Desulfurization of High-Pressure Gasified Coal Using the UC Sulfur Recovery Process

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Abstract

Gasification of carbonaceous feedstocks (e.g., coal) generates fuel-rich gases that may be used for power generation in IGCC, for the synthesis of chemicals or liquid fuels, or for fuel-cell power generation. Gas clean-up is required in all cases. In these applications, a low-temperature absorption process, such as Rectisol or Selexol, is typically employed to scrub the gas free of sulfur compounds. Sulfur-containing species, such as H_2S and COS, plus a major fraction of the CO_2, are recovered as an acid gas by such processes. Sulfur recovery from the stripped gas must also be included. The modified Claus process, coupled with a tail-gas treatment (TGT) process, such as SCOT, is typically used to recover elemental sulfur and produce a dischargeable plant tail gas with ~100 ppm of SO_2 or less. Recovery of co-absorbed CO_2 may also be desired.

The UC Sulfur Recovery Process (UCSRP) uses a solvent with high capacity for H_2S and SO_2 that also catalyzes the liquid-phase reaction of H_2S and SO_2 to sulfur and water. Operation is above the melting point of sulfur, so the sulfur forms a separate liquid phase and is removed by simple decantation. Research at the University of California, Berkeley (UCB), coupled with experimental work at Gas Technology Institute (GTI), shows that UCSRP can be used for direct sweetening of high-pressure sour gas streams. The sour gas (*e.g.*, syngas), mixed with 10% – 20% excess SO_2, is contacted at high pressure (the higher the better) with the UCSRP solvent in an absorber-reactor column at about 260° – 285^oF (125° – 140^oC). Substantially all of the H_2S reacts to form liquid sulfur, leaving the excess SO_2 in the treated gas. The unreacted SO_2 is recovered in a separate absorber/stripper system, which may optionally also serve to dry the treated gas. The sulfur-free gas may optionally also be passed through a second absorber/stripper system for CO_2 recovery. The recovered SO_2 is combined with SO_2 produced by burning one-third of the liquid sulfur in a furnace, compressed and perhaps liquefied, and fed to the reactor column. The furnace employs either air or oxygen. All of the sulfur formed in the reactor is vaporized as it passes through the furnace; the unburned two-thirds condense in the waste-heat boiler. Any organic components dissolved in the sulfur will also be burned. The product sulfur has only a small amount of dissolved SO_2 as impurity. This process has the potential to significantly lower the cost of removing sulfur form syngas and some simple additions to the process can integrate removal of other syngas contaminants such as HCl, NH_3 and trace metals. This paper will discuss the application of UCSRP for syngas desulfurization with optional CO_2 recovery, present the results of exploratory experiments conducted at GTI and highlight the potential economic benefits of the process.

Background

Advanced gasification systems will be needed to provide synthesis gas feed for advanced, combined cycle power plants; for separation systems for hydrogen production or for separating CO_2 for sequestration purposes; or for chemical conversion plants. All of these advanced applications will require that any sulfur-containing species, as well as other contaminants, be reduced to parts-per-million (ppm) or in some cases parts-per-billion (ppb) levels. For acid-gas removal, such as sulfur, technologies that are either currently available or under development include: (1) low-temperature or refrigerated solvent-based scrubbing systems using amines, such as MDEA, or physical solvents (i.e., Rectisol, Selexol, Sulfinol), or (2) high temperature sorbents (not yet demonstrated at commercial scale). However, these gas-cleaning processes operate at temperatures that are either below or above the temperature of the downstream processing operations (for gas turbine fuel systems and catalytic synthesis processes), which are in the range of 300 to 700°F. These temperature differences lead to lower energy efficiencies: the low-temperature clean-up processes require temperature reductions to below 100°F and then reheating to downstream process requirements; the high-temperature sorbent systems operate at 1000°F, leading to unnecessary gas stream corrosivity.

In advanced gasification applications (e.g., IGCC) where a low-temperature absorption process, such as Rectisol or Selexol, is employed to scrub the gas and remove the sulfur compounds, the sulfur-containing species such as H_2S and COS are recovered as an acid gas from either process, which then requires a sulfur-recovery process. The modified Claus process coupled with a tail gas treatment (TGT) process such as SCOT are typically used to recover elemental sulfur and produce a dischargeable plant tail gas.

