# STRIPPER MODEL FOR CO<sub>2</sub> REMOVAL FROM IRON ORE REDUCTION UNIT USING AMINE SCRUBBING PROCESS

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#### ABSTRACT

Iron and steel production is a highly energy intensive process which has been reported to produce about 10% of worldwide CO<sub>2</sub> from fossil fuel. Thus, it has become a potential industry for CO<sub>2</sub> removal process. High energy consumption of amine scrubbing has caused the challenge for the large scale application. Even though recent studies have been done to reduce the energy consumption, there are lacking of focus on the optimization of stripper operating conditions. Thus, the objective of this research is to investigate the relationships of the stripper operating parameters on the reboiler heat duty and CO<sub>2</sub> removal percentage in the stripper. The modeling was done by using ratebased model in Aspen Plus with "MEA Property Insert" which described a MEA-H<sub>2</sub>O-CO<sub>2</sub> system thermodynamically with electrolyte-NRTL model. The column specifications were adapted from a pilot plant in University of Texas, Austin and the flue gas flow and compositions were adapted from Arasto et al. (2012). From the results, it showed that the increase in stripper with higher MEA concentration had reduced the reboiler duty up to 20 % and higher rich solvent temperature were able to reduce the reboiler heat duty. Besides that, the increase of stripper pressure had increased CO<sub>2</sub> removal efficiency in the stripper yet the CO<sub>2</sub> removal percentage was remained constant with the increase in rich solvent temperature. Lower rich solvent loadings with constant lean solvent loadings, molar flow rate of CO<sub>2</sub> exiting the stripper and mass flow rate of MEA solvent enabled the reduction in reboiler heat duty. Even though high stripper temperature enables better performance, the stripper temperature should be maintained below 125  $^{\circ}$ C to avoid MEA degradation. Besides that, it is suggested to use lower lean solvent flow rate so that the output changes can be observed easily. Based on the results, it can be concluded that the hypotheses were accepted. The findings of this study are useful as the reference for future amine scrubbing application on the iron ore reduction unit and to reduce the energy requirement of the process.

Key words: stripper model, iron industry, CO2 removal

#### ABSTRAK

Pengeluaran besi dan keluli dilaporkan sebagai proses tenaga intensif yang telah menghasilkan 10% pelepasan carbon dioksida di dunia daripada bahan api. Oleh demikian, industri tersebut merupakan salah satu industri yang berpotensi dalam proses penyingkiran carbon dioksida. Proses penyentalan amina memerlukan penggunaan tenaga yang amat tinggi dan telah mendatangkan cabaran dalam aplikasi berskala besar. Pelbagai kajian telah dijalankan untuk menggurangkan penggunaan tenaga, namun pengoptimuman terhadap kondisi stripper masih kurang dijadikan tumpuan kajian. Atas sebab tersebut, tujuan kajian ini dijalankan adalah untuk menyelidik hubungan antara parameter operasi stripper terhadap haba pengulang didih dan peratusan penyinkiran carbon dioksida dalam "stripper". Pemodelan ini telah dijalani dengan mengunakan model "rate-based" dalam Aspen Plus dengan "MEA Property Insert" yang menghuraikan MEA-H<sub>2</sub>O-CO<sub>2</sub> sistem elektrolik-NRTL dan model secare termodinamik. Ciri-ciri kolum dalam kajian ini beroperasi berasaskan salah satu "pilot plant" yang bertempat di Universiti Texas, Austin manakala aliran dan komposisi gas bahan api pula berasaskan kajian Arasto et al. (2012). Hasil kajian menunjukkan bahawa peningkatan kepekatan MEA dalam stripper telah menurunkan kadar tugas pengulang didih sebanyak 20% dan peningkatan suhu "rich solvent" pula dapat menurunkan kadar tugas haba pengulang didih. Selain itu, peningkatan tekanan stripper telah meninggikan keberkesanan penyingkiran carbon dioksida dalam stripper. Namun demikian, peratusan penyinkiran carbon dioksida tetap kekal nilainya dengan peningkatan suhu"rich solvent". "Rich solvent loadings" yang rendah dengan nilai tetap untuk "lean solvent loadings", kadar aliran molar carbon dioksida yang keluar daripada stripper dan kadar aliran jisim MEA juga akan menurunkan kadar tugas haba pengulang didih. Walaupun suhu stripper yang tinggi menjamin penyingkiran CO<sub>2</sub> secara lebih efektif tetapi suhu tersebut perlu dikekalkan di bawah 125 °C untuk mengelakkan degradasi MEA. Penggunaan kadar aliran "lean solvent" yang lebih rendah telah dicadangkan supaya perubahan output yang lebih jelas dapat diperhatikan. Hipotesis kajian dikatakan serasi berasaskan hasil kajian yang dikumpul. Hasil tersebut dipercayai dapat membantu dalam mengurangkan penggunaan tenaga aplikasi proses penyentalan amina atas unit penghasilan bijih besi.

