FUPRE Journal of Scientific and Industrial Research Vol.6, (1), 2022 ISSN: 2579-1184 (Print) ISSN: 2578-1129 (Online)

Modelling and Simulation of Carbon Dioxide Capture Plant from Refinery Flue Gas in Nigeria using Aspen Hysys V8.8

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Abstract

The current global trend is to mitigate the release of carbon dioxide (CO₂), a major contributor to greenhouse gases (GHG)). A tangible portion of the flue gas from most fossil fuel is carbon dioxide which can be as much as 10-25%. In petroleum and other industrial plants, CO₂ concentration in exhaust stream depends on the process such as oil refining (8-9 mole% CO₂). Flue gas data obtained from the refinery Fluid Catalytic Cracking Unit (FCCU) was used to study the composition of gas fed into the carbon capture plant and the amount of CO₂ captured by the plantin contact with Monoethanolamine (MEA). A carbon dioxide capture plant was simulated using Aspen Hysys v8.8. It was observed that CO₂ was totally cleaned off from the Sweet gas at the overhead product of the Absorber after contact with Aqueous Monoethanolamine (MEA) which is the absorbent used having compositions 29.997mole% MEA, 66.03mole% H₂O and 4.00mole% CO₂ in the Absorber and then absorbed in the Rich Amine at the bottom exit stream of the column with composition of 3.0mole%. The composition of CO₂ captured was about 93mole% at a temperature of 33°C, a pressure of 0.7703kg/cm² and a molar flow-rate of 282.5kgmole/h.

Key words: CO₂ Capture, Flue Gas, Monoethanolamine

1. Introduction

Carbon capture and storage is the process of capturing waste carbon dioxide (CO_2) usually from large point of sources, such as a cement factory or biomass power plant, transporting it to a storage site, and depositing it where it will not enter the atmosphere, normally an underground geological formation with a view to preventing the release of large quantities of CO_2 into the atmosphere. This is a potential means of mitigating the contribution to Global warming and ocean acidification of carbon dioxide emissions from industry and heating sources (Institute, 2012).

The largest part of the flue gas from most fossil fuel combustion is un-combusted nitrogen since it burns in ambient air which contains about 79 volume percent gaseous nitrogen. Carbon dioxide, the next largest part of flue gas can be as much as 10-25 volume percent or more, and is closely followed in volume by water vapour (H₂O)which results from the combustion of the hydrogen in the fuel with atmospheric oxygen. Carbon dioxide (CO₂) concentration in flue gases depends on the fuels such as coal (12–15 mole-% CO₂) and natural gas (3-4 mole-% CO₂) (Anon., 2018). In the petroleum and other industrial plants, CO₂ concentration in exhaust stream depends on the nature of the process such as oil refining (8-9 mole% CO₂), production of cement (14-33 mole-% CO₂) and iron and steel (20-44 mole-%). From 2004 to 2011, global CO₂ emissions from energy uses increased to 26% (Anon.. 2018).The Nigerian Petrochemical industry is another large contributor to CO₂ emission with a value of 0.44 metric tons per capita in 2016(Anon., 2016). The main anthropogenic emissions of CO₂ come from the combustion of fossil fuels and there is need for the reduction of the amount of CO_2 in the atmosphere.

Carbon Dioxide Removal (CDR) refers to a number of technologies whose objective is large-scale removal of carbon the dioxide from the atmosphere. It can also be the removal of CO₂ from the stack emissions of large fossil fuel point sources, such as power stations and in this case, there is a reduction of emission to the atmosphere but not necessarily a reduction of the amount of carbon dioxide already in the atmosphere. This study is therefore lead to reduction in emission which has been a challenge, reduction in the carbon dioxide source points and ultimately reduction in energy consumption and flaring.

1.1 Carbon capture Technologies and storage

Broadly, three different configurations of technologies for which carbon capture exist: post-combustion, pre-combustion, and oxyfuel combustion:

1.1.1 Post-Combustion

This method is effective for capturing CO_2 from power plants and when applied to power plants, it is referred to as postcombustion capture. This method includes solvent absorption by Monoethanolamine (MEA)and is used extensively (Otto, et al., 2015).

