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Novel Coal Gasification Process: Improvement of Syngas Yield and Reduction of Emissions

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This article is intended to propose and model an innovative process layout for coal gasification that improves the production of syngas and also reduces the sulfur and CO_2 emissions. The typical coal gasification process uses Sulfur Recovery Units to convert H_2S to sulfur, but these have some disadvantage, e.g low sulfur price, coal charge with low sulfur flow rate, use of Tail Gas Treatment unit. Compared to the Claus process, this solution converts H_2S and CO_2 into syngas (economically appealing), reduces emission of H_2S and CO_2 and allows the use of coal charge with high sulfur flow rate, e.g. 9.5% mol/mol. The novel process takes advantage of a double amine wash, a thermal regenerative furnace and considers the recycle of the acid gases coming from the catalytic reactor to further promote the H_2S conversion. In particular, the double amine wash is useful to purify the H_2S stream to be sent to the thermal furnace from the syngas and CO_2, in order to reduce the reactor inlet flow rate. The regenerative furnace is simulated using a large detailed kinetic scheme to appropriately describe the minor species (among them, pollutants like CS_2 and COS). As a result, the recycle appears to substantially reduce the pollutant emissions. In addition, the conversion of the Claus process into the novel process doesn't require any change in the main equipment, just needing for a variation in the layout and the operating conditions.

1. Introduction

Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are two of the most critical chemical by-products discharged by power, petrochemical and manufacturing plants. Despite their massive production, they do not represent a major feedstock or commodity for subsequent industrial purposes. Then, they are pollutants and the venting to atmosphere, when admissible, leads to environmental issues; otherwise, expensive neutralization processes must be adopted. Moreover, H_2S is a poison for industrial catalysts and its combustion products (e.g. SO_X) are strong pollutants. Consequently, desulphurization of hydrocarbons and coal and sweetening of natural gas are mandatory operations. Due to chemical acid behavior, gaseous effluents from desulphurization units are called "acid gases". Since H_2S is toxic, it cannot be vented to atmosphere, but must be properly neutralized. Therefore, acid gases represent a dangerous and costly waste. At H_2S concentrations above 40%, the most important and spread neutralization method is based on oxidation of H_2S by air (i.e. Claus process): the acid gas is fed to a furnace along with a sub-stoichiometric amount of air and then oxidized to sulfur dioxide (SO_2) at high temperature:

$$H_2S + \tfrac{1}{2}O_2 \rightarrow SO_2 + H_2O \tag{1}$$

The SO_2 is next reduced by residual H_2S by means of catalytic reactors for obtaining elemental sulfur:

$$2H_2S + SO_2 \rightarrow \tfrac{3}{x}S_x + 2H_2O \tag{2}$$

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The elemental sulfur is partially used in process industry to produce sulfuric acid; nevertheless, since most portion of sulfur is stocked and commercial demand for sulfuric acid can be weak, the neutralization process represents a significant plant cost.

CO_2 is the major responsible for impacts on ecological and environmental system, involving the greenhouse effect. Due to its thermodynamic stability and low chemical value, CO_2 has presently minor industrial uses (e.g. urea synthesis).

As a result, nowadays H_2S and CO_2 are strongly undesired coal gasification by-products, to be accounted as a huge cost in the budget of industrial plant. Nonetheless, despite his bad reputation, H_2S is quite an interesting chemical since it contains a highly noble species, the hydrogen. Consequently, H_2S should deserve more attention than to be considered just a waste and then oxidized in Claus plants to obtain elemental sulfur and water. Besides, as shown in above reforming synthesis reactions, CO_2 as well is a potential interesting molecule: it may work as oxidizing agent (e.g. reforming synthesis reactions).