Kata kunci: model "stripper", industri besi, penyingkiran CO2

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# LIST OF ABBREVIATIONS

ao	standard quadratic mixing term
$a_1$	additional, asymmetric term
$\alpha_i$	temperature function by Soave
$A_{j}$	constant for equation (3.37)
A <sub>ø</sub>	Debye-Huckel parameter
b	constant in equation (3.19)
$b_i$	constant in equation (3.26)
$B_i$	constant for equation (3.37)
$C_i$	constant for equation (3.37)
d	solvent density
$D_i$	constant for equation (3.37)
$D_{s}$	dielectric constant of the mixed solvent
$D_w$	dielectric constant for water
E	Activation energy
е	charge of an electron
fac(i)	stream scale factor
F(i)	mass flow of stream i
$g^{ex^*}$	molar excess Gibbs free energy
$g^{ex^*,LR}$	molar excess Gibbs free energy contribution from long range forces
$q^{ex^*,local}$	molar excess Gibbs free energy contribution from local forces
$g_{pD\mu}^{ex^*}$	Pitzer-Debye-Hucel contribution
a <sup>ex*,Born</sup>	Born expression
h(i)	enthalpy of stream i
H(i)	heat flow of heat stream i heat flow of heat stream i
I <sub>x</sub>	ionic strength on a mole fraction basis
k	rate coefficient
$k_B$	Boltzmann constant
kij	binary parameters in equation (3.29)
K <sub>j</sub>	equilibrium constant for thermodynamic model
$l_{ij}$	binary parameters in equation (3.31)
$m_i$	constant in equation (3.27)
$M_s$	solvent molecular weight in kg/kmol
No	Avogadro's number
NC	number of components specified by Comps and Comp-Groups
NH	number of combined inlet and outlet heat streams
NM	number of combined inlet and outlet material streams
NSS	number of sub streams specified
NW	number of combined inlet and outlet work streams
$P_{c_i}$	critical pressure of species i
$q_{reaction}$	heat of reaction for desorption of $CO_2$
$q_{reboiler}$	reboiler duty
$q_{sensible}$	energy required for sensible heating of the incoming rich amine solution to the stripper operating temperature.
<i>q<sub>strinner</sub></i>	energy consumed to generate stripping vapour (steam)
R	Universal gas constant
$r_i$	rate of reaction
,	

Born radius of species k
+1 for inlet streams, -1 for outlet streams in equation (3.43) to (3.46)
mass fraction of sub stream j in stream i
temperature in K
temperature in K in equation (3.42)
critical temperature of species i
work of work stream k
molar volume
liquid-phase mole fraction
mass fraction of component k in sub stream j of stream i
charge on species k

## Greek

α	non-randomness parameter
ρ	closest approach parameter
τ	binary energy interaction parameter
$\omega_i$	acentric factor