The development of desulfurization systems that can be matched to the elevated temperature and pressure conditions of gasification processes (i.e., temperatures in the range of 300-700°F and pressures in the range 400-1200 psig) and that can be integrated with the warm-gas cleanup of other contaminants (trace components and heavy metals) is, therefore, of critical importance for early commercialization of advanced gasification technologies being promoted by U.S. DOE in the FutureGen and Clean Coal Power Initiative programs.

Research at the University of California, Berkeley (UCB), coupled with experimental work at Gas Technology Institute (GTI), is leading to the development of an integrated multi-contaminant removal process whereby syngas is sent to a reactor column at a temperature above the melting point (247°F) and below the polymerization temperature (310°F) of elemental sulfur and a gasification pressure of 400 psig or higher. H_2S in the syngas, together with injected SO_2, dissolves in a solvent that is circulated from the bottom to the top of the column. The Claus reaction is carried out in the liquid phase. Sulfur is only sparingly soluble in the solvent and therefore forms a separate liquid phase. The solvent contains a homogeneous liquid catalyst (less than 1% by weight of the solution). The catalyst is a commonly available and inexpensive material that does not degrade nor dissolve in the sulfur. The water formed in the Claus reaction vaporizes and forms part of the syngas. One-third of the sulfur product is burned with oxygen (if an oxygen-blown gasifier is involved this would be a fraction of the oxygen requirement for the process), and fed to the reactor column. Means are also provided to remove COS, HCl, NH_3, and trace heavy metals. The treated gas leaving the reactor column will meet the strict specifications set for H_2S and the other contaminants for turbines, fuel cells, and catalytic processes.

The process is ideal for syngas desulfurization at 285 to 300°F and at any given pressure (the higher the better) and offers a tighter integration with the process for removal of trace contaminants and heavy metals. It is expected to be significantly lower in capital and operating cost compared to conventionally applied amine or physical solvent based acid-gas removal process followed by Claus/SCOT process. Testing done at GTI has shown negligible chemical consumption (including catalyst), unlike typical chemicals costs of $300 - $1000 per ton sulfur removed found in competing processes. There is much less need for stainless steels in the process, and we see no cut-off point in terms of sulfur handling at which Claus/SCOT becomes more economical.

This process differs from liquid redox processes in important ways. There is no need for filtering a solid sulfur paste with attendant handling problems and loss of solvent. The sulfur quality can be as good as Claus sulfur due to the low solubility of the solvent in the liquid sulfur, and to the large density difference and ease of liquid/liquid separation in the process. The process can operate at significantly higher temperatures than the liquid redox or CrystaSulf processes, which is of value in IGCC applications. No foaming of the solution occurs since the solvent is non-aqueous and has no surfactant properties. No sticky or solid sulfur is anywhere present in the system so the problems of liquid redox plugging and pump wear would not be present.

As was described in the papers presented in San Francisco and Amsterdam and published in GasTIPS, see References 5, 6 and 7 below, the UCSRP replaces a typical Claus plant + tailgas unit. The UCSRP-HP process, in addition, employs the reaction between H_2S and SO_2 to sweeten a gas at high pressure in a reactor column under the following conditions:

i) the organic liquid solvent contains a homogeneous catalyst that promotes the liquid-phase reaction

$$2\ H_2S + SO_2 \Rightarrow 3\ S + 2\ H_2O$$

ii) the temperature in the reactor column is above the melting point of sulfur, and
iii) the SO_2 is fed in stoichiometric excess to the H_2S.

The SO_2 is fed separately, at a rate that is in stoichiometric excess to the H_2S. The process is useful for producing a product gas that may be dry and is substantially free of H_2S, SO_2 and other sulfur-containing compounds from a wet H_2S-containing feed gas with the following characteristics:

i) The feed gas contains components of value so that one wishes to remove only H_2S and other sulfur compounds, and sometimes water, to the extent possible while recovering the valuable components as a treated gas.
ii) Although there is no minimum (or maximum) pressure at which the process can operate, the flow of solvent is reduced and reaction rates are increased at higher pressures. This permits the use of smaller equipment and lowers operating costs; hence the process will be most attractive for the treatment of H_2S-containing gases at high pressure.