1.1.2 Pre-Combustion

The pre-combustion capture refers to capturing CO_2 generated as an undesired coproduct of a

Conversion process (Kumar, et al., 2016). In this case, fuel from a power plant is reacted with oxygen to generate a syngas mixture, which is moved out in the gasification step (Li, et al., 2012). Carbon dioxide is then reacted with steam in the second step and finally separation occurs using a physical or chemical absorption process (Corti & Lombardi, 2004).

1.1.3 Oxy-Fuel

In the oxy-fuel combustion technological approach for CO_2 capture, flue gas consisting of pure

Oxygen is burnt. This technological route produces a flue gas stream that is highly saturated with CO_2 (Diego, et al., 2014). The main advantage of this technique is that the flue gas is available at a high CO_2 concentration of approximately 75.7mole%, thereby reducing compression costs and facilitating efficient CO_2 removal (Smit, et al., 2014).

2. Materials and Method

The methodology adopted in this work included mathematical modelling which involved the various units of the plant followed by simulation utilizing the Aspen softwareand material and energy balances over the plant.

2.1 Mathematical Model

The model consists of sub-models for the Absorption and Regeneration towers included in an amine-based CO_2 capture plant. The absorption column, and the regeneration column coupled with a condenser followed by a reflux drum and a re-boiler are included in the model. In this case, the heat exchanger, cooler, make-up and separator tank are not modelled.

2.1.1 Column Models

Column models include the Absorption and Regeneration towers. The Regeneration tower is developed as a combination of the condenser and the re-boiler models together with the column model of the Regenerator. Attention is paid to the heat and mass transfer phenomenon taking inside the traysand towers. The main model equations for the columns are the same for both absorption and the regenerator tower. Specie and energy balances are carried out on both the liquid and vapour phases, and these form the basis for the development of the main model equations.

2.1.2 Model Assumptions

- Each phase in a control volume of the spatially discretized model behaves as a continuous stirred tank reactor (CSTR)
- The gas and liquid phases are ideal
- Inter-phase mass transfer of N₂ and O₂ are neglected
- Only the reactions in the liquid phase are taken into account
- Pressure drop is linear along the columns
- The number of trays in the columns are considered
- Constant volume flow of vapour and liquid is assumed
- Heat loss to the surroundings is assumed negligible.

The set of equations used in the columns are given below:

$$\frac{\partial c_{j,col}^{l}}{\partial t} = \frac{u_{col}^{t}}{\lambda} \frac{\partial c_{j,col}^{l}}{\partial z_{col}} + \frac{1}{\lambda} \dot{n}_{j,coltrans}^{m} + \dot{n}_{j,col,gen}^{m} \tag{1}$$

$$\frac{\partial C_{j,col}}{\partial t} = \frac{U_{col}^{v}}{(1-\lambda)} \frac{\partial C_{j,col}^{t}}{\partial z_{col}} - \frac{1}{(1-\lambda)} \dot{n}_{j,colgen}^{m}$$
(2)

$$\frac{\partial T_{col}^{l}}{\partial t} = \frac{U_{col}^{l}}{\lambda} \frac{\partial T_{col}^{l}}{\partial Z_{col}} + \frac{h^{m}A_{W}}{\lambda \tilde{c}_{p,col}^{l} \Sigma_{j=}^{l} c_{j,col}^{l}} \left(T_{col}^{v} - T_{col}^{l}\right) + \frac{n_{CO_{2},col,trans}^{m}(-\Delta \tilde{H}_{Abs})}{\lambda \tilde{c}_{p,col}^{l} \Sigma_{j=}^{l} c_{j,col}^{l}} + \frac{\Sigma_{j=1}^{n} n_{j,col,trans}^{m}(-\Delta \tilde{H}_{Vap,j})}{\lambda \tilde{c}_{p,col}^{l} \Sigma_{j=}^{l} c_{j,col}^{l}}$$
(3)
$$\frac{\partial T_{col}^{l}}{\partial t} = \frac{U_{col}^{v}}{(1-\lambda)} \frac{\partial T_{col}^{v}}{\partial z_{col}} - \frac{h^{m}A_{W}}{(1-\lambda) \sum_{j=}^{l} c_{j,col}^{v} \tilde{c}_{p,j,col}^{v}} \left(T_{col}^{v} - T_{col}^{l}\right)$$
(4)

