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### MEA-Based CO<sub>2</sub> Capture Technology and Its Application in Power Plants

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#### 1. Introduction

CO<sub>2</sub> emission has the greatest negative impact on the observed greenhouse effect, causing approximately 55% of the global warming (IPCC, 2005). Currently, it is a mission for the whole world to control and reduce the emission of CO<sub>2</sub>. There is a great amount of CO<sub>2</sub> being released from coal-fired power plants. Coal is the most abundant fossil fuel, and its resources are more evenly distributed all over the world than those of oil or natural gas. Coal is expected to continue to be a prominent fuel for electricity production in the future (Thitakamol et al., 2007; Romeo et al., 2008; IEA, 2003).

For coal-fired power plants,  $CO_2$  capture technologies can be divided into pre-combustion, oxyfuel and post-combustion method based on the position of  $CO_2$  captured. Meanwhile, it can also be divided into chemical absorption method, adsorption method, membrane separation method and so on.

 $CO_2$  capture based on monoethanolamine (MEA) is one of the most mature chemical absorption methods of post-combustion technologies. There has been extensive research on  $CO_2$  capture system based on MEA. But MEA based  $CO_2$  capture system needs thermal energy to regenerate MEA, which leads to the energy penalty to the power plant.

#### 2. Related work

#### 2.1 Research progress on MEA based CO<sub>2</sub> capture system

It has been concluded that the energy penalty is about 2.57-4.2GJ/tCO<sub>2</sub>, based on the simulation in software Aspen plus (Romeo et al., 2008; Mimura et al., 1997; Desideri et al., 1999). Recently, outstanding studies have analyzed different alternatives to reduce the heat duty on the reboiler and the thermal integration requirements on the power cycle (Mimura et al., 1997; Desideri et al., 1999; Mohammad et al., 2007; Ali, 2004; Bozzuto et al., 2001; Singh et al., 2003). There are mainly two ways to reduce the energy penalty. One is to optimize CO<sub>2</sub> capture system based on MEA, while the other is to optimize the integration of CO<sub>2</sub> capture system and power plant. The thermal efficiency reduction for the power plant is about 6.82% with the energy supplied by steam extractions from the turbines (Romeo et al., 2008). Besides the method of steam extractions, building new reboilers or gas turbines have also been discussed (Romeo et al., 2008). The parameters that affect the energy penalty of the system have been analyzed and optimized (Mohammad et al., 2007). It has been found that the thermal energy requirement for MEA process is a major part of the process overall

operating cost (Singh et al., 2003). By modeling the MEA process for a 400 MWe coal fired power plant, a specific thermal energy requirement equal to 3.8 GJ/ton CO<sub>2</sub> has been found. Other studies have focused on the location of turbine steam extractions and the re-injection of condensate from stripper to steam cycle. Power reduction around 17% has been reported, for a 90 MW coal-fired power plant (Mimura et al., 1997), where 611 t/h of CO<sub>2</sub> are captured and compressed, using 737 t/h of steam, which is the 54% of the steam leaving the boiler. Some researchers have calculated power reduction up to 26%, with a decrease in power plant efficiency of 11.6 points for a 320MW coal-fired power plant (Desideri & Paolucci, 1999).

However, in the previous research, MEA based  $CO_2$  capture system itself has been given too much concentration, and power plants are usually treated as black boxes. Although the effects on the power plant due to installing  $CO_2$  capture have been mentioned, the effects have not been fully discussed. It has been proposed that a typical range of energy required is between 0.72 and 1.74 MWt per MWe generated in a coal-fired power plant (Ali, 2004).

#### 2.2 Contributions of our work

In this chapter,  $CO_2$  capture process based on MEA will be introduced firstly. Then a 600MW coal fired power plant will be taken as the base case, and the integrations of this plant with MEA-based  $CO_2$  capture processes will be discussed.