Treatment of Synthesis Gas from Coal Gasification

When coal is gasified, the syngas produced may contain not only H_2S, but also NH_3 and HCl and heavy metals, such as As, Cd, Hg and Se. Before the syngas is used as fuel for a gas turbine or further processing to methane, liquid hydrocarbons or hydrogen, all of the above should be reduced to very low values. A PFD demonstrating one application of UCSRP to this problem is shown in UCSRP-HP4.

a) Reactor: The countercurrent reactor column is divided into two sections: the scrub section and the reactor section. The sour gas feed enters scrub section, 2A, where it is contacted with a stream of diethylene glycol (DEG) or other glycol ether. At the pressure, temperature and water content of the syngas, the DEG will have a steady-state water content of about 10 to 20 wt%. It will also have substantially smaller, but significant, steady-state contents of NH_3 and H_2S. As a result, the HCl content of the feed gas will be absorbed very effectively to form highly soluble NH_4Cl. A small but significant concentration of NH_4HS will also be present in the liquid phase, and the heavy metals As, Cd and Hg will be absorbed to form their respective, very insoluble sulfides. Selenium will be present in the syngas as H_2Se and will be absorbed to form highly soluble $(NH_4)_2Se$ under these conditions. At the bottom of the scrub section the DEG stream is withdrawn and circulated by pump back to the top. A small slipstream of the DEG stream may be withdrawn, perhaps intermittently, for filtration and other treatment to remove the accumulated impurities, and then returned. The gas stream leaving the scrub section passes into the reactor section through a chimney that effectively prevents the mixing of the solvent in the two sections.

In the operation of the reactor column, 2B, a stream of glycol ether, such as diethylene glycol methyl ether (DGM) is circulated from the bottom of Stripper 1 to the top of the reactor section. The temperature of this stream may be increased or decreased by the heater-cooler, depending on the heat balance in the reactor section. This lean solvent stream, depleted of SO_2 and NH_3, effectively absorbs those components from the gas stream flowing upward in the reactor section. NH_3 passes through the reactor section without being oxidized but is absorbed as an ammonium salt through its reaction with SO_2. The solvent has a water content that is essentially in equilibrium with the syngas. A stream of liquid SO_2 is injected into the reactor section at one or more points below the entry of the solvent stream, and is mixed with the solvent flow within the column. The quantity of SO_2 fed into the column exceeds that required to react with the H_2S in the feed stream by an amount between 0.5 and 1 mole per mole of NH_3 in the feed stream. The solvent catalyzes the reaction between H_2S and SO_2. The water formed by the reaction remains in the vapor phase. The sulfur forms a second liquid phase. The two liquids flow from the bottom of the reactor section to a liquid/liquid separator. The solvent stream then flows to Stripper 1, STR1, by way of HX2. The liquid sulfur stream flows to the furnace.

b) NH_3 and SO_2 Removal: The gas stream leaving the reactor section of the reactor column has passed through a section in which the gas has been contacted with a solvent stream that is depleted in NH_3 and SO_2, but has a water content that is in near equilibrium with the gas. Depending on the water content of the solvent, NH_3 and SO_2 will be absorbed as the separate compounds, as the ion pair or as ammonium sulfite and/or bisulfite. The treated gas leaving the process has a temperature and water and CO_2 content that are little changed from those of the feed stream but is substantially free of H_2S, NH_3, HCl, SO_2 and heavy metals. The solvent stream that exits the reactor section of the reactor column exchanges heat with the bottoms stream as it flows to Stripper 1, which operates at near-ambient pressure. The overhead vapor from Stripper 1 is condensed to form a solution of ammonium sulfite and bisulfite. The water stream entering the condenser is provided to insure that no solid salts are formed. As was noted

above, the flow of SO_2 to the reactor column is regulated so that the molar ratio of SO_2 to NH_3 stripped out of the fat solvent stream fed to Stripper 1 is between 0.5 and 1. Both can therefore be absorbed in the water stream (plus the water from the condensed overhead vapor) and pumped as a solution to the furnace to moderate the combustion temperature, destroying the NH_3 and recovering the SO_2.

