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Reduction and Capture of Green House Gas Emissions from an Oil Refinery with Amine/Piperazine-and Amine/Sulfolane-Based Solvents

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This paper focuses on the emissions of greenhouse gases (GHG) from petroleum/petrochemical refineries which are predominantly in the form of CO_2. A refinery located in the Gulf is selected and methodologies to reduce and capture CO_2 are presented. The refinery emits approximately 775 tonnes/year CO_2. A sound energy policy, robust process control, careful operation of motor driven equipment and process heaters could lead to appreciable reduction of these emissions. After reduction, the capture of remaining CO_2 emissions with PZ (piperazine) and sulfolane-based smine solvents is simulated and optimized to get minimum re-boiler duty in the stripper. The process simulator ASPEN software is used for simulations. The optimization results indicate that PZ-based amine solvent performs better than sulfolane-based amine when H_2S in the flue gas is in small amounts. The re-boiler duty seems to depend upon the temperature of the stripper feed. It is proposed that heat exchanger design be improved that exchanges heat between lean and rich amines.

Keywords: GHG, emissions reduction, carbon capture, refineries, amines.

Introduction

To halt and reduce global warming, world nations have reached a consensus called “Paris Climate Accord”. The purpose of agreement is to keep global temperature increase below 2 °C above pre-industrial levels and to support and assist efforts to limit the temperature increase even further to 1.5 °C.

In November 2017, 6 UNFCC members signed the agreement and 170 became party to it. In the Paris Agreement, each country is supposed to work out her own plan to control greenhouse gas (GHG) emissions that cause global warming (UN Paris Agreement for Climate Change, 2015).

If Paris agreement is not properly implemented, then it is expected that the world temperature would rise by 1.5 °C around 2040, which could lead to dramatic climate change such as ice-free Arctic, 90% destruction of Coral Reef, and a 10 cm rise in ocean levels (IPCC Report, 2013). In its efforts to honor the Paris Agreement and to avoid 2040 scenario, Saudi Arabia is making several attempts to reduce GHG emissions. Among those are attempts to increase the use of renewable energy, improving energy efficiency, enhancement and utilization of carbon capture, methane recovery and flare minimization. Unfortunately, the country's plan to use 54 GW of renewable and 17 GW of nuclear energy by 2032 has been downscaled. In the "Vision 2030", the renewable power plans are lowered to 9.5 GW. This might lead to additional emissions of 74–135 Mt CO_2 in 2030 compared to the scenario with a renewable energy target of 54 GW and a nuclear energy target of 17 GW by 2032. In February 2017, in a step towards meeting its scaled-down renewable energy target, Saudi Arabia launched its renewable energy tender program, the National Renewable Energy Plan (Khondaker et al., 2015).

Apart from harnessing renewable energy, the efficient use of fossil fuel-based energy can also lead to significant reduction of GHG emissions. According World Resource Institute Report (2019), the Industrial and Manufacturing sector contributes to almost 20% of GHG emission. Of 20%, the share of refineries to GHG emissions is estimated to be 5%. This is because oil exploration and refining are a very complex industry that runs on crude oil – fossil fuel – and produces a diverse range of fuels and petrochemicals. Refinery relies heavily on physical and chemical operations such as distillation, cracking, thermal reforming and treatment. Most of these processes require a huge amount of process heating and steam consumption. The burning of fossil fuel to run these operations accounts for 80% of the total oil and gas sector GHG emissions.

A survey conducted by the US government agency (NAICS 324110) has indicated annual energy consumption and GHG emissions of all refining sector in the USA. From the survey, energy consumption and related GHG emissions are categorized either as offsite emissions and onsite emissions. Offsite emissions come mainly from electricity generation (72%) and steam generation (28%). On the other hand, onsite emissions are released from process heaters and boilers as well as from several processes such as fluid catalytic cracking unit (FCCU), reforming unit, liquefied petroleum gas (LPG), recovery unit, hydrogen production units and sulfur recovery plants, which have significant process emissions of CO_2. Methane emissions are largely due to equipment leaks, crude oil storage tanks, asphalt blowing, delayed coking units and blow down systems. Asphalt blowing and waste gas to flare also contribute to overall CO_2 and CH_4 emissions at any refinery.