Here Equations, (1), (2), (3) and (4) represent the rate of change of specie concentrations and temperatures of the liquid and vapour phases inside the towers, respectively. The main reaction between CO_2 and MEA, given in Equation (5) is considered in the computation of the rate of specie generation.

$$CO_2 + 2MEA \leftrightarrow MEAH^+ + MEACOO^-$$

(5)

The reflux flow, which enters the column in the first control volume from the top of the regeneration tower, introduces changes which are given in Equations (6) and (7).

$$\frac{dC_{1}^{l}}{dZ} = \frac{U_{1}^{l}}{\frac{U^{l}_{1}}{\lambda}} \left(\frac{C_{1,3}^{l} - C_{1}^{l}}{\Delta Z} \right) + \frac{U_{2}^{l}}{\lambda} \left(\frac{C_{1,2}^{l} - C_{1}^{l}}{\Delta Z} \right)$$
(6)

$$\frac{U^{l}}{\lambda}\frac{dT^{l}}{dZ} = \frac{U_{1}^{l}}{\lambda}\left(\frac{T_{1}^{l}-T^{l}}{\Delta Z}\right) + \frac{U_{2}^{l}}{\lambda}\left(\frac{T_{2}^{l}-T^{l}}{\Delta Z}\right)$$
(7)

Here u_1^l and u_2^l are the velocities of the amine flow from the absorption tower and the reflux from the reflux drum. Concentrations $c_{j,1}^l$ and $c_{j,2}^l$ represent the concentrations of the rich amine leaving the absorption tower and the reflux stream, respectively. Temperatures T_1^l and T_2^l are correspond to the rich amine flow and the reflux flow at the inlet to the regeneration tower.

2.2 Condenser and Re-boiler models

The condenser of the regeneration column is modelled with a reflux drum to hold the liquid until it is refluxed. A flash calculation is performed on the feed stream to the condenser at constant pressure and temperature and the liquid and vapour fractions leaving the condenser and their compositions can be obtained. The liquid and vapour flows leave the condenser and enter the reflux drum and the gas consisting mainly of CO_2 leaves for the compressor.

The reflux drum is assumed to have constant cross-sectional area. The temperature inside the drum and the liquid phase densityare also assumed to be constant. Specie and overall mass balances are carried out for the liquid phase inside the tank so as toobtain the rate in the change of the liquid height in addition to the liquid phase composition which are obtained through Equations (8) and (9).

$$\frac{dH_{RD}^l}{dt} = \frac{1}{A_{RD}\rho^t} \left(\dot{m}_{RD,jn}^l - \rho^l \dot{V}_{RD}^l \right) \tag{8}$$

$$\frac{dC_{RD}^l}{dt} = \frac{1}{A_{RD}H_{RD}^l} (\dot{n}_{i,RD,jn}^l - \frac{C_{i,RD}^l}{\rho^l} \dot{m}_{RD}^l) \quad (9)$$

Here $m_{RD,in}^{l}$ is the mass flow rate of liquid into the reflux drum, which is found from the molar flow into the reflux drum.

$m_{RDin}^l = \sum \left(n_{j,RD,in}^l M_i \right)$

where M_i is the molar mass of specie i. Liquid height, specie concentration, liquid density and cross-sectional area of the reflux drum are given by H^l_{RD} , c^l_{iRD} , ρ^l and A_{RD} respectively. When the liquid phase composition and the mass flow rate from the reflux drum are known, then the conditions of the reflux stream are known.

The re-boiler is modelled using a fixed vapour to feed fraction.

Temperature and pressure control in the reboiler are assumed to be ideal.