c) SO_2 Generation: The stream of liquid sulfur leaving the reactor column flows directly to the furnace**,** where, when time-averaged, exactly one-third of it is burned with a stream of oxygen to form the SO_2 required for the process. The high pressure in the reactor column, about 10 bar absolute, makes it advantageous to use oxygen for the combustion, so that the SO_2 formed may readily be condensed and pumped as a liquid to reactor pressure. The aqueous solution from Stripper 1 is used to moderate the temperature of combustion in the furnace. The high temperature that would result when one-third of the sulfur combusted reacts with oxygen could damage the materials in the furnace if such moderation were not provided. The NH_3 content of the aqueous stream is converted to N_2 and H_2O as it passes through the furnace. The presence of S_2 vapor prevents any NO_x formation. The combustion gas raises steam in the boiler and then passes through the condenser, where liquid sulfur is collected. The wet SO_2 gas then flows to a cooler, where liquid water, saturated with dissolved SO_2, is condensed. The SO_2 stream leaving the cooler is converted to liquid in another condenser, and then pressurized to the pressure of the reactor column by a pump as shown. This pump must also be able to handle the small amounts of N_2 and CO_2 that will be present.

d) CO_2 Capture: An option for non-IGCC facilities would be to capture the CO_2 for sequestration. Here, the gas stream leaving the reactor column is cooled to near-ambient temperature in the heat exchanger(s) before entering a dryer column, where it is contacted with a part of the solvent stream from a CO_2 column. The solvent absorbs mercaptans, SO_2 and H_2O, together with some CO_2 and syngas components. The dissolved CO_2 tends to desorb from the solvent as mercaptans, SO_2 and H_2O are absorbed, which reduces the temperature rise that might otherwise occur. The reboiler at the bottom of column heats the solvent sufficiently to strip out a large fraction of the CO_2, and syngas dissolved in it while retaining substantially all of the mercaptans, SO_2 and H_2O. The solvent stream then flows to the SO_2/H_2O stripper.

The gas stream leaving the dryer column flows to the CO_2 column and is contacted with freshly stripped, cooled solvent. A major fraction of the CO_2 in the natural gas stream is absorbed. The reboiler at the bottom of the CO_2 column heats the rich solvent sufficiently to strip out a large fraction of the syngas while retaining substantially all of the CO_2. The reboiler serves also to cool the stream leaving the solvent strippers. The product gas leaving the CO_2 column will have a CO_2 content of 1 vol % or less, will be substantially free of SO_2 (1 ppmv or below), mercaptan (0.01 ppmv or below), and will be dried to a dew point of 0^oC or to meet process specifications. The CO_2-rich solvent then flows to the CO_2 stripper, which operates near ambient pressure and removes most of the CO_2 from the solvent. The solvent contains about 1 wt% water, so that most of the stripping vapor in the reboiler of the CO_2 stripper is H_2O and the temperature is low enough to prevent thermal degradation of the solvent. No water is removed from the system in the CO_2 stripper; the water vapor condensed at the top is returned as a reflux that prevents loss of solvent vapor. The captured CO_2 can then be compressed for transfer to a sequestration facility.

d) Syngas Temperature Recovery: To maximize thermal efficiency, it is preferable to minimize the temperature drop during sulfur removal. This process is preferably operated above the melting point (247^oF) and below the polymerization temperature (310^oF) of elemental sulfur. Therefore, if the temperature of the sour syngas feed to the reactor is above this range, stream 1 will be passed through a

gas-gas heat exchanger, HX1. The feed gas temperature will be reduced to about 280 to 300°F by exchange with the treated syngas stream 5. This way we expect that almost all heat will be recovered and the maximum temperature differential between sour feed gas and treated sweet gas will be around 30 to 40°F.

Experimental Basis

The UCSRP technology is based on extensive laboratory experimentation. Numerous graduate projects were undertaken in the Department of Chemical Engineering at UC Berkeley, some of which are reported in References 1 - 4 cited below. These established the mechanism and chemical kinetics of the reaction and determined the solubilities of elemental sulfur and various gases as functions of temperature and pressure for the glycol ether solvents of interest.

