218 OPTIMAL DESIGN AND CONTROL OF ACID GAS REMOVAL PROCESSES WITH PHYSICAL ABSORPTION

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The objective of this work is to capture the acid gas (H_2S and CO_2) from coal gasification outlet stream in order to solve the CO_2 emission and catalyst poison problems. Design specifications of hydrogen sulfide and carbon dioxide recovery percentages are 99.9% and 90.2%. Because of high pressure operations, physical SELEXOL absorption method is used to absorb acid gas. Two process flowsheets are taken into consideration: “flowsheet 1” (SWGS outlet stream feeds into H_2S removed process and then feeds into CO_2 capture process) and “flowsheet 2” (H_2S removal unit runs first and the effluent stream is sent to WGS reactor and CO_2 capture process) . The processes were simulated by using Aspen Plus software. From the sensitivity analysis, the optimal variables of the two process flowsheets were absorber tray no.(N_A), stripper tray no.(N_S), absorber column pressure(P_A), stripper column pressure(P_S), stripper feed stage(N_F) and stripper feed tray temperature(T_F) which dramatically affected the total annual cost (TAC) of each process flowsheet. Acid gas removal processes were designed based on minimal TAC while maintaining product specifications. The optimal result shows that “flowsheet1” gave a lower TAC than flowsheet 2. Finally, the control structures were designed for each process flowsheet by using sensitivity analysis. After controllers tuning, the dynamic simulation was performed to assess the controllability of each process with set-point and load concentration changes.

1. INTRODUCTION

Recently some research has investigated gasification technology with coal and biomass material for generating power and chemical products. Convectional pulverized coal combustion power plants generate amounts of anthropogenic greenhouse gas, causing global climate change. According to the International Energy Agency, the CO_2 emissions from the electricity and heat production were about 41% of the total global emissions from fossil fuels. Coal gasification of IGCC plants is promising technology for power generation in view of their higher efficiency and lower level CO_2 emissions [1]. The syngas mainly consists of H_2, CO and CO_2. After H_2 is produced by the water gas shift reaction, H_2–rich stream is then fed into a combustion turbine to generate power [2] or the H_2/CO ratio is adjusted to generate chemicals such as methanol [3] and ammonia products. The resulting CO_2 can be separated and storaged. CO_2 removal from fossil fuels by means of physical solvents has been practiced since the 1950s.The IGCC plant, operates under high pressure conditions, so the physical absorption method is used to capture CO_2. due to its relatively lower energy requirements and lower investment costs [4].

More and more papers have used steady-state simulation and analysis tools to evaluate IGCC plant performance and efficiency, including the impact of different CO_2 capture technology. Very few papers including[3] have studied the optimal flowsheet, dynamics and control issues .There are two different configurations of water-gas-shift reactor and acid gas removal processes are discussed.

2. PROCESSES DESCRIPTION

In this work, design of coal to methane processes was investigated. The optimal economic flowsheet sequences of sour water gas shift reaction (SWGS) and acid gas removal (AGR) processes were taken into consideration. In order to fit the methation processes specification, the H_2/CO ratio of SWGS reactor effluent stream was adjusted to 3:1. Most of the COS hydrolysis converted to H_2S in the reactor, and then was sent to acid gas removal processes which included H_2S removal and CO_2 capture units.

2.1 Modeling

SWGS and acid gas removal processes were simulated with Aspen plus software and Peng-Robinson equation of state was used to describe the gas-liquid phase behavior. The composition of physical absorption solvent (SELEXOL) consists of a mixture of dimethyl ether of polyethylene glycol and the formula is $CH_3O(C_2H_4O)_XCH_3$ where x can be between 3 to 9. X was set at 5 and the component is named DEPG [3]. Relative solubility of various gases in the SELEXOL solvent are different and can be used to separate gas mixtures such as H_2S and CO_2. The outlet gas from the acid gas removal processes still contained trace sulfur impurity which can be adsorbed in the ZnO bed.

2.2 Process Flowsheets

The optimal economic flowsheet sequences of sour water gas shift reaction (SWGS) and acid gas removal (AGR) processes were taken into consideration. Two flowsheets were discussed in the later sections.

2.2.1 Flowsheet 1 (FS1)

The syngas from the gasifier outlet was sent to sour water gas shift reactor (SWGS) to adjust the outlet stream specification H_2/CO to 3:1. The syngas from the coal contained a quantity of the H_2S and COS in the gasifier, most of the COS was converted to H_2S in the WGS reactor by COS hydrolysis reaction. The WGS reaction and COS hydrolysis reaction are represented by Eqs. (1) and (2) [5-6].

