly led to 6 additional units in the solid waste gasification industry; and the experience gained with these gasifiers has led to the selection of LO CAT Technology for use in coal gasification projects in the United States, China and South Africa. A summary of LO CAT units treating syngas is shown here in Table 2. As can be seen, the technology has been adopted to treat syngas in an array of applications having an equally diverse spectrum of feedstocks. These LO CAT units operate across a wide range of pressures, removing H_2S from either syngas or the acid gas extracted from syngas. As has been the case with the introduction of LO CAT into each new market, the projects started out small with sulfur removal capacities of less than one ton/day have quickly grown to removal capacities greater than 25 tons/day.

Table 2: LO CAT GASIFICATION APPLICATIONS

LO CATion	Start	Gasification	LO CAT Type	Application	Flow rate MMSCFD	Inlet H2S ppmv	Outlet H2S ppmv	Sulfur ton/day
South Africa	2011	UCG Underground Coal Gasification	Conventional	SNG Power Generation	267,000	2,000	< 10	18
China	2010	CTC Coal to Chemicals	Autocirculation	Ammonia Production	7,100	6 vol%	< 5	15
China	2009	IGCC Integrated Gasification Combined Cycle	Autocirculation	SNG Power Generation	4,700	4,000	< 10	25
China	2008	CTC	Direct / Conventional	Acetic Acid Production	31,000	4,000	< 0.1	5
USA	2008	CTL Coal to Liquids	Conventional	Fischer Tropsch Fuels	400	8 vol%	< 1	1
Italy	2006	MSW (Municipal Solid Waste)	Conventional	SNG	21,000	2,600	< 10	2
Japan	2006	MSW	Conventional	SNG, Methanol, Ammonia, Hydrogen	20,000	4,100	< 40	2
Japan	2005	MSW	Conventional		27,500	3,000	< 40	<1
Japan	2005	MSW	Conventional		6,000	400	< 20	3
Japan	2004	MSW	Conventional		18,000	400	< 20	<1
Japan	2003	Waste Plastics	Conventional	Ammonia Fertilizer	33,000	140	< 1	<1
Japan	2001	Car Shredder Dust	Conventional	Confidential	7,400	300	< 10	1
USA	1993	COG (Coke Oven Gas)	Autocirculation	SNG	1,700	2.5 vol%	< 10	14
USA	1990	COG	Conventional	Pilot Plant	-	-	-	<1
USA	1990	COG	Conventional	Pilot Plant	-	-	-	<1
USA	1989	COG	Conventional	Pilot Plant	-	-	-	<1

Process Chemistry

LO CAT® Technology was developed to provide an isothermal, low operating cost method for carrying out the modified Claus reaction:

(modified Claus reaction) $H_2S + 1/2\ O_2 \rightarrow H_2O + S°$

As embodied in LO CAT Technology, the basic modified Claus reaction is divided into five sequential steps:

1 - Absorption of H_2S $H_2S\ (Gas) + H2O\ (Liquid) \leftrightarrow H_2S\ (Aq) + H2O\ (Aq)$

2 - Ionization of H_2S	H_2S (Aq)	↔	$H^+ + HS^-$
3 - Sulfide Oxidation	$HS^- + 2Fe^{+++}$	→	$S° + 2Fe^{++} + H^+$
4 - Absorption of Oxygen	1/2 O_2 (Gas) + H_2O (Liquid)	↔	$^1/_2$ O_2 (Aq) + H^2O (Aq)
5 - Iron Oxidation	1/2 O^2 (Aq) + H^2O + $2Fe^{++}$	→	2 OH^- + $2Fe^{+++}$

Equations 1 and 2 represents the absorption of H_2S into the aqueous, chelated iron solution and its subsequent ionization, while equation 3 represents the oxidation of hydrosulfide ions to elemental sulfur and the accompanying reduction of the ferric (active) iron to the ferrous (inactive) state. Equations 4 and 5 represent the absorption of oxygen (from ambient air) into the aqueous solution followed by oxidation of the ferrous iron back to the ferric state.