$$CO_2 + CH_4 \rightarrow 2CO + H_2 \tag{3}$$

All these considerations have pushed research and development for a captive use of H_2S and CO_2, to improve the accounting of these by-products. In this work, proven and mature technology used in the Claus process has been realized to be potential source of innovation. Taking advantage of extensive scientific works and operating experience on acid gas oxidation by air at high temperatures, H_2S and CO_2 have been observed under a different light, like a couple of oxidizing and reducing species; so, reduction of CO_2 by means of H_2S looks to be a promising and valuable new route. Although some aspects are still unresolved, thermodynamics, kinetics (Manenti et al., 2013a) and process control (Signor et al., 2010) of Claus process have been plentifully studied so far; consequently, the H_2S and CO_2 conversion process starts from a conceptual and technological validated basis. This new technology, developed in this study, presents three principle advantages: the recycle of acid gas (i.e low H_2S emissions), the reduction of CO_2 that is vent into atmosphere and the production of H_2 and CO that is economically appealing. Therefore, this technology can be used not only for coal gasification, as in this case, but also for all chemical process in which there are acid gases, such as hydrodesulfuration.

2. Novel Process Description

In this section, the overall layout of the novel coal gasification process is discussed and then each part is analyzed. For each section, some numerical results are presented in order to prove the validity of the process and highlight the possible advantages and disadvantages. The process is simulated with the use of an industrial plant simulation software: Aspen Hysys. A Peng-Robinson equation of state is used for the entire process except for the amine wash section where is used the amine package, included in Aspen Hysys. The *Figure **1*** shows a simplified BFD of the novel process.

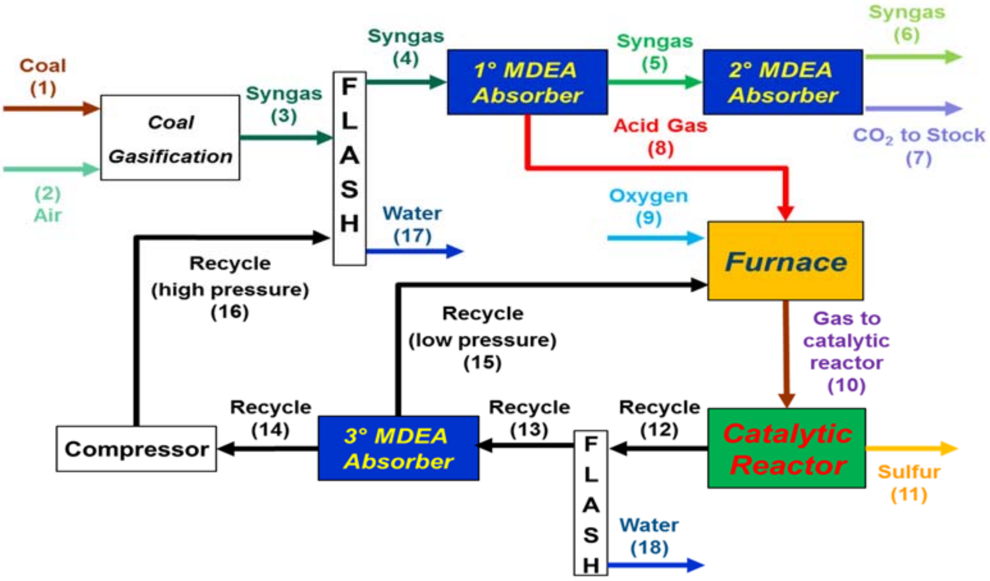

Figure 1 Process layout

The case study simulation, developed in this work, is built up starting from a syngas stream coming from the gasification section (Table 1). This is a typical composition of coal gasification products launching from coal charge with a high sulfur flow rate, e.g. 9.5% mol/mol.

Table 1 Syngas stream composition coming from coal gasification section

	x_{CO}	x_{H2}	x_{CO2}	x_{H2O}	x_{CH4}	x_{Ar}	x_{N2}	x_{H2S}	x_{COS}	x_{O2}	n_{tot} [kmol/h]
Syngas from Coal Gasification (3) – vapor	0.19	0.13	0.09	0.55	0.00	0.00	0.00	0.03	0.00	0.00	3375.68