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41.7 kJ/mole \qquad (1)$$

$$COS + H_2O \rightarrow H_2S + H_2 \qquad (2)$$

Because the syngas contained a quantity of the sulfur before entering the SWGS reactor, sulfur tolerant Co/Mo catalysts was chosen. The kinetic of the catalysts are shown as follows.

$$r_{WGS} = k_{WGS} P_{CO}{}^{0.7} P_{H_2O}{}^{0.14} \left(1 - \frac{P_{CO_2} P_{H_2}}{K_{WGS} P_{CO} P_{H_2O}}\right) \qquad (3)$$

Where $K_{WGS} = \exp\left(\frac{4577.8}{T} - 4.33\right)$

$$r_{COS} = \frac{k_1 K_3 P_{COS} P_{H_2O}}{1 + K_3 P_{H_2O}} \qquad (4)$$

Where $k_1 = 2.778 \times 10^{-4} \exp\left(0.835 - \frac{3039}{T}\right)$

$K_3 = 1.000 \times 10^{-3} \exp\left(-15.89 + \frac{10{,}010}{T}\right)$

The outlet stream from the SWGS reactor was cooled from 604.9°F to 103°F and passed through a knockout drum to remove most of the water prior to entering the absorber. The syngas fed into the bottom of the absorber where most of the H_2S gases were physically absorbed with the SELEXOL solvent from the top of the absorber. The syngas exited the top of the H_2S absorber which was ready for CO_2 capture process. The H_2S-rich solvent coming out of the bottom of the H_2S absorber was preheated with the lean solvent prior to stripper column. The stripper distillate was cooled to 110°F by a partial condenser to ensure most of the water condensed. The vapor generated from the reflux drum and was sent to Claus process to obtain sulfur component. As some water was lost in the process, more water was added to the reflux drum. In order to balance SELEXOL solvent loss, some solvent was added to the bottom of the stripper. The lean solvent from the bottom of the stripper was recycled back to the top absorber at 1ppm H_2S. The recycled solvent was cooled from 145.8°F to110°F.

Removal process for CO_2 was similar to H_2S process; however the significant difference was that the CO_2 capture process needed a larger amount of SELEXOL than H_2S removal process because the solubility of the CO_2 is less than H_2S. The solvent of CO_2 process used a stripper to recycle back to the CO_2 absorber. The stripper distillate was compressed to 150 bar to sequestration, and the treated gas from the top of the CO_2 absorber was fed into a methanation process. The processes flowsheet is shown in Fig. 1.

2.2.2 Flowsheet 2 (FS2)

FS2 is different to FS1, the configuration of FS2 is that the syngas from the gasifier was sent to H_2S removal process where most of the H_2S was removed. Then the treated gases entered the WGS reactor which contained the commercial catalyst $Cu/ZnO/Al_2O_3$. The outlet gas was finally sent to CO_2 capture process. The lean solvent with 0.01 mole fraction CO_2 was recycled back to the absorber. In both of the processes, in order to obey air emission standards and downstream limitation of H_2S concentration to methanation process, the specification of H_2S and CO_2 recovery percentages are 99.9% and 90.2%, respectively.

2.3 Optimization

2.3.1 Objective Function

The objective function of these processes was to find the minimal total annual cost (TAC). The objective function is represented Eq. (5).

$$TAC = Operating + \frac{Capital}{3} \qquad (5)$$

The payback period was 3 years, and the equipment cost functions are represented in Eqs. (6-9)[7]

$$Column\ vessel = \left(\frac{M\&S}{280}\right) * 1548.9 * D_C{}^{1.066} L_C{}^{0.802} \qquad (6)$$

$$Column\ tray = \left(\frac{M\&S}{280}\right) * 12.69 D_C{}^{1.55} L_C \qquad (7)$$

$$Heat\ exchanger = \left(\frac{M\&S}{280}\right) 101.3 A^{0.65} \left(2.29 + \left(F_d + F_p\right) F_m\right) \qquad (8)$$