Equations 3 and 5 are very rapid. Consequently, iron-based systems generally produce relatively small amounts of byproduct thiosulfate ions. However, equations 1 and 4 are relatively slow and are the rate controlling steps in all chelated iron processes. It is interesting to note that the chelating agents do not appear in the process chemistry, and in the overall chemical reaction, the iron cancels out. So the obvious question is why is chelated iron required at all, if it doesn't take part in the overall reaction. The iron serves two purposes in the process chemistry. First, it serves as an electron donor and acceptor, or in other words, a reagent. Secondly, it serves as a catalyst in accelerating the overall reaction. Because of this dual purpose, the iron is often called a "catalytic reagent". Although there are many metals which can perform these functions, iron (Fe) was chosen for LO CAT Technology because it is inexpensive and non-toxic. The chelating agent(s) do not take part at all in the process chemistry. Their role is simply to hold the iron ions in solution. Neither ferrous (Fe++) nor ferric (Fe+++) ions are very soluble or very stable in aqueous solutions. Iron will ordinarily precipitate at low concentrations as either ferric hydroxide Fe(OH)3 or ferrous sulfide (FeS). The chelating agents are organic compounds that wrap around the iron in a claw-like fashion, preventing the iron ions from forming precipitates. LO CAT Technology uses a proprietary system of chelating agents to hold the iron in solution over a very wide pH range. LO CAT has developed into a very versatile processing scheme for treating gas streams containing moderate amounts of H_2S. Advantages of these systems include the ability to treat both aerobic and non-aerobic gas streams, removal efficiencies in excess of 99.9%, essentially 100% turndown on H_2S concentration and quantity, and the production of innocuous products and byproducts.

Process Flow Schemes

In applying this chemistry to a wide range of gas streams in diverse industrial processes, many different flow schemes have been successfully employed. The two most common LO CAT® processing schemes utilized in Chinese coal gasification applications, are illustrated in Figures 1 and 2.

Figure 1 illustrates a *direct* treatment of syngas and incorporates a "Conventional" LO CAT processing scheme, where hydrolysis reactors are utilized to convert COS to H_2S and destroy HCN. When using the Conventional LO CAT scheme, Merichem's treating approach; follow the syngas pretreatment steps that remove: tar, particulates, and chlorides; and starts with the removal of a large portion of the water vapor that is present by cooling the syngas thus reducing the amount of gas to be treated. The syngas is then directed through two integrated conversion and removal stages. The conversion of sulfur species into H_2S and cyanides into NH3 is accomplished with catalytic hydrolysis.

Because these hydrolysis reactions are equilibrium limited a two stage approach is required. The H_2S concentration in the syngas feeding the first hydrolysis reactor increases to a level which subsequently limits deep conversions of COS and CS_2. The first LO CAT absorber then reduces the H_2S level to <1 ppmV thus removing the equilibrium constraints and allowing the second hydrolysis reactor and LO CAT absorber to achieve a very high overall total sulfur removal and cyanide destruction.