Experiments have been performed in the laboratories at GTI during the past two years to verify both the stability of the solvent at ambient temperature and the feasibility of operating the reactor at high pressure while maintaining the temperature at about 140°C. The stability test was carried out for a period of about 1000 hours. Both gases were fed continuously, with H_2S in excess, to a stirred-tank reactor while the product sulfur was drained off intermittently. Solvent samples were taken daily and tested by gas chromatography to detect the possible formation of solvent degradation products. None were found. The sulfur balance was 100% within experimental accuracy.

The specific purpose of the second experiment was to investigate the degradation of the solvent used in UCSRP that might be due to various gases present in the syngas as well as the H_2S conversion to elemental sulfur when SO_2 is added to the reactor. The experiment was conducted in a 4-liter batch autoclave reactor at 300 psia and 140°C for about 150 hours. Small liquid samples (5-10 mL) were withdrawn from the reactor at regular intervals and analyzed by GC. Gas samples were also analyzed at the start and at the end of the experiment and at the midpoint, before SO_2 addition to the reactor. The experiment progressed as expected and no solvent degradation was observed after 150 hours of continuous exposure to simulated syngas. The initial gas phase composition was about 63.4% H_2; 24.5% CO; 5.0% N_2; 4.9% CO_2; 2.1% H_2S and 1083 ppmv of COS. The gas phase H_2S concentration in the reactor dropped from initial 2.1% to 2400 ppm at the end of the experiment. Also, at the completion of the experiment, the COS and SO_2 levels in the gas phase were undetectable. The results from this exploratory experiment lead us to conclude that it is possible to convert H_2S in the syngas directly into elemental sulfur using UCSRP technology without any adverse affect on solvent performance. Further process evaluations tests should be done using a laboratory-scale co-current or counter-current trayed column reactor with the ability to continuously remove liquid sulfur from the solvent and change reactor parameters.

Anticipated Economic Benefits

The UCSRP-HP is ideal for syngas desulfurization at 285 to 300°F and at any given pressure and offers a tighter integration with the process for removal of trace contaminants and heavy metals. It is expected to be significantly lower in capital and operating cost compared to conventionally applied amine or physical solvent based acid-gas removal process followed by Claus/SCOT process. A GRI sponsored techno-economic evaluation of the related process (i.e., low pressure UCSRP) done by Halliburton KBR has found significant advantages (40% reduction in each of capital and operating cost)

for the proposed scheme compared with conventional treating approaches., i.e., Claus plus SCOT tail gas treating. Testing done at GTI has shown negligible chemical consumption (including catalyst), unlike typical chemical costs of $300 - $1000 per ton sulfur removed found in competing processes. There is much less need for stainless steels in the process and we see no cut-off point in terms of sulfur handling at which Claus/SCOT become more economical. In this process there is no need for filtering a solid sulfur paste with attendant handling problems and loss of solvent. The sulfur quality can be as good as Claus sulfur due to the low solubility of the solvent in the liquid sulfur, and to the large density difference and ease of liquid/liquid separation in the process. The process can operate at significantly higher temperatures than the liquid redox or CrystaSulf processes, which is of value in IGCC applications. No foaming of the solution occurs since the solvent is non-aqueous and has no surfactant properties. No sticky or solid sulfur is anywhere present in the system so the problems of liquid redox plugging and pump wear would not be present. The heat losses in the process are expected to be minimal.

Conclusions

The papers presented in San Francisco and Amsterdam and published in GasTIPS, see References 5, 6 and 7 below, showed that the UCSRP replaces a typical Claus plant + tailgas unit. The papers also reported an engineering study by Kellogg, Brown and Root showing that both capital and operating costs are cut by one-third or more. UCSRP-HP offers additional savings by replacing the typical alkanolamine absorber/stripper used to sweeten a high-pressure gas as well as the sulfur-recovery system that follows. In some cases, no tail gas at all is produced and chemical costs are nearly eliminated. Most of the unit operations are conventional, but the reactor column is unique and will require a pilot plant both to obtain plate-efficiency data and to demonstrate the process. GTI has been awarded a contract from the U.S. DOE to study the reactor column, as well as reaction kinetics, trace gas removal effectiveness, solvent degradation and corrosion. The next phase will be scale-up to a pilot unit in the field. The University and GTI would welcome an industrial partner to undertake this important step. The technology described in this paper is the subject of several patents and a pending patent application, with rights assigned to the University of California.