# LIST OF ABBREVIATIONS

CCS	Carbon capture and storage
DEA	Diethanolamine
DGA	Diglycolamine
DIPA	Di-isopropanolamine
EOS	Equation of state model
EU ETS	European Union Emission Trading Scheme
GHG	Greenhouse gas
GCEP	Global Climate and Energy Project
GDP	Gross Domestic Product
IEA	International Energy Agency
IISI	International Iron and Steel Institute
IPAE	2-Isopropylaminoethanol
IPCC	Intergovernmental Panel on Climate Change
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
NBS	National Bureau of Statistics
NCDC	National Climatic Data Center
NRTL	Non-random-two-liquid
OSHA	Occupational Safety and Health Administration
PENG-ROB	Peng-Robbison
<b>RK-SOAVE</b>	Redlich-Kwong-Soave equation

## **1** INTRODUCTION

#### 1.1 Background

It has been known that global warming is one of the most serious environment issues that pose a threat to the humankind and the living things in this world. Climate change is negatively affecting the economy, health and communities and the scientists have concerned that the conditions would be disastrous if no action is taken to control the situation. One of the initial causes of climate change is the increasing of the CO<sub>2</sub> concentration in the atmosphere which leads to the greenhouse effect. Carbon dioxide is the primary greenhouse gas that contributes the most to climate change because of both its abundance and long atmospheric lifetime (Simon, 2013).The greenhouse effect is exerted on the Earth's surface which absorption and emission of infrared radiation by gases in the atmosphere cause the increasing surface temperature of Earth (Kiehl & Trenberth, 1997).

There are several sources of  $CO_2$  emission that are mainly caused by the human activities such as the generation of electricity and heat, industry processes, transportation, agriculture and fuel combustion since decades ago. IPCC (2005) has reported that the using of carbon-based fossil fuel as the primary source of fuel is expected to be continued for many years from now and the largest source of the global  $CO_2$  emission is due to the burning of fossil fuels. The increase of energy demands due to the fast economic development in the world has caused the problem to be more critical. The future  $CO_2$  concentration seems to be substantially higher as the rate of  $CO_2$  emission accelerates unless there are significant changes made. One of the methods that had been proposed was the storage of the pure  $CO_2$  stream in a variety of carbon sink in a long period to reduce or eliminate the accumulation of greenhouse gas in the atmosphere (GCEP, 2005).

One of the potential  $CO_2$  removal industries is iron and steel production since the production produces a high amount of  $CO_2$  gas from the making processes which includes the fossil fuel power generator and the release of  $CO_2$  during the reduction process from iron ore (Arasto et al., 2012). This statement can be further confirmed by the report of global steel production sector which has been reported to have maintained

an upward trend for the last five years. The production had even reached up to 1058 million tons of crude steel in 2004 (IISI, 2005). Moreover, iron and steel industry is the largest energy-consuming manufacturing sector in the world which is accounting for 10-15% of total industrial energy consumption (IEA GHG, 2000). Iron and steel industry is responsible for 10% of worldwide CO<sub>2</sub> emission which is corresponding to 5% of overall global greenhouse gas emission (IEA, 2008). The increasing trend is predicted for the amount of CO<sub>2</sub> to be produce in this sector since the demand for iron and steel has rapidly increased in the countries that have been in a primary stage of rapid economic growth especially in China and India (Simon, 2013). The two most common steel making processes, Blast Furnace and Basic Oxygen Furnace-based route (BF + BOF route) and the Electric Arc Furnace route (EAF route) have contributed for about 99% of the global crude steel production (Worldsteel, 2010) and they are the main sources for the CO<sub>2</sub> emission from the iron ore reduction plant. Since coke is used as reducing agent in the production of iron and steel by using the BF + BOF route which causes the emission of relatively high CO<sub>2</sub> concentration, improvements should be done in order to reduce the amount of CO<sub>2</sub> gas emitted (Arasto et al., 2012).