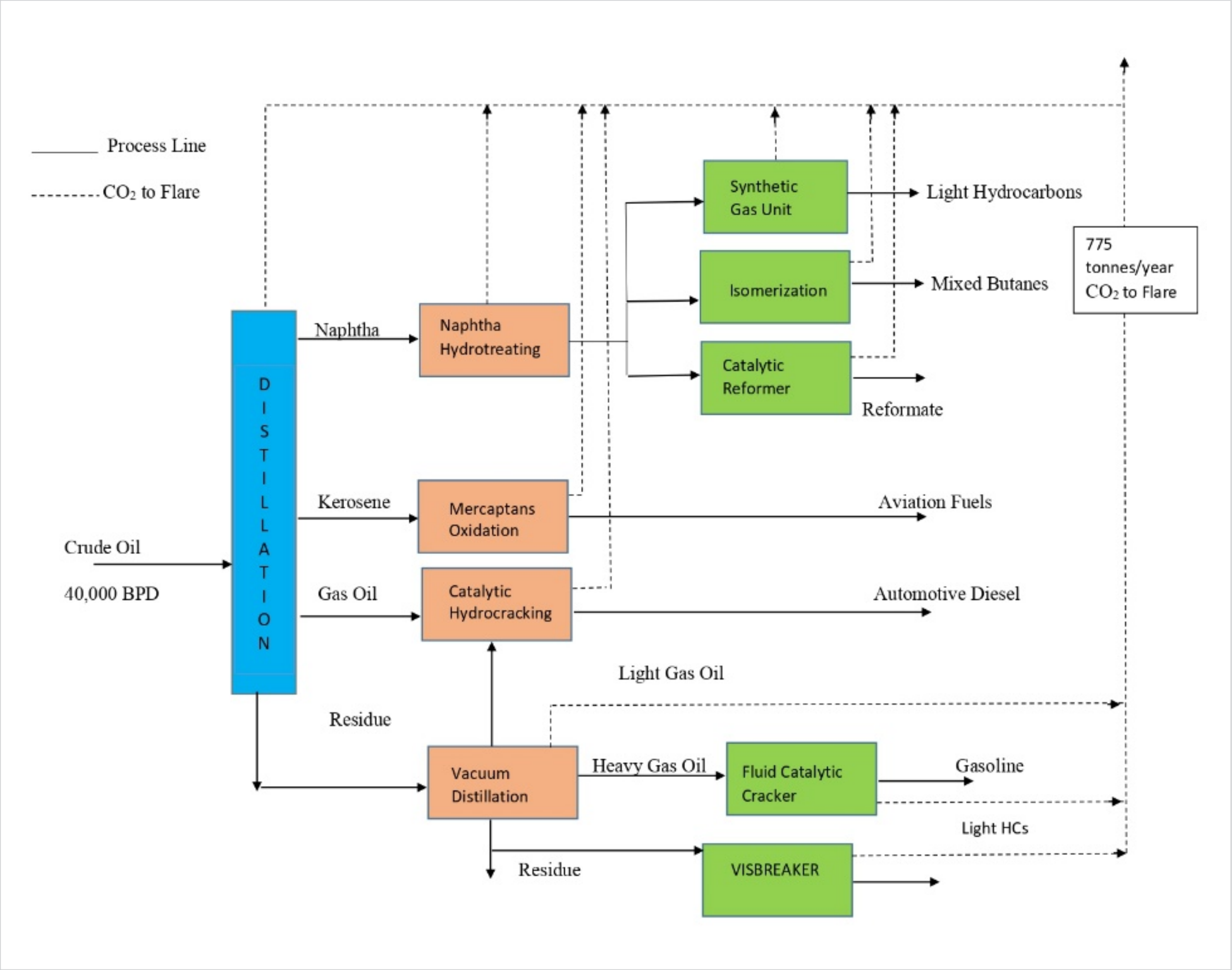
This work considers an oil refinery located in Saudi Arabia and assesses how to reduce CO_2 emissions by using operational and management methods. In addition, the work evaluates the feasibility of using two amine-based solvents, namely, PZ in monodiethanol amine or MDEA, and sulfolane in MDEA to capture CO_2 and H_2S in the refinery flue gases. For the first time, we presented an approach where the stress is first to curtail the emissions and then capture to reduce load on the carbon capture technologies.