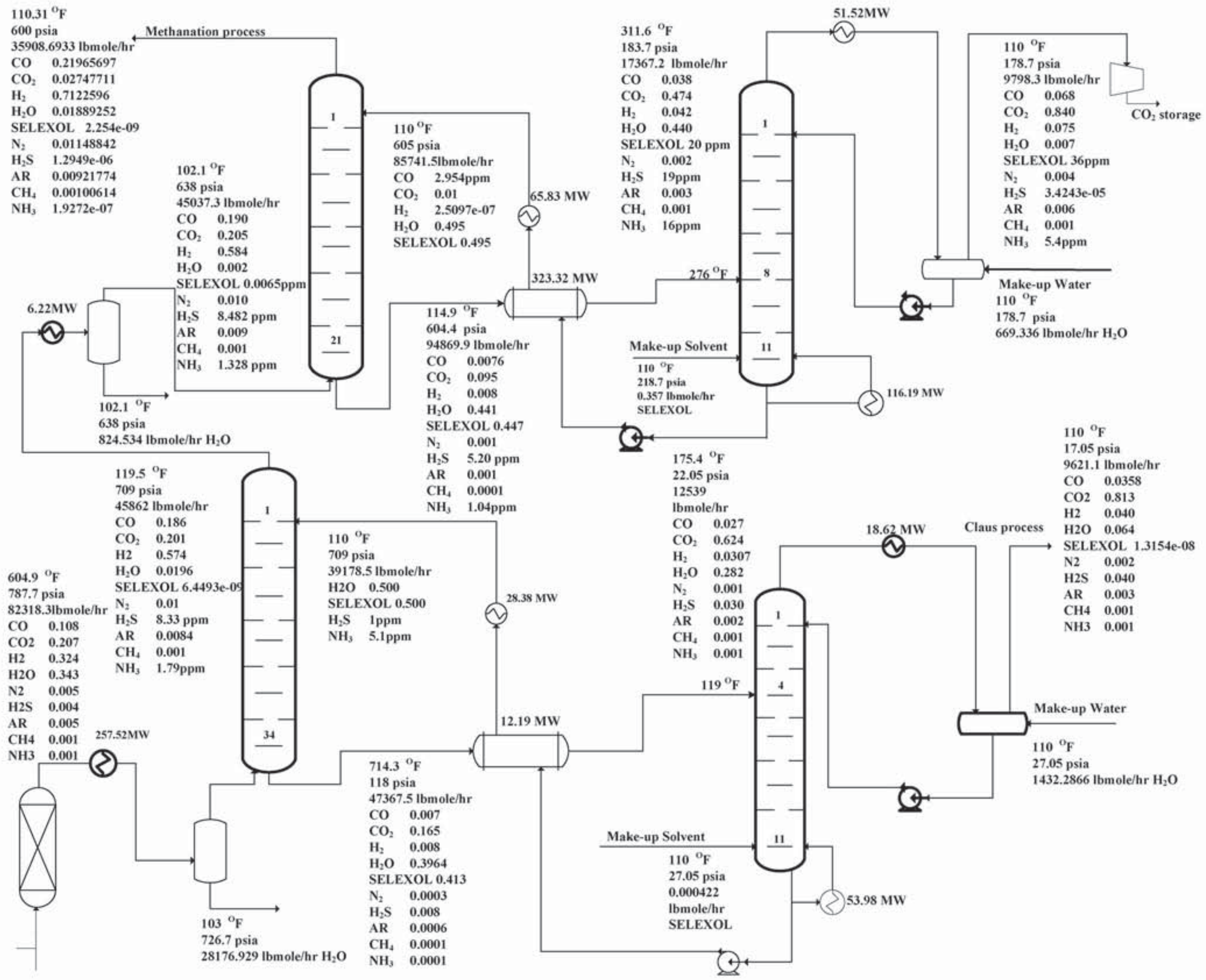

Fig. 1 Optimal result of WGS/AGR FS1

$$\text{Gas compressor} = \left(\frac{M\,\&\,S}{280}\right) * 517.5 * bhp^{0.82} * (2.11 + F_C) \qquad (9)$$

The equipment of the H_2S and CO_2 removal processes was designed so that sieve trays and tray spacing of 2 ft were used. The overall heat transfer coefficient, U, was 150BTU/(h • ft^2 • °F). The operating cost included cooling water at $0.03/1000gal, chilled water at $ 4.00/GJ, electricity at $0.04/kwhr and steam at $3.4/lb depending on the steam pressure needed in the reboiler. An economic M&S index was $1536.5 in year 2011.