There are several technologies have been developed to capture carbon dioxide from flue gas. Movagharnejad and Akbari (2011) has stated that there are numerous techniques that have been used for the post combustion capture for carbon dioxide from the flue gases such as chemical absorption, physical absorption, membrane separation and adsorption. Currently, chemical absorption is the most preferred method for the low pressure flue gases. According to IEA (2008), amine scrubbing is the post combustion chemical absorption technique which is the commonly used method to remove CO<sub>2</sub> since 1930 which involves the use of various amines such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). The simplest and most used amine for CO<sub>2</sub> removal is MEA (monoethanolamine) which is relatively inexpensive, low molecular weight, and has a high enthalpy of solution with CO<sub>2</sub> which tends to drive the dissolution process at high rates (GCEP, 2005). Generally, amine scrubbing has been recognized as one of the potential techniques to solve the climate change problem by reducing the  $CO_2$  emission in large scale (Arasto et al., 2012). This has brought a possibility to utilize this technology in the iron and steel production sector. Rochelle (2009) also has suggested amine scrubbing is useful with the steel works with 25% CO<sub>2</sub> and modeling studies by Gielen and Moriguchi (2001) has

indicated that  $CO_2$  removal might be an attractive strategy for the iron and steel production sector. However, this removal process has a high consumption of thermal energy due to the amine regeneration in the stripper and increases the cost of the  $CO_2$ removal process.

#### **1.2** Motivation and problem statement

The accelerating rate of the CO<sub>2</sub> concentration has concerned the public about the global warming which leads to serious consequences such as the climate change and the rising of the average sea level which is expected to be critical by the year 2100 (IPCC, 2005). In addition, a further global warming of minimally 1.8 to 4  $^{\circ}$ C in this century and at the worst case of 6.4  $^{\circ}$ C is expected. This can be avoided if the people around the world decrease the greenhouse gas (GHG) emissions. Iron and steel industry has proven to be one of the largest sources of CO<sub>2</sub> which contribute 10% of worldwide CO<sub>2</sub> emission and 5% of overall global greenhouse gas emission (IEA, 2008). Consequently, the application of the CO<sub>2</sub> removal system should be done in this industry as one of the practical ways to reduce the global CO<sub>2</sub> emission effectively to avoid the conditions to be worsened.

Amine scrubbing process which involves the removal of carbon dioxide is a technically feasible method of making effective and continuous reductions of CO<sub>2</sub> emissions. This can be done by reducing the CO<sub>2</sub> concentration in the atmosphere to a controllable level and focus on the increase of the efficiency of energy conversion and/or utilization in the amine scrubbing plant by substituting the current fossil fuel power generators to renewable sources of energy (Li, 2008). The main advantage of amine scrubbing is it can be installed to the existing power plants without major modifications (Arachchige et al., 2012). As mentioned by Alie et al. (2004), amine scrubbing process consists of an absorber and a stripper as the main unit operations which are important for CO<sub>2</sub> removal. Stripper is especially important in this process to regenerate the amine solvent so that the CO<sub>2</sub> removal percentage is kept in high values. Many researchers have done the studies on the amine scrubbing process but the studies mainly focused on chemical reaction mechanism, mass transfer, gas/liquid equilibrium, and other related aspects of CO<sub>2</sub> absorption (Aroonwilas et al., 1999; Soave & Feliu, 2002; Freguia & Rochelle, 2003). However, the most challenging issue is the large quantities of energy required to regenerate the amine solvent within the CO<sub>2</sub> capture process. Large amount of energy is needed especially in the stripper's reboiler and  $CO_2$  compression which is higher than the capital cost. This cost of implementation is too high to be applied in the large scale industry and many researchers start to focus on the design of amine scrubbing units which are mainly consisting of absorber, stripper and heat exchanger in order to reduce the energy consumption and the cost of the process. By varying the stripper parameters in this process, the performance and the cost are highly affected in the system. Thus, stripper operating parameters have been labelled as the primary factors for the energy reducing in the amine scrubbing system.