The re-boiler heat duty (Q_{RB}) is calculated using the following equation:

$$\dot{Q}_{RB,in}\hat{C}_{p}^{l}\Delta T_{RB} + \sum \left(\dot{n}_{i,RB}^{v}\Delta \widetilde{H}_{vap,i}\right) + \Delta H_{ab}$$

(10)

- The energy required to heat up the feed is given by $(\dot{m}_{RD,in}^t \hat{C}_p^l \Delta T_{RD})$
- Energy required to generate vapour from the feed is $\sum (\dot{n}_{i}^{v} \Delta \tilde{H}_{vap,i})$, and
- Heat of desorption of CO_2 is (ΔH_{ab}) .

Where $\Delta T_{RB} = T_{RB} - T_{RB,in}^{l}$

The feed flow into the re-boiler, specific heat capacity of the liquid and the molar rate of vapour leaving the re-boiler are given by $\dot{m}_{RD,jn}^{l}$, \hat{C}_{p}^{l} and $\dot{n}_{i,RB}^{v}$ respectively.

2.3 The Simulation

2.3.1 Aspen Hysys-Based Model

The model utilized was simulated using the flue gas data obtained from Refinery Fluid Catalytic Cracking(FCC) Unit. The plant was assumed to operate at steady state. The process flow diagram is shown in Figure 1.



Figure 1: Simulated process flow diagram of the carbon capture plant.

2.3.2 Absorber

The process that occurs here is the Absorption process also referred to as chemical absorption. Here, the CO_2 which is to be captured is contacted with a chemical solvent in this case MEA in the absorption column. High pressure and low temperature

favour absorption, and the operating pressure in this with 20 traycolumn is 50.99kg/cm². The sweet gas which contains no CO₂ leaves at the overhead of the column while the CO₂ rich amine, absorbed in MEA flows out at the bottom of the column to a separator.



Fig 2: Absorption column

2.3.3 Separator

The function of the separator in this plant is to remove excess water in the rich Amine in addition to some traces of Nitrogen and Carbon monoxide while the aqueous mixture of CO_2 , water and MEA is passed to the heat exchanger.



Figure 3: Separator

2.3.4 Heat exchanger

This heat exchanger is used in the plant to raise the temperature of the mixture from 96.20°C to 100° C, the pressure drop across the heat exchanger is 0psi and the heat flow across the heat exchanger is 2.95×10^{5} kJ/hr.



Figure 4: Heat Exchanger

2.3.5Regenerator

This unit is used to separate CO_2 from MEA where CO_2 and water is produced at the rectifying section of the column at a temperature of 83.35°C. The amine is recovered and flows out at the stripping section at 105°C. The regenerator operates at 1.22kg/cm² has 30 trays and operates at a reflux ratio of 3.



Figure 5: Regenerator unit

2.3.6 Cooler

The cooler is used to reduce the temperature of the distillate product from the rectifying section of the regenerator in order to properly separate water and CO_2 therebyand in this process a higher yield of CO_2 is obtained. This process is also known as cryogenic process.

2.4 Material and Energy Balance 2.4.1 Overall Material Balance

The Aspen Hysys process simulator used employs the law of conservation of mass to perform the material balances based on the assumptions stated earlier.(The rate of mass inflow (kg/h)) + (The rate of mass generated (kg/h)) = (The rate of mass outflow (kg/h)) + (The rate of mass accumulation (kg/h) 11 A steady state process was assumed; therefore, the accumulation is zero. Since the process is entirely physical, mass inflow equals mass outflows

 Table 1: Overall Material Balance

Feed stream	Rate of mass inflow(kg/ h)	Product stream	Rateofmassoutflow(kg/h)
FCC Flue	75261.845 0	Sweet Gas	63456.2004
WATER MU1	9.3784	Purge 2	0
MEA MU1	0	Overhead	699.5348
WATER MU2	5130.3925	Steam condensa te	50912.7372
MEA MU2	12.1278	Purge 1	0.02675
SATURATE D STEAM	50912.737 2	CO ₂	11927.4561
		Distilled water	4298.1911

2.4.2 Energy balance

The general energy balance equation is given as:

Rate of energy accumulation = (Rate of energy inflow to the system (kJ/h)) – (Rate of energy outflow from the system (kJ/h)) + (Energy generated within the reactor (kJ/h)) + (Rate of work done on the system)

(12)

At steady state,

Rate of energy accumulated = 0 and no work is done on the system, hence:

Rate of energy inflow to the system (kJ/h) + Rate of energy generated within the reactor (kJ/h) = Rate of energy outflow from the system (kJ/h)

 Table 2: Total energy balance

Equipme	Rate	Equipme	Rate
nt Duty	energy	nt Duty	of
	inflow to		energ
	the		У
	system(kJ/		outflo
	h)		w
			from
			the
			syste
			m
			(kJ/h)
L-R	5.266e6	Heater 1	8.001e
Exchange			6
r			
Pump	2.221e6		

3. Results and Discussion

The results obtained from the simulation of the carbon capture plant using the chemical solvent, MEA as the absorbent for CO_2 from the flue gas are shown below.

Table 3: Composition of flue gas fromFCCU

COMPONEN	COMPOSITIONS(M
TS	ole %)
CO2	10.25
O2	1.3
CO	6.98
H_2S	0.00
H2	2.915
N2	78.555

Stream Name	FCC FLUE	Vapour Phase
Vapour / Phase Fraction	1.0000	1.0000
Temperature [C]	656.3	656.3
Pressure [kg/cm2]	1.870	1.870
Molar Flow [kgmole/h]	2600	2600
Mass Flow [kg/h]	7.526e+004	7.526e+004
Std Ideal Liq Vol Flow [barrel/day]	2.102e+004	2.102e+004
Molar Enthalpy [kJ/kgmole]	-2.780e+004	-2.780e+004
Molar Entropy [Btu/lbmole-F]	10.50	10.50
Heat Flow [Btu/hr]	-6.850e+007	-6.850e+007
Liq Vol Flow @Std Cond [barrel/day]	4.822e+004	4.822e+004
Fluid Package	Basis-1	
Utility Type		

Figure 6: The properties of the flue gas from the FCCU

	Mass Fractions
MEAmine	0.2997
H2O	0.6603
CO2	0.0400
H2S	0.0000
Hydrogen	0.0000
CO	0.0000
Oxygen	0.0000
Nitrogen	0.0000

Total

Figure 7: Lean MEA absorbent composition for absorption

Stream Name	Lean Amine	Aqueous Phase
Vapour / Phase Fraction	0.0000	1.0000
Temperature [C]	41.45	41.45
Pressure [kg/cm2]	50.99	50.99
Molar Flow [kgmole/h]	1.616e+004	1.616e+004
Mass Flow [kg/h]	3.805e+005	3.805e+005
Std Ideal Liq Vol Flow [barrel/day]	5.771e+004	5.771e+004
Molar Enthalpy [kJ/kgmole]	-2.877e+005	-2.877e+005
Molar Entropy [Btu/lbmole-F]	-47.04	-47.04
Heat Flow [Btu/hr]	-4.406e+009	-4.406e+009
Liq Vol Flow @Std Cond [barrel/day]	5.451e+004	5.451e+004
Fluid Package	Basis-1	
Utility Type		

1.00000

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	Mole Fractions	Vapour Phase
MEAmine	0.0000	0.0000
H2O	0.0022	0.0022
CO2	0.0000	0.0000
H2S	0.0000	0.0000
Hydrogen	0.0324	0.0324
CO	0.0775	0.0775
Oxygen	0.0144	0.0144
Nitrogen	0.8735	0.8735

Figure 8: Lean MEA properties for absorption

Figure 9: Sweet gas composition at the rectifying section of the Absorber

Stream Name	SweetGas	Vapour Phase	Aqueous Phase
Vapour / Phase Fraction	1.0000	1.0000	0.0000
Temperature [C]	41.21	41.21	41.21
Pressure [kg/cm2]	50.99	50.99	50.99
Molar Flow [kgmole/h]	2332	2332	9.914e-005
Mass Flow [kg/h]	6.346e+004	6.346e+004	1.799e-003
Std Ideal Liq Vol Flow [barrel/day]	1.883e+004	1.883e+004	2.723e-004
Molar Enthalpy [kJ/kgmole]	-8925	-8925	-2.844e+005
Molar Entropy [Btu/lbmole-F]	-4.955	-4.955	-38.22
Heat Flow [Btu/hr]	-1.973e+007	-1.973e+007	-26.72
Liq Vol Flow @Std Cond [barrel/day]	3.113e+004	3.113e+004	2.720e-004
Fluid Package	Basis-1		
Utility Type			