#### 3. Carbon capture process based on MEA

#### 3.1 System description

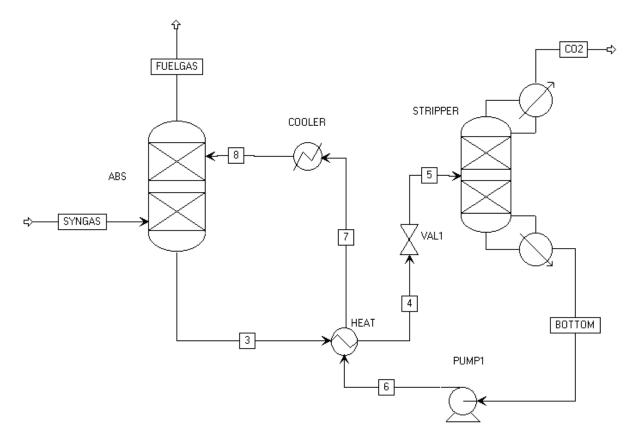


Fig. 1. Diagram of MEA based CO<sub>2</sub> capture system

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MEA based CO<sub>2</sub> capture system has been shown in Fig.1 (Zhai et al., 2008; Zhai et al., 2009). The main components are the absorber, stripper, pump, heat exchangers and so on. The flue gas from the power plant enters the absorber to have CO<sub>2</sub> absorbed, and then the untreated gases go out from the top of the absorber. The rich solution with CO<sub>2</sub> is pumped into the stripper to separate CO<sub>2</sub> from the rich solution. The CO<sub>2</sub> stream will be pressurized, while the lean solution without CO<sub>2</sub> will go back to the absorber to form a cycle. Besides, there is a heat exchanger between the rich solution and lean solution to recovery the heat.

#### 3.2 Modeling and evaluation

The flowsheet in Fig.1 can be simulated by ASPEN PLUS. The ELECNRTL physical property option set was selected. This was done to enable more accurate predictions of ionization equilibrium and the heats of solution. The absorber with 7 equilibrium stages is modeled in ASPEN using RadFrac, a rigorous, 'plate-to-plate' equilibrium stage model that allows for chemical reactions as well as phase equilibrium at each stage. The stripping column is modeled using RadFrac and contains 15 equilibrium stages. The main reactions taking place in aqueous systems of MEA and CO<sub>2</sub> are:

 $2H_2O \Leftrightarrow H_3O^+ + OH^ CO_2 + 2H_2O \Leftrightarrow H_3O^+ + HCO_3^ HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{-2-}$  $2MEA + CO_2 \Leftrightarrow MEAH^+ + MEACOO^ MEA^+ + H_2O \Leftrightarrow MEA + H_3O^+$ 

$$MEACOO^{-} + H_2O \Leftrightarrow MEA + HCO_3^{-}$$

Tempera	ture °C	37.8	
Pressur	e MPa	1.7	
	СО	0.44	
	CO <sub>2</sub>	24.6	
Mole	$H_2$	31.9	
Fraction (%)	H <sub>2</sub> O	0.35	
	$N_2$	41.5	
	Others	1.21	

The component of the SYNGAS is showed in Table 1. And the main assumptions made for the  $CO_2$  recovery process is showed in Table 2.

Table 1. The composition of syngas

The methodology 'Specific Consumption Analysis' based on the second law of thermodynamics was proposed by Prof. Song Zhiping in 1992. In this paper, the raw material consumption for the unity end product is referred to as 'specific consumption'. Unless otherwise stated it is always defined with respect to the 'total energy system' from the very input of primary energy until it reaches the end-users.

Parameters	Value
Absorber's inlet temperature °C	38 (gas)/38(liquid)
Absorber's outlet temperature °C	70 (top)/77(bottom)
Absorber's pressure MPa	1.7
Stripper's inlet temperature °C	83
Stripper's outlet temperature °C	38 (top)/112(bottom)
Stripper's pressure MPa	0.1
Stripper's reflux ratio	0.54
CO <sub>2</sub> recovery rate %	95

Table 2. Assumptions made for the CO<sub>2</sub> absorption

As can be seen in Table 3, the AspenPlus flow sheet does, reasonably well, predict the plant data.