2.1 Main Amine Wash

The syngas must be purified form acid gases (H_2S and CO_2). For this work is decided to use an amine wash, using MDEA (Methyl DiEthanolAmine) that is chosen for its industrial application and its specific selectivity to hydrogen sulfide. Furthermore, MDEA has low vapor pressure, high resistance to degradation and requires low energy absorption for the regeneration (approximately 100 kg of steam for 1 m^3 of MDEA) compared to DEA (DiEthanolAmine) and MEA (MonoEthanolAmine). In the process, is used two distinct amine washes (*Figure **1***):

1) The first amine wash aims to remove almost all of the H_2S from the acid gas stream. Simultaneously is limited the absorption of CO_2, that is the main source of CO and at the same time a "heat absorber" in the furnace. If there is an excess of CO_2, more oxygen should be required to reach the desired temperature, leading to a major consumption of H_2S for oxidation instead of consumption of H_2S for pyrolysis.
2) The second amine wash aims to remove the CO_2 from the syngas stream. However, a small percentage of CO_2 remain in the stream but in several processes, such as methanol synthesis, it can be useful. The output syngas is used for sale or for some other downstream processes, while the stream with high concentration of CO_2 is sent to burner or to storage.

2.2 Reaction Section (Furnace and Catalytic Reactor)

In industry, there is a different configuration of the Claus furnace, called "regenerative", which allows to produce a greater amount of H_2. This configuration (*Figure **2***) present a preheating for input acid gas stream before the combustion of gases. Then, the gases are sent, as usual, to the WHB (Waste Heat Boiler).

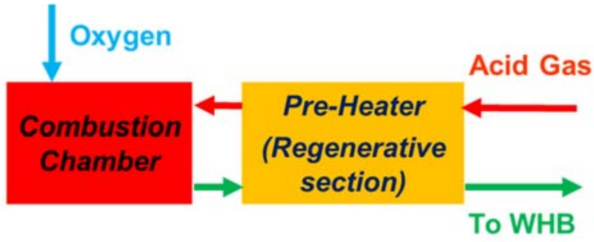

Figure 2 Regenerative Furnace Scheme

The hydrogen is produced almost all by the H_2S pyrolysis (Binoist et al., 2003). Therefore, if the temperature of the acid gases rises up to 750-850°C before the combustion, the oxygen flow rate, required to reach the standard temperatures in the furnace (1200-1300°C), is lower and so the H_2S available for pyrolysis is greater. Another advantage of this configuration is that a stream of pure oxygen is used. This lead to limit the effects of "heat absorber" of nitrogen.

This reactor is modeled as a series of ideal reactors (Manenti et al., 2012):

1) Plug Flow Reactor with a linear temperature profile. The inlet temperature is the same of acid gas stream (about 200-250°C) while the output temperature (before the combustion chamber) is about 750-850°C.
2) "Gibbs Reactor" (Reactor implemented in Hysys that minimized the Gibbs energy). This reactor simulate the combustion chamber.
3) Plug Flow Reactor with a linear temperature profile. The inlet temperature is given by the output stream from the Gibbs Reactor, while the output temperature is evaluated from heat balance with the reactor (1).
4) Non-isothermal PFR reactor with fixed external temperature and heat transfer coefficient. This reactor simulates the WHB.

It is important to emphasize that the reactors (1), (3), (4) are simulated through the use of DSMOKE (software for ideal reactor simulation with a detailed kinetic scheme), which is integrated within Aspen Hysys with the use of Visual Basic programming. This allows to use a detailed kinetic scheme within a commercial package for the simulation of chemical plants. The detailed scheme is made up of three different subsets reaction that describe the kinetic of Carbon (methane oxidation (Ranzi et al., 1994b), propane and n-butane oxidation (Ranzi et al., 1994a) with later revision of CO-H_2 system (Frassoldati et al., 2007)), Sulfur (Glarborg studied the effect of SO_2 (Glarborg et al., 1996), Binoist studied the pyrolysis of H_2S (Binoist et al., 2003) and Manenti revised the kinetic scheme with particular attention to H_2S and COS species (Manenti et al., 2013)) and Nitrogen (Faravelli et al., 2003).