Recent studies have been done in many aspects in order to reduce the energy consumption of amine scrubbing process. However, there are limitations such as insufficient comparisons between the parameters involved in the studies especially in the iron and steel industry. There are a lot of attentions are paid to the power plants but less in the iron and steel industry. The studies have been done are based on the case study in the steel mills that currently exist around the world such as in Finland (Arasto et al., 2012). Arasto et al. (2012) had focused on only three different heat production scenarios and the amount of  $CO_2$  can be captured based on these three scenarios and the best amine solvent has been evaluated by comparing the CO<sub>2</sub> removal percentage of each solution. Goto et al. (2012) has only investigated on the types of absorbent that can result the highest CO<sub>2</sub> absorption rate based on the pilot plant scale experimental method in Japan with 2-Isopropylaminoethanol (IPAE) aqueous solution. Cheng et al. (2010) also has used the pilot plant scale experimental method to investigate the CO<sub>2</sub> removal percentage by using more parameters such as types of solvent, the speed of the rotation of rotating packed bed column for absorber, temperature, gas flow rate and the liquid flow rate for solvent in the rotating packed bed.

The introduction of innovative configurations of stripper (Van Wagener & Rochelle, 2011) might increase the operating cost of the  $CO_2$  removal since the unit operations involved would be increased even though the introduction of more complexity to the process flow by means of splits, recycles, and multiple pressure stages can reduce the existing driving forces to cut down on total energy loss. According to Van Wagener and Rochelle (2011), the reduction of the driving forces and the total compressor work can be done by introducing the more complex configurations with compressor by collecting high-pressure  $CO_2$ .

On the other hand, the invention of the new solvents and additives which are added into the amine solution in order to fasten the reaction kinetics are still in research and development progress (Cullinane & Rochelle, 2004) such as the potassium carbonate/piperazine solvent. Even though it has been proven that this solvent can ensure very high  $CO_2$  absorption rate without limiting the lean solvent loading in 0.40 mol  $CO_2$ /mol solvent but the price is much higher compared to MEA and the stability of the solvent is still under investigation.

There are limited studies by previous researchers focused on the effects of stripper operating parameters on the energy consumption reduction in the  $CO_2$  removal process. Hence, this study aimed to investigate the effects of stripper operating parameters such as the rich solvent loading (mol  $CO_2$ /mol MEA),  $CO_2$  removal percentage, MEA concentration, reboiler heat duty, stripper operating pressure and rich solvent temperature on the energy consumption of the  $CO_2$  removal process which is directly affecting the operation cost. The optimization of these parameters not only can reduce the energy consumption and investment costs but it also can ensure the secure operation safety.

The most precise way to study the effects of the stripper parameters is via experiments. However, there are some critical issues regarding experimental procedures since amine scrubbing covers a large range of operating conditions from normal atmosphere with supercritical state, and involve multi-component mixtures (Li, 2008). Besides that, MEA solvent is also hazardous to the human body and overexposed to this amine solution would possibly cause the irritation of the respiratory system and excretory system (OSHA, 2013). Moreover, for research purposes, a large scale of  $CO_2$  capture plant is very expensive to build and time consuming. Consequently, process simulation and modeling play an important role in process optimization and in evaluation of the various process alternatives. In this research, Aspen Plus® will be used as the simulation tool to develop the model.

### 1.3 Objective

This study aims to investigate the influence of stripper operating parameters on the overall energy consumption of  $CO_2$  removal from iron ore reduction unit by amine

scrubbing process which is directly affecting the cost of operation by using Aspen Plus®.

### 1.4 Scope of the research

The following are the scopes of this study:

- Modeling of stripper for CO<sub>2</sub> removal for an iron ore reduction unit using amine scrubbing process based on the case study on Ruukki Metals Ltd.'s Raahe steel mill which was done by Arasto et al. (2012).
- Modeling analysis of stripper operating parameters on the energy consumption of the amine scrubbing process.