Methods

Saudi Aramco Oil Refinery

The GHG emissions and their reduction from a Saudi Aramco Refinery are presented here. The block flow diagram of the oil refinery indicating major units is shown in *Fig. 1*. The refinery processes 400,000 bbl/day of crude oil and overall generates about 775 tonnes CO_2 per year. The refinery has a crude distillation unit (CDU), a vacuum distillation unit (VDU), a merox unit, a fluid catalytic cracking unit (FCC), a naphtha hydro-treating unit (NHT), an isomerization unit (ISOM), a catalytic cracking unit (CCU), a stabilized gas processing unit (SGP), a catalytic hydrodesulfurizer unit

Fig. 1. *Saudi Aramco refinery block diagram*



(CHD), and a visbreaker unit. The distillation and reaction units require high degree temperatures which are achieved by burning fossil fuels such as fuel oil and the natural gas causing significant release of CO_2. In addition, CO_2 is emitted at the boiler house to generate steam. At present, the refinery does not have any mitigation procedure to control GHG emissions. To begin with, this study estimated unit-wise CO_2 emissions which are given in *Table 1* (refinery mostly uses fuel oil for heating purposes).

From *Table 1*, it is obvious that the emissions are mostly from the boiler house followed by CCR+ISOM units. Several CO_2 reduction measures were considered which are discussed below.

Table 1. *Unit wise CO_2 emissions per day based on fuel oil consumption*

Unit	Fuel oil burned (kg/day)	CO_2 (kg/day)
Crude distillation + vacuum distillation	535	460
Visbreaker	254	218
Hydro-treating (NHT + merox + CHD)	574	494
FCC	687	591
ISOM+CCR	728	625
Boiler house	2160	1858

Reduction of CO_2 emissions

This study suggested following measures to cut down CO_2 emissions.

Improvement of energy efficiency

As shown in *Table 1*, the CO_2 emissions are directly proportional to the quantity of energy (fuel) used. Obviously, by improving energy efficiency that is performing a particular refinery operation with lesser energy consumption would generate lower CO_2 emissions. Energy efficiency can be achieved by considering new technologies, improving existing ones and putting in place a strong energy management system (EMS). Such a type of a system helps greatly to manage energy and chalk out continuous improvement. Although refiners can define their own EMS, energy management standards are available for purchase from the American National Standards Institute (ANSI), ANSI 2000:200, and ISO 5001. Additionally, free access to the US EPA energy management standard is available on their site.

Implementation of robust process control systems

Process monitoring and control systems play a crucial role in successful refinery operations. Accurate monitoring and robust control reduces wastes, downtime, maintenance, costs, and processing time as well as improve safety and emission control. Valero and ASPEN Tech have developed a model to control plant wide intake of energy which is expected to save overall energy usage by 2–5%. In general, process control systems save 5% energy intake (Worrel and Galitsky, 2005).

Energy reduction at motor driven equipment

It is estimated that 70% to 80% of electrical energy used in a typical refinery goes to pumps, compressors, fans and blowers. Any improvement in these machines and their operation procedures can lead to significant savings in energy and hence CO_2 emissions (Worrel and Galitsky, 2005).

Energy reduction in process heating (combustion)

As mentioned above, process heating is responsible for the highest CO_2 emissions in refineries (about 70%). Consequently, a great deal of improvement is necessary to reduce CO_2. Process heating at a refinery is divided into steam generation and stationary combustion.

Steam generation in a refinery gives around 30–40% of total CO_2 emissions. These can be reduced by taking several measures such as improved insulation, evaluation of boiler feed water, generation of steam not more than the required pressures, enhanced heat recovery from flue gases and blowdowns, careful maintenance of steam traps, installation of condensed return lines, etc. (Worrel and Galitsky, 2005). After taking these measures, energy savings of 5–10% are expected.

Process heaters release about 40% of total refinery CO_2 emissions. Several measures can be carried out to reduce these emissions. For instance, proper draft control would reduce unnecessary excess air and hence minimize energy usage. Installation of a combustion air pre-heater has been found to save 10% of energy. Improved burner design and maintenance could also reduce energy consumption.

The suggestions from this study are under review and implementation at the refinery. It is intended to publish emissions reduction data in the next article. The composition of the acid gas leaving the refinery is tabulated in *Table 2*.