The catalytic reactor is modelled as a series of four reactors that are already implemented in Aspen Hysys. These reactors are characterized as follows:

1) Conversion reactor for CS_2 hydrolysis: in this reactor, the following reaction occurs at complete conversion:

$$CS_2 + H_2O \rightarrow COS + H_2S \tag{4}$$

2) Conversion reactor for COS hydrolysis: in this reactor, the following reaction occurs at complete conversion:

$$COS + H_2O \rightarrow CO_2 + H_2S \tag{5}$$

3) Conversion reactor for Claus reaction: in this reactor, the following reaction occurs at complete conversion:

$$2H_2S + SO_2 \rightarrow {}^{3}\!/_{2}\, S_2 + 2H_2O \tag{6}$$

4) Equilibrium reactor. This the reactor allows, at different temperature, to evaluate the different composition between the various allotropic species of sulfur.

The hydrolysis and the Claus reaction are evaluated at complete conversion because is consider that the system works in the most favorable conditions for the sustainability of the process. In fact, the hydrolysis reactions produce H_2S, which can be recycled to the regenerative furnace and can be further source of H_2. The Claus reaction allows to complete the conversion of SO_2. In this way can be produced the greatest amount of sulfur.

2.3 Secondary Wash Section

This wash is located after the catalytic rector. It is similar to the first amine wash of the main section and has the purpose of separating the H_2S (with a low percentage of CO_2) from the syngas and the remaining CO_2. Moreover, this stream (syngas and CO_2) is sent to the compressor and then again to section of the main wash (Figure 1). This stream has a reduced flow rate, consequently is reduced the compression costs. Instead, the stream containing H_2S is sent directly to the furnace.

3. Results and Discussions

In this paragraph are presented and discussed the results of the case study simulations for each section.

3.1 Main Amine Wash Results

The numerical results of this section are summarized in Table 2. Is possible to note that:

- The configuration of the first amine wash is suitable for stripping of all H_2S from the syngas stream by ensuring that only a part (about 25%) of CO_2 remains in the acid gas.
- The configuration of the second amine wash is suitable for complete stripping of CO_2 and H_2S present in the syngas stream from the first wash. In the syngas stream is left an amount of CO_2 equal to about 4% molar.
- In the syngas stream to be sold, there is not H_2S.
- The other output stream ("CO_2 to Stock") is sent to a burner or stored under pressure. This is the only outlet stream in which there is H_2S. However, its amount is about 40 ppm and so the aim of reducing emissions is achieved.
- The yield of syngas washing is:

$$\frac{(H_2S + CO)_{out}}{(H_2S + CO)_{in}} 100 = 99.2\% \tag{7}$$

The surplus syngas produced deserves a special mention. In fact, the comparison between the input syngas with the output syngas should be made with the amount of syngas "clean" obtained from the same amount of initial syngas (Table 1), making one wash that allows to completely remove acid gases (traditional process). Therefore, is simulated a traditional washing section in Aspen Hysys in order to obtain an output syngas stream "clean" with a percentage of H_2S and about 4% of CO_2. In the syngas stream "clean", the hydrogen flow rate is equal to 445.86 [kmoli/h], while carbon monoxide flow rate equal to 639.60 [kmoli/h]. So is calculated the surplus of syngas as follow:

$$\frac{((H_2+CO)_{new\,process}-(H_2+CO)_{traditional})}{(H_2+CO)_{traditional}}100=1.17\% \tag{8}$$

Table 2 Simulation results of the main amine wash section

	x_{H_2}	x_{H_2O}	x_{CO}	x_{N_2}	x_{O_2}	x_{CO_2}	x_{H_2S}	x_{SO_2}	x_{COS}	x_{CS_2}	n_{tot} [kmol/h]
Syngas to 1st amine wash (4) - vapor	0.28	0.00	0.40	0.00	0.00	0.25	0.06	0.00	0.00	0.00	1635.40
Acid Gases from 1st amine wash (8) - vapor	0.00	0.05	0.00	0.00	0.00	0.50	0.41	0.00	0.03	0.00	226.48
Syngas to 2nd amine wash (5) - vapor	0.32	0.00	0.46	0.01	0.00	0.21	0.00	0.00	0.00	0.00	1416.37
CO_2 to Stock (7) - vapor	0.00	0.05	0.00	0.00	0.00	0.94	0.00	0.00	0.00	0.00	269.58
Syngas Out (6) - vapor	0.39	0.00	0.56	0.01	0.00	0.04	0.00	0.00	0.00	0.00	1156.01