First of all, the process flow diagram for amine scrubbing was modified by referring to Harun et al. (2012) and the flue gas flow rate and composition are adapted from the Arasto et al. (2012) based on the case study on Ruukki Metals Ltd.'s Raahe steel mill. The thermodynamic and transport properties are modeled by using "MEA Property Insert" (Abu-Zahra et al., 2006). Then, the identification of all the parameters, physical properties, column specifications and constants is done. In this study, the stripper operating parameters such as rich solvent loading (mol CO<sub>2</sub>/mol MEA), rich solvent temperature and stripper operating pressure are set as the input variables while the performance indicators are including reboiler heat duty and CO<sub>2</sub> removal percentage in the stripper which are proven to be important leads to a significant cost due to energy consumption. The mass balance and energy balance are calculated based on the formulas stated in Chapter 3. All the data are inserted into the system and the baseline case simulation is run as the standard for further comparisons among the variables. The baseline case is defined by using the standalone absorber and a variation of the pure MEA solvent flow rate of 30 wt. % to determine the amount of CO<sub>2</sub> being absorbed and the column specifications are shown in Chapter 3 which is referred to the pilot plant from University of Texas that is validated by Kvamsdal et al. (2009) and Lawal et al. (2009). After the simulation is done, the analysis on the performance is done based on the results and comparison is carried out with the previous studies.

Several hypotheses are made in this study. First, the thermal energy requirement for reboiler decreases with increasing rich solvent loading and the increase in  $CO_2$  removal percentage would increase the energy consumption. It is also expected that a significant

amount of energy can be saved by increasing the MEA concentration in the absorber/stripper but the high MEA concentrations may cause corrosion in the absorber/stripper and solvent degradation. Besides that, the increase of stripper pressure is expected to cause a higher efficiency of the amine regeneration and would reduce energy consumption.

#### **1.5** Organisation of this thesis

The structure of the reminder of the thesis is outlined as follows:

Chapter 2 provides a description of the problems, background, and applications of amine scrubbing process for  $CO_2$  removal in iron and steel industry. Besides that, general descriptions of the characteristics of the technique, as well as the theories that are related for the modeling are presented. This chapter also provides a brief discussion of the studies available for the simulation, mentioning their applications and limitations for energy consumption reduction analysis. A summary of the previous study on amine scrubbing as well as in other fields such as  $CO_2$  removal in the power plant is also presented.

Chapter 3 gives a review of the procedures and detailed property model with the theory that are applied for the modeling of amine scrubbing process for  $CO_2$  removal. All the correlation, formulas and equations that are applied in this modeling are stated and explained accordingly. Justifications are stated to clarify the reasons of the usage. A standalone absorber is used as a baseline case to obtain the parameters needed to complete the whole process modeling and the description of a complete process flow diagram of the amine scrubbing is supported with the figures.

Chapter 4 shows the result and it is discussed accordingly based on the data used and the results obtained.

Chapter 5 concludes the result and discussion which had obtained from the simulation and recommendations are given based on the result and discussion made.

### **2 LITERATURE REVIEW**

#### 2.1 Overview

In this chapter, the problems and motivations that lead to the development of  $CO_2$  removal by using amine scrubbing process are clearly discussed. Then, the explanation is done to justify the application of this technology should be done in iron and steel industry and a summary of the limitations based on references from past studies is stated and discussed. Modeling is the best way to analyse the influence of stripper conditions on energy consumption of the amine regeneration and the properties of the modeling are explained at the end of this chapter.

#### 2.2 Global warming and CO<sub>2</sub> emissions

The growth in the world gross domestic product (GDP) was the main contributor to the recent increase in  $CO_2$  emissions (Raupach et al., 2007) and it is directly affecting the rising of global surface temperature significantly for the past decades. This condition has become even more pronounced in recent decades. Human activities such as fossil fuel burning, waste gas emission from the industries and deforestation are the main sources of greenhouse gases, especially carbon dioxide which acts as a primary greenhouse gas that contributes the most to climate change (Simon, 2013). The increase of energy demands due to the fast economic development in the world has caused the problem to be more critical as the rate of  $CO_2$  emission accelerates, hence, the authorities, engineers and scientists are working hard to solve this international problem without affecting the current investments. Figure 2.1 shows the annual world greenhouse gas emissions in 2005 according to sectors. The  $CO_2$  emissions (Herzog, 2009).