2.3.2 Optimization Variables

The optimal variables of the two process flowsheets were absorber tray no.(N_A), stripper tray no.(N_S), absorber column pressure(P_A), stripper column pressure(P_S), stripper feed stage(N_F) and stripper feed tray temperature(T_F) which dramatically affected the total annual cost (TAC) of each process flowsheet.

2.3.3 Optimization

Optimization flow steps were followed as: 1. fixed the H_2S recovery specification at 99.9%, a given absorber/stripper pressure, a given absorber /stripper tray number, a given feed stage, the TAC was obtained by varying the feed temperature. 2. Fixed the H_2S recovery specification, a given absorber pressure, a given stripper tray number and a given feed temperature, the TAC was obtained by varying the stripper pressure and feed stage. 3. Fixed the H_2S recovery specification, a given absorber/ stripper pressure, a given stripper tray number, a given feed stage, the TAC was obtained by varying the absorber tray number. Consequently, the optimal result was found by following these flow steps, and the TAC with optimal variables is shown in Fig. 2. The minimal TAC of H_2S removal process is US$11,827,469 including the capital cost of $5,747,667 and the operating cost of $6,079,802.

In the CO_2 capture process, the CO_2 gas was compressed to 150 bar from the stripper so that the operating cost increased significantly. Similar to the optimal flow steps of H_2S process, the minimal TAC of the CO_2 capture is US$41,946,495 including the capital cost of $17,256,521 and the operating cost of $24,689,973. The optimal CO_2 process in FS1 is shown in Fig. 3. The total economic optimal flowsheet is shown in Fig. 1. The minimal TAC of the H_2S and CO_2 in FS2 is obtained by the above mentioned method, and the result is represented in Table 1.

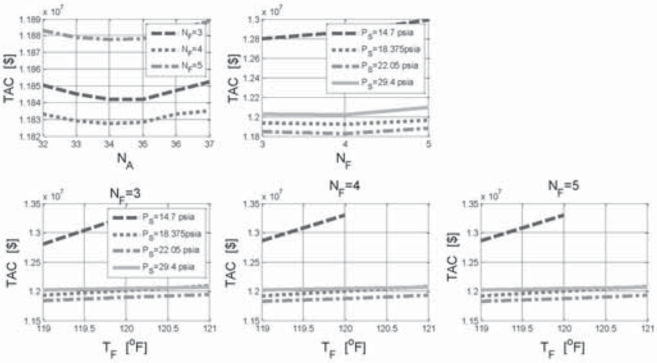

Fig. 2 Optimal design of H_2S removal process (FS1)

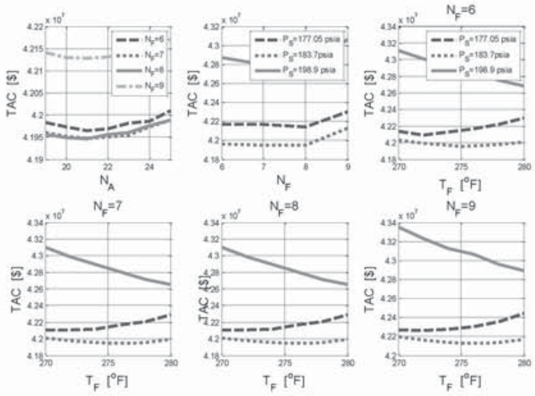

Fig. 3 Optimal design of CO_2 capture process (FS1)

Table 1. Cost of the two flowsheets.

	WGS	H_2S	CO_2
Case1			
Catalyst cost	$1,135,384.9		
Total capital cost	$1,381,773.3	$5,747,667.1	$17,256,521.7
Total operating cost		$6,079,802.0	$24,689,973.4
TAC	$2,517,157.3	$11,827,469.1	$41,946,495.1

	WGS	H_2S	CO_2
Case2			
Catalyst cost	$145,032.3		
Total capital cost	$905,017.7	$4,224,248.2	$21,795,075.4
Total operating cost	$7,115,017.9	$4,738,462.3	$31,935,189.1
TAC	$8,165,066.9	$8,962,710.5	$53,730,264.5

2.4 Result and Discussion

From the afore mentioned optimization analysis, the optimal TAC of FS1 and FS2 are obtained. Based on the result, the cost of FS1 is US$14,566,919 cheaper than FS2 and the main reasons are discussed as follows:

WGS reactor: Due to the outlet gas from the gasifier in the FS1 containing enough water, steam is not required to achieve the specification in FS1. On the contrary, the gasifier outlet stream is firstly sent to H_2S removal unit where most of the water is removed in FS2. Hence the WGS reactor required additional high pressure steam to reach the outlet molar ratio (H_2 /CO = 3:1).