Table 2. *Refinery acid gas data*

Process Parameter	Value
Inlet gas temperature	40 °C
Inlet gas pressure	1 bar
Inlet gas flowrate	1918052 kmol/hr
CO_2 in inlet gas	4.8 mole %
H_2S in inlet gas	0.05 mole %
Water in inlet gas	3.2 mole %

Capture of CO_2 emissions

There are three possible routes to capture CO_2 emissions viz. oxy-firing, pre-combustion and post combustion (Xiaoxing and Chunshan, 2020). In this paper, we consider post combustion capture of CO_2 because this is the most popular method of emission control in oil refineries. Numerous post combustion processes have been developed which typically fall into one of the five categories, i.e., chemical solvent absorption, physical solvent absorption, adsorption, membranes and cryogenic fractionation. Among them, the chemical/physical absorption processes are the most widely used.

Selection of the solvent

Physical solvents, such as dimethyl ether of polyethylene glycol (DEPG), propylene carbonate (PC), N-Methyl-2-Pyrrolidone (NMP) and methanol (MeOH), etc., are used commonly under conditions when the partial pressure of the acid gas is high, concentration of heavy hydrocarbons is low, and chemical solvents are corrosive (@aspentech white paper). Conversely, chemical solvents, such as MDEA, MEA, DEA, PZ, PZ+MDEA, DGA, DIPA, etc., are used. The regeneration of chemical solvents is done by heating, whereas for physical solvents pressure of the stripper is reduced without the application of heat. In view of the plant data, the choice of amine solvents for acid gas cleaning is made.

Working with amines

Until now, the most feasible chemical solvent method to remove CO_2 from flue gas is its absorption and reaction in aqueous amine solutions (Lang et al., 2017; Erfani et al., 2015; Chavez and Guadarrama, 2015). Historically, three different types of amines have been used viz. mono-ethanolamine (MEA), di-ethanolamine (DEA) and methyl-di-ethanolamine (MDEA). Among them, the MEA has been most widely used. However, with MEA, the energy demand by desorption is very high as well as accelerated corrosion of the system cannot be ignored (Peter et al., 2017). They concluded that although low temperature of the lean solvent favored DEA and MDEA, overall MEA was found to be performing better because it needs half of the amount at almost same heat exchanger duty.

Recently, studies have been initiated to use a mixture of amines to overcome undesired characteristics of single amines such as those mentioned above (Zarogiannis et al., 2015). Ongoing efforts are focused on MEA/MDEA (Singh, 2011). Aroonwillas and Veawab (2007) conducted pilot-plant studies of an MEA/MDEA mixture and showed significant heat reduction by using the MEA/MDEA mixture instead of single MEA. AMP (2-amino-2-methyl-1-proponal) has been used with MEA and was found to give more efficient recovery of CO_2 compared to MEA/MDEA (Mandal et al., 2001). AMP has also been tested with DEA (Adesosun and Abu Zahrah, 2013) and EDA (Kemper et al., 2011). Both combinations were found to give less energy requirement for stripping and a high absorption rate.

Thus, a large number of possible combinations of amine and other compounds exist (Hamborg, 2011; Bruder et al., 2012; Singh, 2011; Zhang et al., 2012). The selection of the best combination requires careful estimation and analysis of mixture properties from group contribution methods, equation of state and activity coefficient models. Zarogiannis et al. (2015) presented a comprehensive approach for the selection of the best mixture. In their approach, they selected 6 primary or second amines and 5 tertiary amines based on their good candidacy to remove CO_2 and developed 29 binary amines mixtures from them. Based on their assessment of mixture performances, they recommended that mixtures of 10% (N, N-Dimethyl-1,3-Propanediamine + Di-N-Propylethylamine), 90% (Di-N-Propylethylamine + N-Butyl-1-Butanamine) and 90% (Di-N-Propylethylamine+ N-(1-methylethyl)-1Butaneamine) should further be investigated for CO_2 capture.

In this study, ASPEN simulations are used to investigate new combinations of amines with other compounds. The main objective is to find the best solvent mixture that can lower energy requirement in the stripper with a high CO_2 removal rate. Instead of adopting Zarogiannis approach, we conducted parametric studies of each solvent mixture. Specifically we chose PZ (Piperazine) + MDEA, and sulfolane + MDEA mixtures.