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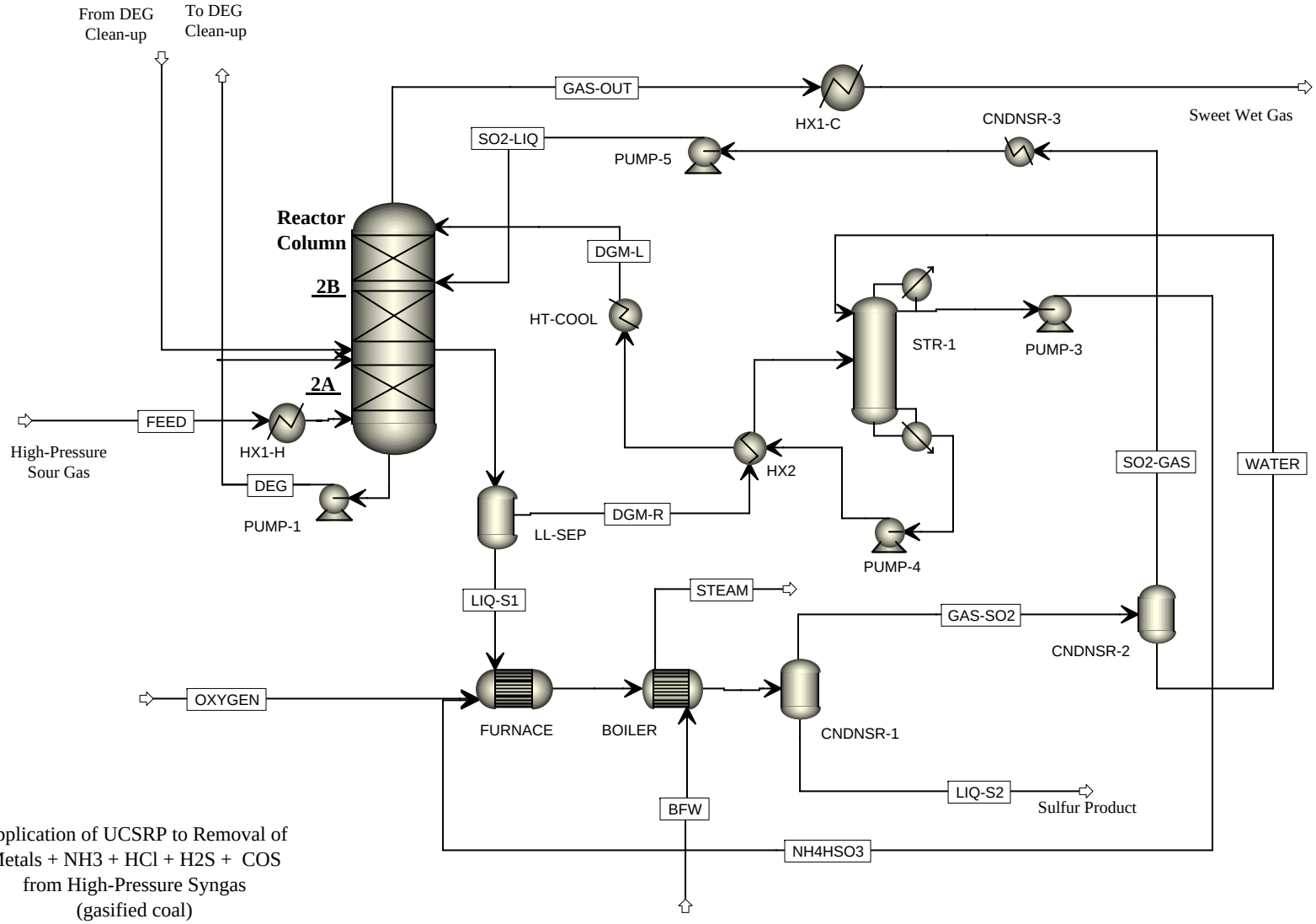
UCSRP-HP4



Application of UCSRP to Removal of
Metals + NH3 + HCl + H2S + COS
from High-Pressure Syngas
(gasified coal)
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