H_2S removal unit: In the FS1, the CO_2 generated from the WGS reaction reduces the H_2S partial pressure. Thus the need for more SELEXOL solvent increases the capital and operating cost.

CO_2 capture process: In the FS2, the syngas from the WGS outlet is sent to CO_2 capture process. To achieve the CO_2 recovery specification, more solvent is required. Consequently, the capital and operating cost increase. After stripping the CO_2, the CO_2 rich stream is compressed and used for sequestration. Therefore, the compression cost for FS2 is greater than FS1.

3. SENSITIVITY ANALYSIS

In order to effectively control the specifications of the absorber distillate and the stripper bottom stream H_2S concentration, control structures must be developed. In our process, once the inventory control was implemented, the sensitivity analysis was used to confirm the quality control loops. The manipulated variable of the H_2S removal process absorber in FS1 was analyzed by singular value decomposition (SVD). A minor change in the feed flow rate +1% did not affect the tray temperature. As a result, the solvent flow rate was used to control the H_2S concentration at the top of the absorber. The H_2S concentration of the stripper bottom stream was adjusted by reboiler duty. Stage 6 is most temperature sensitive given 1% of reboiler duty change. This suggests that manipulating reboiler duty can maintain product specification. Also, from SVD analysis of CO_2 process, the results show that stage 9 of absorber and stage 11 of stripper are most temperature sensitive.

4. CONTROL STRUCTURE

Once the inventory control was implemented, including liquid level and pressure control as shown in Fig. 5, the quality control loops of WGS were determined and are described below:

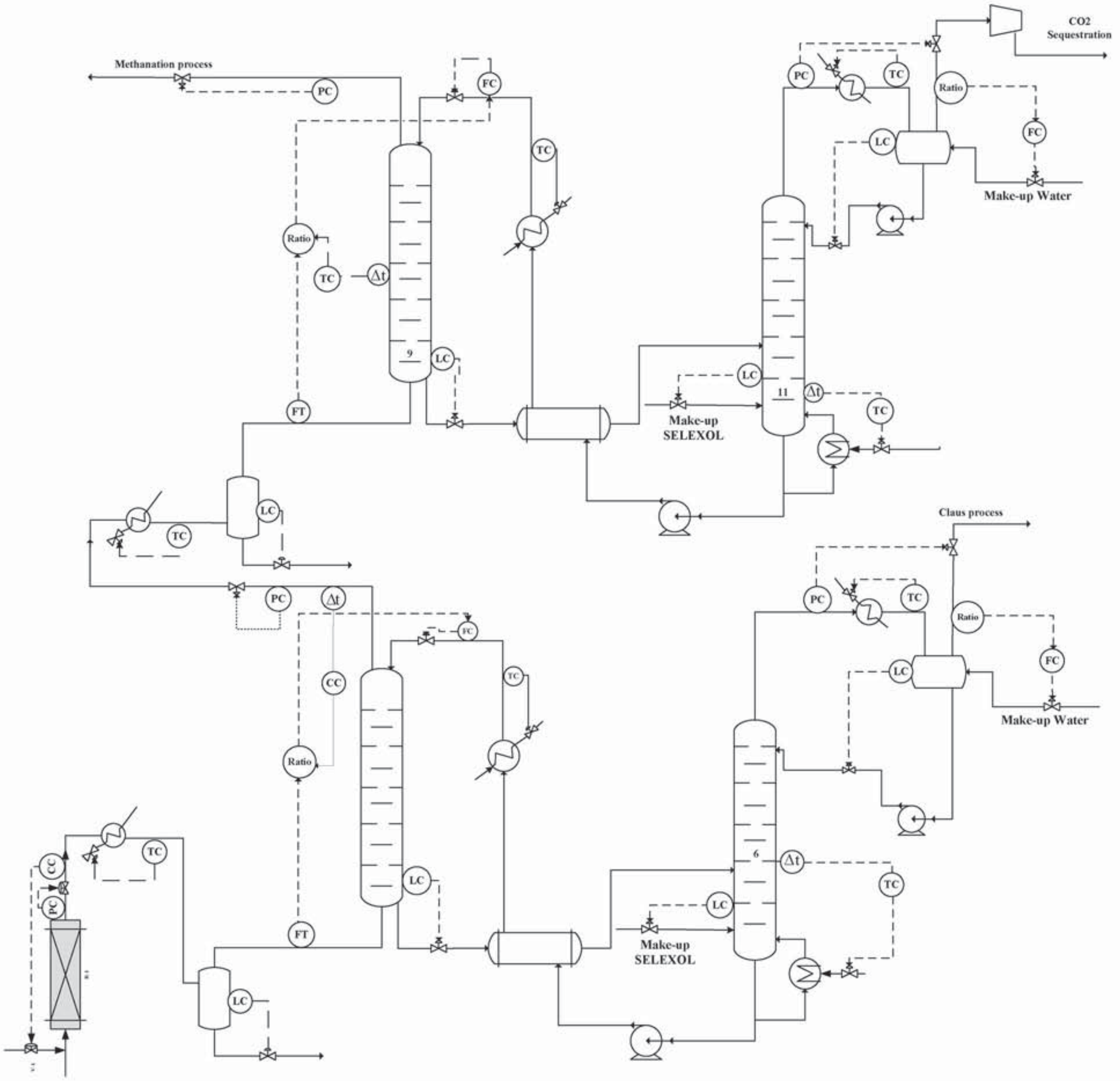

Fig. 4 FS1 control structure

(1) H_2/CO ratio from the WGS outlet is adjusted by feed steam flow rate.

The quality control loops of H_2S removal process are described below:

(1) Flow rate of the solvent is in ratio to the flow rate of feed. The ratio is adjusted by a composition controller which maintains the H_2S concentration.

(2) Stripper reboiler duty is manipulated to control stage 6 temperature.

The quality control loops of CO_2 capture process are described below:

(1) Flow rate of the solvent is in ratio to the flow rate of feed. The ratio is adjusted by the temperature controller to control stage 9.

(2) Stripper reboiler duty is manipulated to control stage 11 temperature.

5. OPERABILITY

To respond the product demand and feed composition disturbances, the quality control loops of WGS, H_2S and CO_2 are tested with operability analysis which was observed the H_2/CO ratio of the WGS, molar fraction from absorber top stream and reboiler duty of H_2S and CO_2 processes .Their quality control could operate flexibly within ±20% changes of the feed flow rate and the component disturbances.

6. CONCLUSION

The purpose is to compare the optimal economic of FS1 and FS2. Based on the result, the cost of FS1 is \$14,566,919 cheaper than FS2 and the main reason are:

1. Due to the outlet gas from the gasifier in the FS1 containing enough water, high pressure steam is not required to achieve the specification. 2. The CO_2 generated from the WGS reduces the H_2S partial pressure in the FS1. Thus the demand for more solvent increases the operating cost. 3. In the FS2, the syngas from the WGS outlet is sent to CO_2 capture process. To achieve the CO_2 recovery specification, more solvent is required. Therefore, FS1 is a more desirable option regarding the less TAC. Once the inventory control was implemented, the quality control loops were determined with SVD analysis. The H_2S absorber used a composition controller which maintains the H_2S concentration and stripper reboiler duty is manipulated to control stage 6 temperature. The CO_2 absorber used the temperature controller to control stage 9 and stripper reboiler duty is manipulated to control stage 11 temperature. To respond the product demand and feed composition disturbances, the quality control of FS1 could operate flexibly within ±20% changes of the feed flow rate and the component disturbances.

NOMENCLATURE

A = area [ft^2]
bhp = break horsepower [bhp]
D_C = diameter [ft]
F_C = design type of compressors [-]
F_d = design type of heat exchanger [-]
F_m = shell-and-tube material [-]
F_p = design pressure [psi]
k_1 = rate constant [mol/s kg cat Pa]
k_3 = rate constant [1/Pa]
k_{WGS} = rate constant [mol/atm$^{0.841}$ h gcat]
K_{WGS} = equilibrium constant [-]
L_C = height [ft]
$M\&S$ = marshall and swift cost index [$]
N_A = absorber tray number [-]
N_F = stripper feed stage [-]
N_S = stripper tray number [-]
P_A = absorber column pressure [psia]
Pi = partial pressure [atm]
P_S = stripper column pressure [psia]
r_{COS} = reaction rate of COS [mol/s kgcat]
r_{WGS} = reaction rate of WGS [mol/h gcat]
T_F = stripper feed tray temperature [-]

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