Thermodynamic model

For chemical solvent modeling, the acid-gas chemical solvent property package in ASPEN was used. It employs electrolyte non-random two-liquid (Electrolyte NRTL) for electrolyte thermodynamics and Peng-Robinson equation of state for vapor phase properties. The package extensively provides VLE and heat of absorption data for many chemical solvents used in industry.

Selection of process simulation type

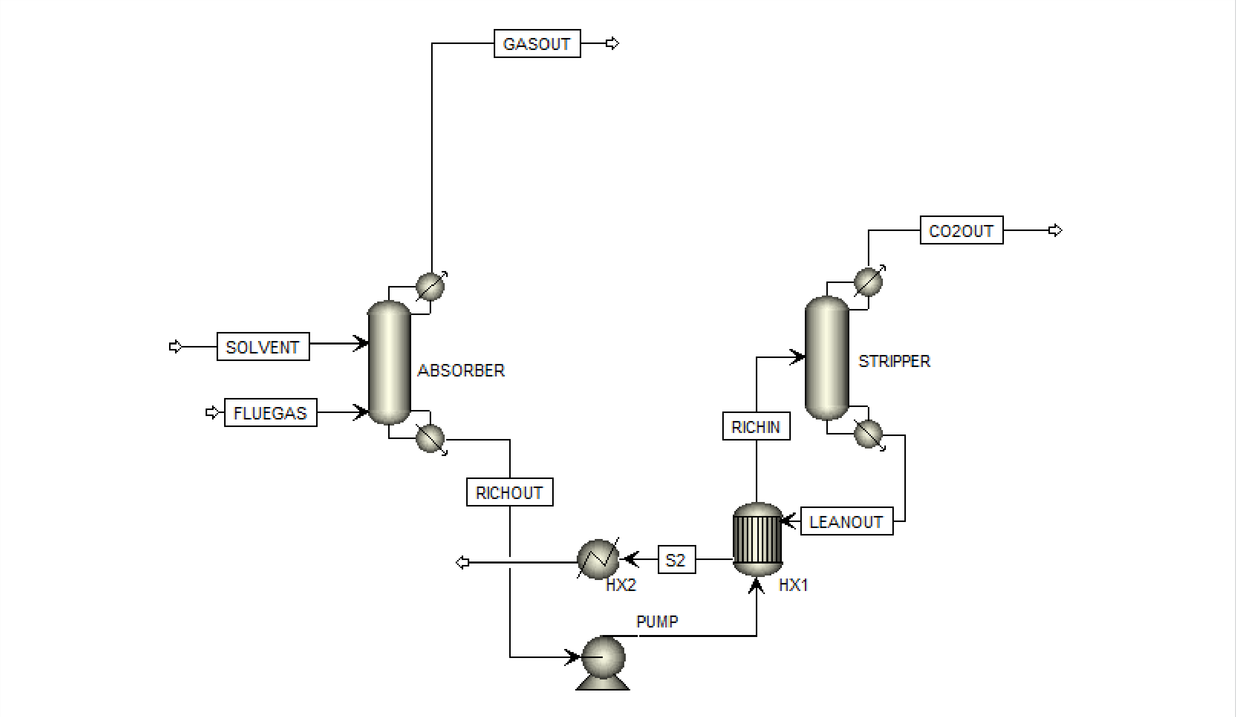
Process simulation of absorption towers can be done via two approaches viz. rate-based and equilibrium-stage. Rate-based simulation is done by assuming mass transfer and heat transfer occurrence between the phases. Thus, information about heat and mass transfer correlations together with tray/packing geometry is required. This approach can be used more accurately over a wide range of operating conditions. On the other hand, equilibrium models require empirical tuning for accurate calculations.

In ASPEN, two models are available for absorber/regenerator units, i.e., efficiency and advanced. In the advanced model, Maxwell-Stefan theory is used to calculate heat and mass transfer rates by ignoring VLE for each stage. On the other hand, the efficiency model employs an equilibrium stage model to simulate the column. To capture non-equilibrium behavior, the efficiency model calculates rate-based efficiency for CO_2 and H_2S at each stage. The simple efficiency model solves the column much faster compared to the advanced model. ASPEN recommends using the advanced model only when contaminants other than acid gases are present in the flue gas. In this work, the approach of the efficiency model was used.