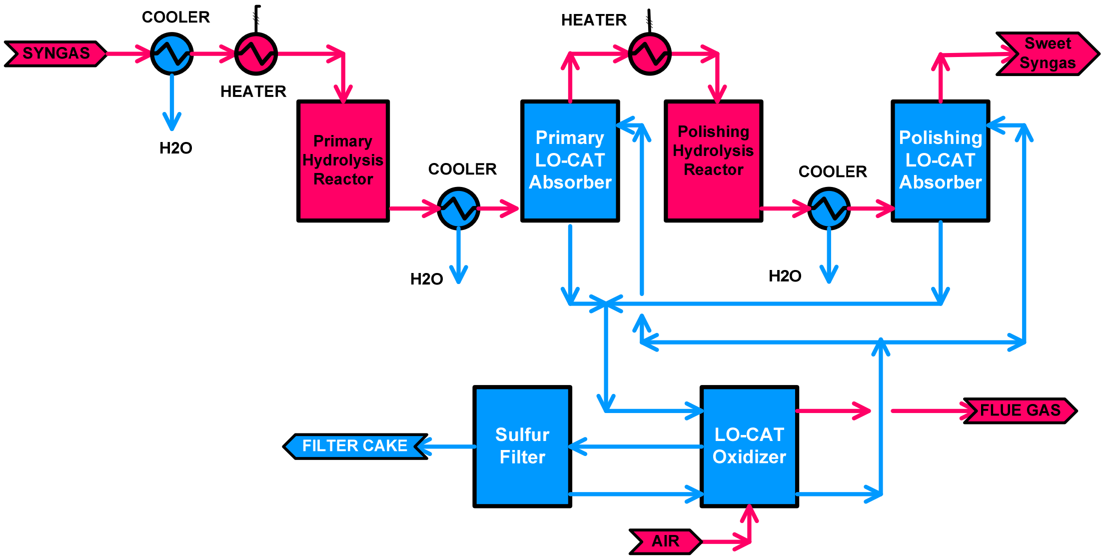

Figure 1 – *Direct* treatment of Syngas using Conventional LO CAT scheme

Figure 2 illustrates an *indirect* treatment of syngas that utilizes an "Autocirculation" LO CAT processing scheme, which is used when treating an acid gas stream where the syngas is pretreated first using a solvent system to separate acid gas from the syngas. When using the Autocirculation LO CAT scheme, Merichem's treating approach typically follows either a physical or chemical solvent system. The processes of choice are typically either: Rectisol, Selexol or Amine. Because these processes only remove the acid gases from the syngas they must be followed by a sulfur removal step. The type of sulfur recovery system required is dependent on the required sulfur recovery efficiency, the quantity of sulfur to be removed and the concentration of the H_2S in the acid gas. The required sulfur removal/recovery efficiency from this acid gas stream will vary depending on the geographic LO CATion of the facility and local regulations; typically an Autocirculation LO CAT processing scheme is guaranteed to reduce H_2S to less than 5 ppmV

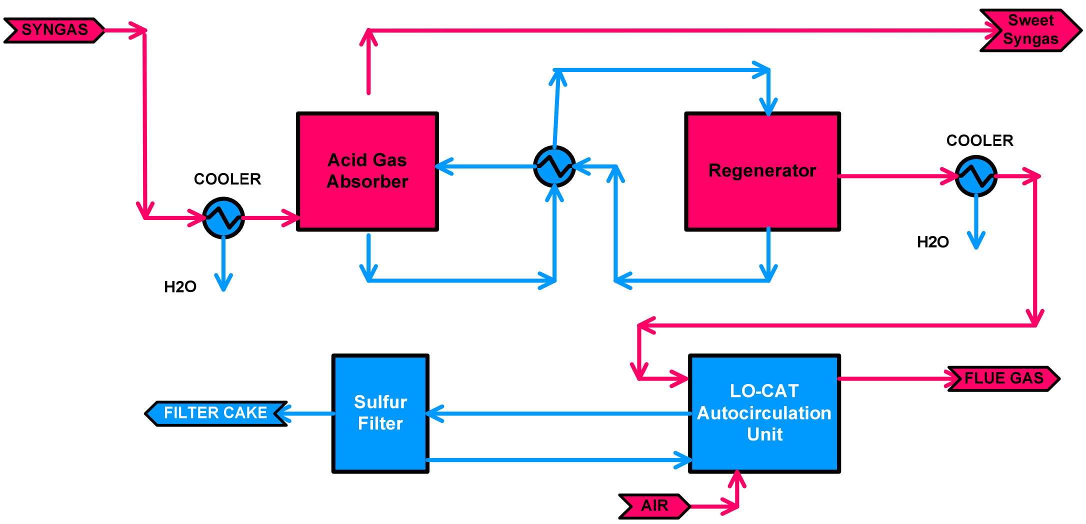

Figure 2 – indirect treatment of Syngas using Autocirculation LO CAT scheme

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