Stream		Field data	AspenPlus
Gas	CO <sub>2</sub> in	24.6%	24.6%
	CO <sub>2</sub> out	93.5%	93.2%

Table 3. Validation of AspenPlus flow sheet

In accordance with the advanced exergo-economic approach, specific consumption is composed of the theoretically minimum specific consumption  $(b_{\min})$  and the specific consumption accruals  $(b_I)$ , where subscript I = 1, 2, ..., n is the order number of the subsystem in question. The theoretically minimum specific consumption  $b_{\min}$  arises in a hypothetical ideal energy system which is conceived as an entirely reversible energy system with an infinite lifetime and without any fixed costs. It follows that the theoretically minimum specific consumption for a system can be shown as

$$b_{\min} = (F / e_F) / (P / e_P) = e_P / e_F$$
(1)

Where  $e_p$  and  $e_F$  refer to the exergy for per unit product and the exergy for per unit material respectively.

Any irreversibility results in a raw material accrual and a relevant accrual of specific consumption b. Consider an energy system consisting of n subsystems and m streams. The specific consumption accruals in terms of a column vector due to irreversibility are

$$\mathbf{b} = [b_1 \ b_2 \ \dots \ b_n]^{\tau} = (b_{\min} \ / \ P) \mathbf{A} \mathbf{E}$$
<sup>(2)</sup>

where, P the total exergy amount of the end product

**E** the column vector of m stream exergies

 $A = [a_{ij}]$  the incident matrix with elements  $a_{ij} = 1$  (if stream *j* flows into subsystem *i*);  $a_{ij} = -1$  (if stream *j* flows out of subsystem *i*);  $a_{ij} = 0$  (if stream *j* has no direct connection with subsystem *i*)

The specific consumption of the end product equals its theoretically minimum specific consumption plus the sum of the specific consumption accruals, i.e.

$$b = b_{\min} + \sum_{0}^{n} b_{I} \tag{3}$$

The specific consumption of the  $CO_2$  recovery process can be identified as the MEA mole needed for the absorption of 1 mol  $CO_2$ .

The degree of carbonation in the absorber refers to the mole of  $CO_2$  that can be absorbed by 1 mol MEA, i.e. the  $CO_2$  solubility in 1 mol MEA.

The ideal degree of carbonation refers to the maximum mole of  $CO_2$  that can be absorbed by 1 mol MEA in the absorber. And the minimum specific consumption is the reciprocal of the ideal degree of carbonation. In this paper, the ideal degree of carbonation is 0.16 molCO<sub>2</sub>/molMEA, i.e. the minimum specific consumption is 6.25molMEA/molCO<sub>2</sub>.

In addition, based on the definition above, the specific consumption of the system is the mole of MEA needed for absorbing 1 mol  $CO_2$ , taking the component losses into consideration. And the reciprocal of the specific consumption is defined as the nominal degree of carbonation, which is the nominal mole of  $CO_2$  that can be absorbed by 1 mol MEA in the absorber. According to the flowsheet in Fig.1, the relationship between components and streams can be depicted in Table 4.

	SYNGAS	3	4	5	6	7	8	FLUEGAS	BOTTOM	CO <sub>2</sub> H	Ieat stream
Absorber	1	-1	0	0	0	0	1	-1	0	0	0
Heat exchanger	0	1	-1	0	1	-1	0	0	0	0	0
Condenser	0	0	0	0	0	1	-1	0	0	0	0
Pump	0	0	0	0	-1	0	0	0		0	0
Valve	0	0	1	-1	0	0	0	0	0	0	0
Stripper	0	0	0	1	0	0	0	0	-1	-1	1

Table 4. The incident matrix between components and streams

	[1	-1	0	0	0	0	1	-1	0	0	0 ]
	0	1	-1	0	1	-1	0	0	0	0	0
The incident matrix A=	0	0	0	0	0	1	-1	0	0	0	0
The incident matrix A=	0	0	0	0	-1	0	0	0	1	0	0
	0	0	1	-1	0	0	0	0	0	0	0
	0	0	0	1	0	0	0	0	-1	-1	1

According to the calculations based on Eq.2, the specific consumption accruals in components are showed in Tab.V. The total exergy amount of the end product P, the exergy of the  $CO_2$ , is 277000kW.