Flowsheet development

The standard acid gas process was simulated by using ASPEN v11. The simulated flowsheet is shown in *Fig. 2*. The acid gas sent to the bottom of the absorber column flows upward, counter-current to the amine mixture solvent, which is introduced in one or more stages around the top of the absorber. The cleaned gas exits the top of the column. The solvent with the absorbed acid gas is sent to a second "stripper" column, to be regenerated by means of heating. In this study, we did not consider the closed loop system, that is, the lean amine is not recycled back to the absorber. This is because the factors we are focusing here have little to do with the recycle. Additionally, the simulation becomes easier to handle numerically in case of an open loop.

Fig. 2. *ASPEN flowsheet of amine absorption*



In this work, the target of 95 mole % of CO_2 to be removed from the flue gases was maintained for all combinations of solvent. The inlet flue gas conditions to the proposed plant are given in *Table 2*. The gas is compressed to a pressure of 1.2 bar to overcome the liquid hydrostatic pressure in the absorber.

Parameter selection for an absorber and a stripper

For the two columns, the parameters selected were the number of theoretical stages (N), temperature and composition of the solvent mixture, and the ratio of CO_2/solvent loading. The values selected are given in *Table 3*. The parameters were selected based on the previous research attempts (Aroonwilas and Veawab, 2007; Hamborg, 2011).

Table 3. *Simulation specification for the two columns*

Parameter	Absorber	Stripper
Number of theoretical plates (N)	13	11
Solvent temperature (°C)	30	40
Solvent composition (mass %)	30	-
Column pressure (P, bar)	1.2	2.2
Molar ratio (CO_2/amine)	0.35	-

PZ+MDEA mixture

Piperazine or PZ is added to MDEA (aq.) to aid in CO_2 absorption (Haghtalab et al., 2014). Compared to pure MEA (aq) and MDEA (aq.), the mixture shows improved resistance to thermal and oxidative degradation (Closmann et al., 2009). In the literature, only kinetics of absorption has been discussed and no simulation has been reported so far to check its feasibility at the industrial level.

In simulating the PZ+MDEA mixture, the formations of compounds and ions considered are H_2O, CO_2, H_3O^+, OH^-, HCO_3^-, CO_3^{--}, $MDEAH^+$, PZH^+, PZH^{++}, HPZCOO, $PZCOO^-$, $PZCOO^{--}$, N_2, O_2, and H_2. The ratio of MDEA/PZ in the solvent is kept at 3.0. The following equilibrium reactions are incorporated:

1 $2H_2O \leftrightarrow H_3O^+ + OH^-$
2 $HCO_3^- + H_2O \leftrightarrow CO_3^{--} + H_3O^+$
3 $PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
4 $HPZCOO + H_2O \leftrightarrow PZCOO^- + H_3O^+$
5 $MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+$
6 $CO_2 + OH^- \rightarrow HCO_3^-$
7 $HCO_3^- \rightarrow CO_2 + OH^-$
8 $PZ + CO_2 + H_2O \rightarrow PZCOO^- + H_3O^+$
9 $PZCOO^- + H_3O^+ \rightarrow PZ + CO_2 + H_2O$
10 $PZCOO^- + CO_2 + H_2O \rightarrow PZCOO^{--} + H_3O^+$
11 $PZCOO^{--} + H_3O^+ \rightarrow PZCOO^- + CO_2 + H_2O$
12 $MDEA + H_2O + CO_2 \rightarrow MDEAH^+ + HCO_3^-$
13 $MDEAH^+ + HCO_3^- \rightarrow MDEA + H_2O + CO_2$

The kinetics of forward reactions (6–13) are modeled as the power law. The values of the kinetic rate parameters, i.e., the rate constant 'k' and the activation energy 'E" are given in *Table 4*. The simulation is run by varying operating parameters. The range of the operating parameters is given in *Table 5*. The operating parameters varied for both the absorber and the stripper are the number of theoretical plates for the absorber and the stripper (Na and Ns), Fs (flow rate of solvent), Ts (temperature of the solvent), CO_2 recovery, and composition of the lean solvent (Xs). The range of these parameters is given in *Table 7*.