Figure 2-1: Annual world greenhouse gas emissions in 2005 according to sectors by Herzog (2009)

Based on Figure 2-1, the  $CO_2$  emission is highly depending on the electricity and heat generation with the fuels which is 24.9% of overall global greenhouse gas emission.

Besides that, industry and transportation are also the important contributors to the high concentration of  $CO_2$  in the atmosphere. Both of them have made up of 14.7% and 14.3% respectively. This has meant that industry is also one of the focus points to stabilize the global  $CO_2$  concentration.

According to IPCC (2007), global warming has been detected in natural systems such as sea level rise and critical increase in Earth's surface temperature. Besides that, hundreds of millions of people are affected by flooding, low water supplies, increased malnutrition and increased health issues due to the climate change. Moreover, it has caused a huge impact to the extinction of many species and reduced diversity of ecosystems (Schneider et al., 2007). It was proven by the researchers that warming above 3  $\$  could reduce the crop yields and lead to a reduction in global food production. Figure 2-2 shows the global annual average temperature measured over land and oceans.



Figure 2-2: Global annual average temperature measured over land and oceans by NCDC (2013)

Red bars indicate temperatures above and blue bars indicate temperatures below the 1901-2000 average temperature. The black line shows atmospheric carbon dioxide concentration in parts per million. Based on this graph, the global average temperature shows an increase of approximately 1.4 F since the early 20th century. The data were collected based on the air temperature data over land and sea-surface temperatures observed from ships, buoys and satellites. Even though the graph does not show a continuously increasing trend for every year but it is clear that this is a long-term global warming trend. The fluctuations in temperature for several years are due to natural processes, such as the effects of El Ninos, La Ninas, and the eruption of large volcanoes. According to the graph, 20 warmest years have all occurred since 1981, and the 10 warmest have all occurred in the past 12 years (NCDC, 2013).

### 2.3 Iron and steel production

The industrial activities which involve the large primary material industries such as chemicals and petrochemicals, iron and steel, cement, pulp and paper, and aluminium have supplied most of the  $CO_2$  in the atmosphere although some of these industries have produced less  $CO_2$  from the improvements in energy efficiency and material flow management. However, the demand for industrial products is expected to double or triple over the next 40 years. Thus, they would become the main  $CO_2$  emissions sources in the future.



Figure 2-3: Direct  $CO_2$  emissions in industry by sector and by region in 2007 by IEA (2010)

Based on Figure 2-3, iron and steel, cement and chemicals had accounted for almost three-quarters of  $CO_2$  emissions in industry in 2007 and China is the world largest  $CO_2$  emission country in that particular year. According to Farla et al. (1995), iron and steel production is a highly energy intensive process which can produce up to 20 million tons of  $CO_2$  annually. This phenomenon is estimated to be more critical in the following years since the demands for steel have rapidly increased in the countries that have been in a primary stage of rapid economic growth especially in China and India (Simon, 2013). Gielen (2003) also stated that the development of iron and steel industry has provided the largest point source of energy related  $CO_2$  emissions in the world and makes it as one of the largest potential  $CO_2$  removal industry.



Figure 2-4: China's crude steel production and share of global production (1990–2010) by Hasanbeigi et al. (2013)

Figure 2-4 has shown that the China's crude steel production has increased significantly from the pass 10 years and it is predicted to continue the trends for the coming decades. Starting in the 1990s, the industry development has accelerated and exceeding more than 100 million metric tons (Mt) in 1996. After that, steel production in China has continued to increase rapidly and it makes China to become the world's largest crude steel producer for 14 continuous years. Furthermore, Worldsteel (2011) and NBS (2012) have stated that the average annual growth rate of crude steel production in China was 18.5% between 2000 and 2009. In 2010, the iron and steel production in China had consumed around 461 TWh of electricity and 14,872 PJ of fuel which represented 46.6% of the world steel production in that year. Guo and Fu (2010) has also reported that the three main emission sources in the processes of iron and steel production which are direct on-site burning of fossil fuels, indirect emission from electricity consumed during the production process and direct non-energy related emissions are the  $CO_2$  emission sources and the first and second sources are the main cause of  $CO_2$  discharges.