	Absorber	Cooler	Pump	Heat exchanger	Valve	Stripper
Exergy loss kW	14089.5	22040.3	580.0	1845.0	12006.5	69044.8
Specific consumption accruals kW	0.32	0.50	0.01	0.04	0.27	1.56
Ratio	11.78%	18.43%	0.48%	1.54%	10.04%	57.73%
				ノノト、ノノハ、		

Table 5. Specific consumption accruals in components

It can be seen in Table 5, the stripper has the highest specific consumption accruals, accounting for more than 57.73% of the total specific consumption accruals. The salt formed in the reaction between  $CO_2$  and MEA is relatively stable, which needs great heat to depose, about 4.25MJ/kgCO<sub>2</sub>. And the cooler has the second highest specific consumption accruals, about 18.43% of the total specific consumption accruals. The specific consumption accruals for the heat exchanger, pump and valves are relatively small, because there are no chemical reactions in these components.

The specific consumption for the system is 8.95molMEA/molCO<sub>2</sub>, calculated by Formula 3, increasing by about 43.18% of the theoretically minimum specific consumption. And the normal degree of carbonation is 0.11 molCO<sub>2</sub>/molMEA, lower than the ideal degree of carbonation, which is caused by the component losses. Based on the analysis above, the components should be improved to reduce the specific consumption of the system, especially the stripper.

#### 3.3 Discussions and conclusions

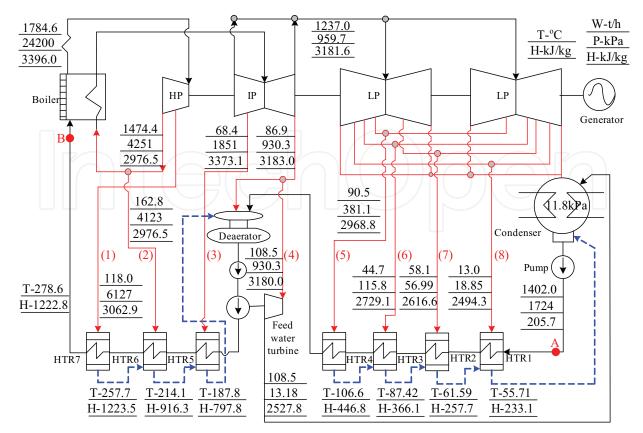
A novel method for chemical process evaluation was proposed in this paper. The specific consumption analysis is now accessible to perform optimizing studies using exergy analysis for amine based  $CO_2$  removal technology. It can be used to find leads to lower the energy consumption, either by optimization of the current flow sheet or by more structural improvements.

## 4. Integration and evaluation of a power plant with a MEA based CO<sub>2</sub> capture process

#### 4.1 System description

The layout of MEA-based CO<sub>2</sub> capture process has been shown in Fig.1. It is assumed that the fraction of CO<sub>2</sub> captured is about 65%. The energy required for CO<sub>2</sub> capture is calculated to be around 3.5GJ/tCO<sub>2</sub> in Aspen plus.

The base power plant used is shown in Fig.2. The combustion of coal takes place in the boiler. The unsaturated boiler feedwater from the condenser enters into the boiler after going through four low-pressure reheaters (HTR1, HTR2, HTR3, HTR4), three high pressure reheaters (HTR5, HTR6, HTR7) and a deaerator (Deaerator). The outlet superheated steam from the boiler is transported to the high pressure cylinder to produce power, and then the exhaust steam drives intermediate pressure and lower pressure cylinders after being reheated in the boiler. In the end, the final exhaust is condensed in the condenser. The extractions from different positions of the cylinders ((1)-(8)) are used to heat the feedwater via feedwater reheaters.



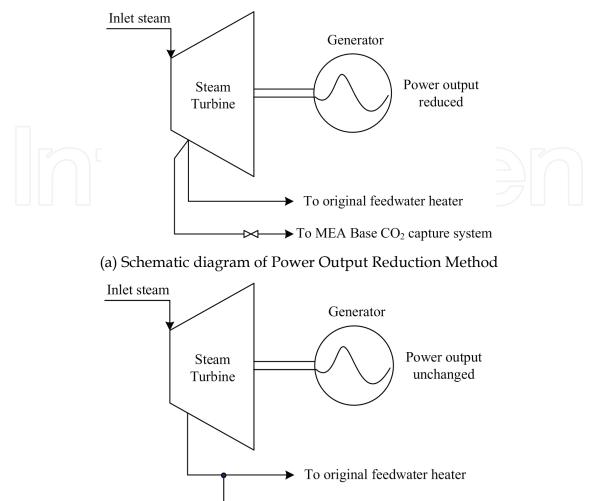
\* (1)-(8) denote the stream conditions.