Table 4. *Reaction rate parameters for MDEA+PZ*

Reaction No.	k	E (cals/mole)
Reaction 6	$4.32 \cdot 10^{13}$	13 249
Reaction 7	$2.38 \cdot 10^{17}$	29 451
Reaction 8	$4.14 \cdot 10^{10}$	8038
Reaction 9	$7.94 \cdot 10^{21}$	15 758
Reaction 10	$3.62 \cdot 10^{10}$	8038
Reaction 11	$5.56 \cdot 10^{25}$	18 372
Reaction 12	$2.22 \cdot 10^{7}$	9029
Reaction 13	$1.06 \cdot 10^{16}$	25 424

Sulfolane + MDEA mixture

Sulfolane and MDEA mixture is used when H_2S is present in the acid gas (Liu, 2021). This is because aqueous amines solutions do not remove H_2S properly.

Previous studies (Macgregor and Mather, 1991) have measured the absorption of acid gas in a sulfolane + MDEA aqueous mixture but until now the solvent has not been used in the modeling and simulation of absorption processes. In simulating the sulfolane and MDEA mixture, the formations of compounds and ions considered are $C_4H_8O_2S$, MDEA, H_2O, CO_2, H_3O^+, OH^-, HCO_3^-, CO_3^{--}, HS^-, S^{--}, $MDEAH^+$. N_2, and O_2. The ratio of sulfolane/MDEA in the solvent is kept at 1.45. The following equilibrium reactions are incorporated:

1 $2H_2O \leftrightarrow H_3O^+ + OH^-$
2 $HCO_3^- + H_2O \leftrightarrow CO_3^{--} + H_3O^+$
3 $PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
4 $MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+$
5 $CO_2 + OH^- \rightarrow HCO_3^-$
6 $HCO_3^- \rightarrow CO_2 + OH^-$
7 $MDEA + H_2O + CO_2 \rightarrow MDEAH^+ + HCO_3^-$
8 $MDEAH^+ + HCO_3^- \rightarrow MDEA + H_2O + CO_2$
9 $H_2S + H_2O \leftrightarrow HS^- + H_3O^+$

The kinetics of forward reactions (4, 5, 8, and 9) are modeled as the power law. The values of the kinetic rate parameters, i.e., the rate constant ‘k’ and the activation energy ‘E” are given in *Table 5*. The simulation was run by varying operating parameters. For comparison, the range of operating parameters is the same as those of the PZ+MDEA mixture.

Table 5. *Reaction rate parameters for MDEA + sulfolane*

Reaction No.	k	E (cals/mole)
Reaction 4	$1.32 \cdot 10^{17}$	13 249
Reaction 5	$6.62 \cdot 10^{16}$	25 656
Reaction 8	$6.85 \cdot 10^{10}$	9029
Reaction 9	$6.62 \cdot 10^{17}$	22 131

Table 6. *Simulation parameters for two solvent mixtures*

Parameter	Min	Max
Na, number of plates, absorption	13	13
Ns, number of plates, stripper	11	11
Fs, flowrate of solvent	200	250
Ts, temperature of solvent	35	45
% CO_2 recovery	92	98
Xs, molar ratio CO_2/solvent	4.5	5.5

Results and Discussions

The parametric study was conducted to optimize the operational parameters to reach the minimum demand of re-boiler heat in the stripper column. The number of stages in the absorber and the stripper were fixed at 13 and 11 for both the solvents whereas the feed plate was chosen to be second from the top. The minimum temperature of the incoming aqueous solvent was varied between 35 to 45 °C as is usually kept in refineries. The molar ratio CO_2/solvent entering to the absorber was varied to get the minimum heat duty at the re-boiler. The optimized results are shown in *Table 7*.

Table 7. *Simulation optimized results*

Parameter	PZ + MDEA	sulfolane + MDEA
$R_{mol\ CO2/mol\ ls}$	0.55	0.52
$T^{t\text{-}abs}$(°C)	35.3	35.3
$T^{b\text{-}abs}$(°C)	40.7	40.9
$T^{t\text{-}strip}$(°C)	45.1	52.2
$T^{b\text{-}strip}$(°C)	92	98
$Q_{re\text{-}boiler}$ (KJ)	3000	2990

The results given in *Table 7* indicate a lower heat duty requirement and higher CO_2 loading for the PZ+MDEA solvent for the same amount of the solvent flowrate, the number of stages and the solvent composition. However, the sulfolane + MDEA solvent completely removed H_2S.