3.2 Reaction Section (Furnace and Catalytic Reactor) Results

In Tables 3, 4 and 5 the results of a case study simulation of the reaction section are reported. It is useful to highlight that the gases are preheated in the "regenerative" furnace up to a temperature of 800°C before coming in contact with oxygen. Looking at the numerical results it can be stated that:

- The amount of sulfur is lower (about 40%) than that of a classic Claus process, but it is a possible revenue that can financially support the process.
- The recycling stream (Table 5) is the heart of the process. This makes it possible to reuse all the H_2S and to have no emissions. In fact, in a traditional Sulfur Recovery Unit, this stream must be sent to a tail gas treatment process.

Table 3 Simulation results of reaction section (1): Furnace

	x_{H_2}	x_{H_2O}	x_{CO}	x_{N_2}	x_{O_2}	x_{CO_2}	x_{H_2S}	x_{SO_2}	x_{COS}	x_{CS_2}	x_{S_2}	n_{tot} [kmol/h]
Total Acid Gas to Furnace (8+15) - vapor	0.01	0.05	0.01	0.00	0.00	0.40	0.51	0.00	0.02	0.00	0.00	330.08
Oxygen (9) - vapor	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	45.00
Acid Gases to Catalytic Reactor (10) - vapor	0.01	0.33	0.04	0.00	0.00	0.30	0.15	0.00	0.03	0.00	0.13	379.35

Table 4 Simulation results of reaction section (2): Catalytic Reactor (Xsn (n=2,4,6,8) are the allotropic configuration of Sulfur).

	x_{H_2O}	x_{S_2}	x_{S_4}	x_{S_6}	x_{S_8}	n_{tot} [kmol/h]
Sulfur (11) - liquid	0.14	0.15	0.14	0.29	0.28	16.67

Table 5 Simulation results of reaction section (3): Catalytic Reactor

	x_{H_2}	x_{H_2O}	x_{CO}	x_{N_2}	x_{O_2}	x_{CO_2}	x_{H_2S}	x_{SO_2}	x_{COS}	x_{CS_2}	x_{S_x}	n_{tot} [kmol/h]
Recycle (12) - vapor	0.01	0.33	0.04	0.00	0.00	0.39	0.23	0.00	0.00	0.00	0.00	328.11

3.3 Secondary Wash Section Results

Looking at the numerical results (Table 6) it can be stated that:

- The main purpose of this amine wash (reduction of the stream to be compressed in order to be then recycled), is achieved since the recycle stream is "lightened" by about 40% molar.
- In addition, is prevented that large amounts of H_2S are recycled to the main section of wash. Thus limits the problems of excessive emission of H_2S.

Table 6 Simulation results of secondary wash section

	x_{H2}	x_{H2O}	x_{CO}	x_{N2}	x_{O2}	x_{CO2}	x_{H2S}	x_{SO2}	x_{COS}	x_{CS2}	n_{tot} [kmol/h]
Syngas form 3rd amine wash (16) - vapor	0.00	0.05	0.00	0.00	0.00	0.19	0.76	0.00	0.00	0.00	95.76
Acid Gases from 3rd amine wash (15) - vapor	0.02	0.03	0.11	0.00	0.00	0.84	0.01	0.00	0.00	0.00	132.43

4. Conclusions

In this work is presented a novel process for conversion and treatment of acid gases (in particular H_2S) coming from coal gasification. The idea is to exploit the oxidizing capacity of CO_2 with H_2S to ease the recovery of hydrogen, which is a chemical species more economically attractive than sulfur. Moreover, the emissions of H_2S and CO_2 is reduced without using any units for gas treatment. Given the innovative nature of the process, this technology requires more detailed analysis before it can be use on a real industrial plant, but this first simulation highlight that the novel process is very interesting and economically appealing.

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