Fig. 2. Steam layout of a 600MW supercritical power plant

#### 4.2 Integration methods

It has been stated that the MEA regeneration process in the stripper needs thermal energy. Integration based on power plant internal streams has been discussed in this section. As can be seen in Fig.2, there are eight extractions from the turbines. In order to extract steam for MEA regeneration, there are two kinds of methods. One method is called Power Output Reduction Method (PORM). In this method, more steam is extracted from the original one or more original steam extractions, as shown in Fig.3(a). The other method is called Coal Consumption Rate Increase Method (CCRIM). In this method, the original extractions from the turbines are kept unchanged, and part of the original steam is allocated for MEA regeneration, as shown in Fig.3(b) (Zhai, 2010).

However, not all the steam extractions from the turbines are suitable for MEA regeneration. Bounded to the chemical restrictions of MEA, the regeneration temperature needs to be below 122 °C. If the temperature is above 122 °C, MEA will decay rapidly and may cause corrosion to the reactor (Ali, 2004). If the approach temperature is set to be 10 °C, ideally the saturated temperature of the steam should be 132 °C. However, none of the original eight steam extractions' saturated temperate is 132 °C. The saturated temperatures of extractions (6) to (8) are too low to be suitable for MEA regeneration. But the steam of extractions (1) to (5) can be used supply the heat for MEA regeneration. Valves need to be used to reduce the pressures of the extractions (1)-(5) first. Therefore, the extractions (1) to (5) can be used to supply the heat for MEA regenerations after heat transferring will return to the reheat system.



 $\square$  To MEA Base CO<sub>2</sub> capture system

- (b) Schematic diagram of Coal Consumption Rate Increase Method
- Fig. 3. Integrations using internal energy flows

Based on the above two kinds of methods, nine possible cases have been considered as follows:

**Case 1**: Increasing the steam extraction of stream (1) to supply heat for MEA regeneration;

Case 2: Increasing the steam extraction of stream (2) to supply heat for MEA regeneration;

Case 3: Increasing the steam extraction of stream (3) to supply heat for MEA regeneration;

Case 4: Increasing the steam extraction of stream (4) to supply heat for MEA regeneration;

- Case 5: Increasing the steam extraction of stream (5) to supply heat for MEA regeneration;
- **Case 6**: Keeping all the steam extractions from the turbines unchanged and using the extractions (2)(3)(5) & part of extraction (1) to supply heat for MEA regeneration;
- **Case 7**: Keeping all the steam extractions from the turbines unchanged and using the extractions (1)(3)(5) & part of extraction (2) to supply heat for MEA regeneration;
- **Case 8**: Keeping all the steam extractions from the turbines unchanged and using the extractions (1)(2)(5) & part of extraction (3) to supply heat for MEA regeneration;

Cases 1 to 5 belong to the Power Output Reduction Method, while cases 6 to 9 belong to the Coal Consumption Increase Method.

**Case 9**: Keeping all the steam extractions from the turbines unchanged and using the extractions (1)(2)(3) & part of extraction (5) to supply heat for MEA regeneration.

#### 4.3 Evaluation methodology

Thermal performance evaluation is going to be used in this analysis. Power output, thermal efficiency, heat consumption rate and coal consumption rate are used as the four indicators in this evaluation, as follows:

#### (1) Power output

The turbine can be divided into different stages, and the real power delivered excluding losses is:

$$W_{out} = F_{in} \times e_{stage} \times \Delta H = F_{in} \times e_{stage} \times (H_{in} - H_{out})$$
(4)

Where,  $H_{in}$  is the inlet steam enthalpy;  $H_{out}$  is the outlet stream enthalpy;  $W_{out}$  is the outlet power per unit; and  $\Delta H$  is the enthalpy change in the stages.