Figure 10: Sweet gas properties at the rectifying section of the Absorber

	Mole Fractions	Aqueous Phase
MEAmine	0.1136	0.1136
H2O	0.8487	0.8487
CO2	0.0373	0.0373
H2S	0.0000	0.0000
Hydrogen	0.0000	0.0000
CO	0.0000	0.0000
Oxygen	0.0000	0.0000
Nitrogen	0.0003	0.0003

Total	1.00000

Figure 11: Rich Amine composition from the stripping section of the Absorber

Stream Name	RichOut	Aqueous Phase
Vapour / Phase Fraction	0.0000	1.0000
Temperature [C]	96.25	96.25
Pressure [kg/cm2]	50.99	50.99
Molar Flow [kgmole/h]	1.643e+004	1.643e+004
Mass Flow [kg/h]	3.923e+005	3.923e+005
Std Ideal Liq Vol Flow [barrel/day]	5.990e+004	5.990e+004
Molar Enthalpy [kJ/kgmole]	-2.862e+005	-2.862e+005
Molar Entropy [Btu/lbmole-F]	-43.95	-43.95
Heat Flow [Btu/hr]	-4.455e+009	-4.455e+009
Liq Vol Flow @Std Cond [barrel/day]	5.474e+004	5.474e+004
Fluid Package	Basis-1	
Utility Type		

Figure 12: Properties of Rich Amine from the Stripping section of the Absorber

		Mole Fractions
MEAmine		0.0000
H2O		0.0685
CO2		0.9311
H2S		0.0000
Hydrogen		0.0000
CO		0.0000
Oxygen		0.0000
Nitrogen		0.0003
	Total	1.00000

Figure 13: Composition of the CO₂ captured

Stream Name	CO2	Vapour Phase	Aqueous Phase
Vapour / Phase Fraction	1.0000	1.0000	0.0000
Temperature [C]	33.35	33.35	33.35
Pressure [kg/cm2]	0.7702	0.7702	0.7702
Molar Flow [kgmole/h]	282.5	282.5	0.0000
Mass Flow [kg/h]	1.193e+004	1.193e+004	0.0000
Std Ideal Liq Vol Flow [barrel/day]	2180	2180	0.0000
Molar Enthalpy [kJ/kgmole]	-3.827e+005	-3.827e+005	-2.852e+005
Molar Entropy [Btu/lbmole-F]	1.231	1.231	-38.47
Heat Flow [Btu/hr]	-1.025e+008	-1.025e+008	0.0000
Liq Vol Flow @Std Cond [barrel/day]	2182	2182	0.0000
Fluid Package	Basis-1		
Utility Type			

Figure 14: Properties of the CO₂ captured

From Figure 9, it is observed that CO_2 was totally cleaned off from the Sweetgas at the overhead product of the Absorber after contact with Aqueous MEA which is the absorbent used.The composition is 29.997mole% MEA, 66.03mole% H₂O and 4.00mole% CO₂ in the Absorber. The Rich Amine was fed to the regenerator after its temperature had been raised using the heatexchanger. The Amine used was recovered at the stripping section of the column for reuse.

In Figure13, composition of CO_2 captured was about 93mole% at a temperature of $33^{\circ}C$, a pressure of 0.7703kg/cm² and a molar flow-rate of 282.5kgmole/h as seen in Figure 14.

Conclusion

The CO₂ capture plant was simulated with use of an adequately selected the mathematical model of the CO₂ capture process with a CO₂ rich flue gas feed and a CO_2 free effluent. The amount of CO_2 present in the flue gases of any process plant can be reduced to a minimal level allowing the release of an environmentally friendly or safe effluent to the environment with the use ofMonoethanolamine as absorbent which captures up to 93% from the stream. The plant simulated can be adapted to accept any field flue effluent with slight variations in its defining parameters to accommodate the variations in the plant's products.

Acknowledgments

The contribution of WRPC in providing data for this work is acknowledged.

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