During the reduction process of iron production, large amount of carbon dioxide gas  $(CO_2)$  is produced and causes the iron production less productive and low in quality. Consequently, the capture and removal of the gas has become the excellent solution to improve the quality and yield of products by eliminating the contaminants and thus, reducing coal and coke consumptions and the emissions of  $CO_2$  to the atmosphere (IPCC, 2005). Gielen (2003) also has reported that the capture technology will help the iron production sector to reduce up to 4% of the global  $CO_2$  emissions. However, the number and impact of competing strategies for the removal of  $CO_2$  in the iron and steel production are relatively low compared to the electricity sector such as power plants.



Figure 2-5: Industrial  $CO_2$  emissions reductions from carbon capture and storage compared to the baseline equivalent scenarios by sector in 2050 by IEA (2010)

Figure 2-5 has shown the emissions reductions comparison between 1.7 Gt  $CO_2$  and 2.5 Gt  $CO_2$  need to be achieved through the application of carbon capture and storage (CCS) in industry in the BLUE low-demand and high demand scenarios respectively. From the data, it is expected that there are important  $CO_2$  reduction opportunities for carbon dioxide gas removal in the iron and steel (IEA, 2010) where it showed high percentage values for both of the scenarios.

### 2.4 CO<sub>2</sub> capture technology

There are three types of main approaches to separate the  $CO_2$  generated from a primary fossil fuel such as coal, natural gas or oil, biomass, or mixtures of these fuels. These technologies are post-combustion capture, pre-combustion capture, and oxy-fuel combustion capture. According to IEA (2010), all of these options have resulted in a significant energy penalty to the base plant and it is expected that the energy requirement can be reduced through continuous researches and experimental studies.





• Post-combustion capture is a process that separates CO<sub>2</sub> from combustion products such as nitrogen, oxygen and water. The capture can occur anywhere along the product processing stream from the combustor to effluent exhaust which the flue gas is produced after the combustion of the fuel.

- Pre-combustion is a process of the separation of carbon in the form of CO<sub>2</sub> from a resource after the energy content of the resource is transferred to a carbon-free energy carrier. The most common configuration involves gasification with air or oxygen. The products undergo a water-gas shift to a high concentration stream of CO<sub>2</sub> and H<sub>2</sub>. The CO<sub>2</sub> is then captured and the H<sub>2</sub> is reacted with air.
- Oxy-fuel combustion is the separation of oxygen from nitrogen in the air to produce a nitrogen-free oxidizer stream. During this process, reaction with fuel is occurred to produce a stream composed primarily of CO<sub>2</sub>, oxygen, and water. The water can then be removed through phase separation.

Figure 2-7 has shown the energy consumption according to the source of the steel industry of China in 2004 and coal is the main fossil fuel which can produce large amount of  $CO_2$  through combustion is used to generate the heat for the process. Hence, post-combustion capture is applicable in this industry to separate  $CO_2$  from combustion products.



Figure 2-7: Energy consumption mix of the steel industry of China in 2004 by Guo and Fu (2010)

### 2.5 Amine scrubbing process

There are several  $CO_2$  separation technologies for post-combustion  $CO_2$  capture and chemical absorption is the most developed and preferred technique to capture  $CO_2$  from flue gas (Mofarahi et al., 2008). This chemical absorption process is adapted from the gas processing industry where amine-based processes have been used commercially for the removal of acid gas impurities from process gas streams (GCEP, 2005). Amine based  $CO_2$  capture is well known for many industries such as oil and gas industry and food industry where  $CO_2$  is captured from flue gas and used in several products (Shao &