#### (2) Thermal efficiency

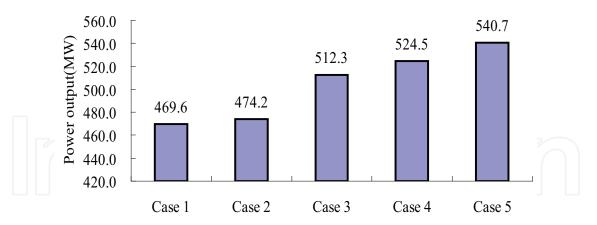
The thermal efficiency is defined as the ratio of net power generated to the total lower heating value of the consumed fuel.

#### (3) Coal consumption rate

The coal consumption rate is defined as the quantity of coal consumed to generate one kWh of electricity. There are various kinds of coal with different heat values. In order to analyzed and compare the total amount of coal, the standard coal needs to be defined. It is defined that the lower heating value of the standard coal is 29306kJ/kg (7000 kcal/kg) (Tian, 2001; You & Xu, 2008).

#### 4.4 Results and discussions

Figures 4 to 6 show the results for the cases, including the power outputs, coal consumption rates and efficiencies.



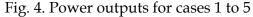


Fig.4 shows the power outputs for cases 1 to 5. The power outputs for cases 1 to 5 increase from 469.6MW to 540.7MW, indicating that the effects of MEA based CO<sub>2</sub> capture system on the power unit for the five cases reduce. There will be smaller power output reduction if the extractions are from low pressure turbines rather than those from high pressure turbines. For example, the power output reduces about 59.57MW with steam extracted from stream (5) (Case 5). The reduction is 54.4% lower compared to the case stream extracted from (1). However, the power output's difference between case 3 and 2 are the highest among all the abut cases, about 38.1MW.

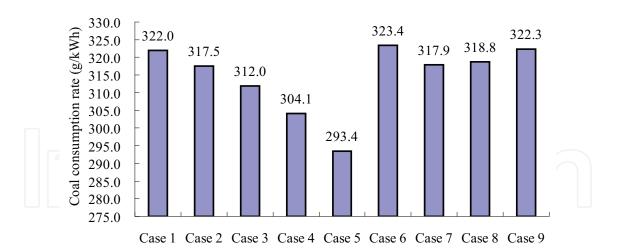
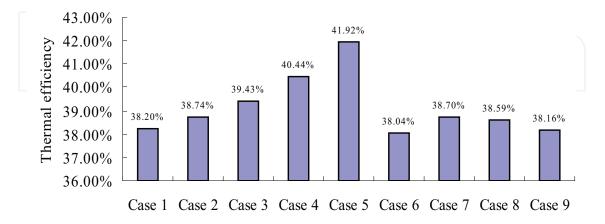


Fig. 5. Coal consumption rates for cases 1 to 9

Fig.5 shows the coal consumption rates for cases 1 to 9. Although cases 1 to 5 are Power Output Reduction Method, the coal consumptions still change. It is because the main steam flowrate reduces due to more steam extracted from the turbines. The coal consumption rates for cases 1 to 5 reduce. For example, the coal consumption rate of Case 5 reduces by about 8.88%, compared to that of Case 1. However, the coal consumption rate's difference between case 4 and 5 are the highest among all the abut cases, about 10.7g/kWh.

Cases 6 to 9 belong to the Coal Consumption Rate Increase Method, and the power output is 600.27MW unchanged. The coal consumption rate of Case 7 is the lowest among cases 6 to 9. However, the average coal consumption rate of cases 6 to 9 is higher than that of cases 1 to 5. Coal consumption rate of Case 7 (the lowest coal consumption rate among the Coal Consumption Rate Increase Method) is still 24.5g/kWh higher than the coal consumption rate of Case 5 (the lowest coal consumption rate among the Power Output Reduction Method). The coal consumption rates of cases 7 and 8 are lower than that of Case 1. It is further indicated that it is not reasonable to extract steam from high pressure turbines. The coal consumption rates for cases 1 to 9 can be sequenced as follows: Case 5<Case 4<Case 3<Case 2<Case 7<Case 8<Case 1<Case 9<Case 6.



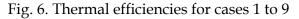


Fig.6 shows the efficiencies for cases 1 to 9. Case 5 has the highest thermal efficiency while Case 6 has the lowest thermal efficiency among the cases. Compared with the thermal

efficiency of the original power plant 45.14%, the thermal efficiency reduction for cases 5 and 6 are 3.22% and 7.1%, respectively. The efficiencies for cases 1 to 9 can be sequenced as follows: Case 5>Case 4>Case 3>Case 2>Case 7>Case 8>Case 1>Case 9>Case 6. This trend is the reversed trend of coal consumption rates for the cases. That's because there is a certain relationship between coal consumption rate and efficiency.

Based on the analysis above, Case 5 is the optimal case. The difference between Case 5 and the reference plant as shown Figure 1 lies in that extra steam of 337.4t/h has been extracted from the original stream (5). The extra steam is used to regenerate MEA, and it then goes back to the deaerator. The parameters of the feedwater heaters have all changed.

After CO<sub>2</sub> stream has been separated, it needs to be compressed from atmospheric pressure, at which point it exists as a gas, up to a pressure suitable for pipeline transport (110bar), at which point it is in either the liquid or 'dense phase' regions, depending on its temperature. Therefore, CO<sub>2</sub> undergoes a phase transition somewhere between these initial atmospheric pressure and final pressure (110bar). Compression of the CO<sub>2</sub> to 110 bar will require around  $0.4 \text{ GJ/tCO}_2$  (IPCC, 2005; IEA, 2004).

The analysis above doesn't take  $CO_2$  compression. The average thermal efficiency reduction of the nine cases is about 6%, while it is only 3.22% for the optimal case (Case 5). If  $CO_2$ compression is taken into consideration, energy of 30.16MW will be consumed for the compression process. The thermal efficiency reduction of Case 5 will increase to 5.56 %. The thermal efficiency reduction for the power plant is about 6.82% with the energy supplied by steam extractions from the turbines (Mimura et al., 1997). Therefore, the calculations in this paper are reasonable.

#### 5. Conclusions and future work

In this chapter, firstly,  $CO_2$  capture processes based on monoenthomal (MEA) have been analyzed from the microscopic angle. Secondly, the integrations of  $CO_2$  capture processes (based on MEA) with power plants have been discussed. The main research findings are as follows:

(1) The MEA based CO<sub>2</sub> capture process has been shown in Fig.1. The performance of the MEA based CO<sub>2</sub> capture process has direct connection with stripper pressure, MEA inlet flowrate and weight percentage, distillate rate and reflux ratio. Based on the specific consumption analysis, the energy consumption is 4.25MJ/kgCO<sub>2</sub>, and the stripper accounts for the most energy loss. Measures can be taken to lower the energy consumption.

(2) The integration of a 600 MW supercritical power plant with a MEA based  $CO_2$  capture process has been discussed. When the system is configured so that more steam is extracted from the low turbine, modeling shows that this system has the highest thermal efficiency, about 41.92% reducing 3.22% compared with the thermal efficiency of the original power plant.

In future work, the optimization of MEA-based capture process integrated with power plants will be examined. The MEA-based capture process needs to be optimized for the operation as well.

#### 6. Acknowledgement

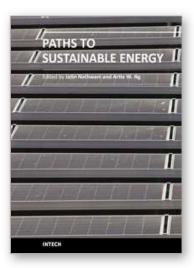
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The world's reliance on existing sources of energy and their associated detrimental impacts on the environment- whether related to poor air or water quality or scarcity, impacts on sensitive ecosystems and forests and land use - have been well documented and articulated over the last three decades. What is needed by the world is a set of credible energy solutions that would lead us to a balance between economic growth and a sustainable environment. This book provides an open platform to establish and share knowledge developed by scholars, scientists and engineers from all over the world about various viable paths to a future of sustainable energy. It has collected a number of intellectually stimulating articles that address issues ranging from public policy formulation to technological innovations for enhancing the development of sustainable energy systems. It will appeal to stakeholders seeking guidance to pursue the paths to sustainable energy.

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