The effect of a stripper feed temperature on re-boiler duty is shown in *Fig. 3*. As the stripper feed temperature was increased, the load on the re-boiler duty decreased. The design of the heat exchanger that exchanges heat between the rich and the lean solvent is therefore of prime importance to decrease the re-boiler duty. Additionally, the sulfolane-based solvent required a little more re-boiler duty compared to the PZ-based solvent.

Fig. 4 shows how the re-boiler duty varies with lean solvent loading of CO_2 in case of both solvents. The heat demand of solvent regeneration decreases

Fig. 3. *Dependence of re-boiler duty on stripper feed temperature*

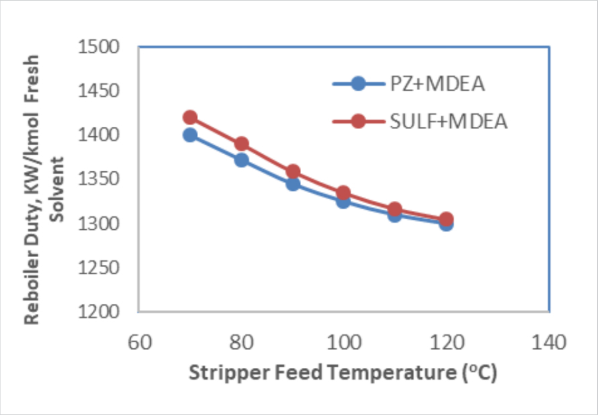
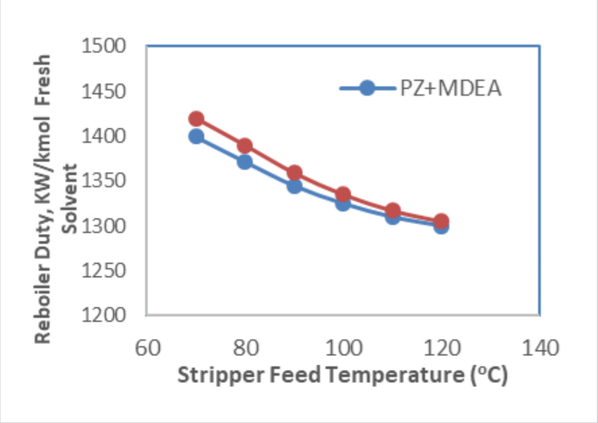


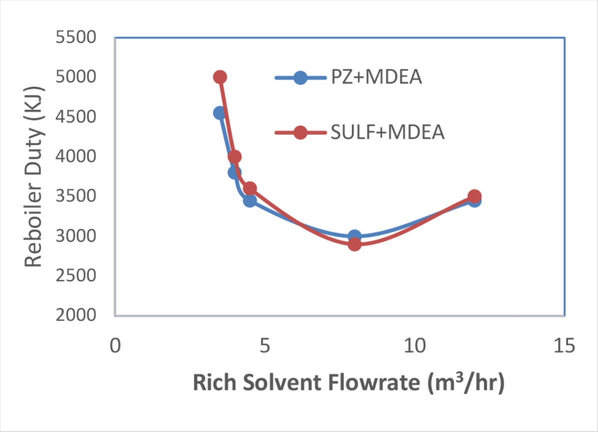
Fig. 4. *Dependence of the re-boiler duty on lean CO_2 loading*



rapidly, reaches a minimum (optimum in this case) and then increases as the lean loading of CO_2 increases. The optimum loading point in case of both solvents is almost 0.55 mol CO_2/ mol fresh solvent. The decrease in the re-boiler duty with an increase in the lean CO_2 loading is due to the fact that the amount of water to evaporate decreases and thus lower heat is required to regenerate the solvent. On the other hand, the increase in the re-boiler duty after the optimum point is because increased temperatures are required to regenerate the solvent probably due to complex solvent-water interactions. Overall, the re-boiler duty is a bit higher in case of the sulfolane-based solvent compared to the PZ-based solvent.

Fig. 5 highlights the effect of the solvent flowrate on the re-boiler duty. As the flowrate increases, the re-boiler duty decreases due to an increase in the solvent contact volume. Then after an optimum point of about 3000 KJ, approximately for both solvents, the re-boiler duty starts to increase due to shorter residence time in the stripper column.

Fig. 5. *Dependence of the re-boiler duty on the rich solvent flowrate*



Conclusions

Petroleum refineries emit CO_2 significantly due to fossil fuel-based operations. To curtail these emissions, a systematic approach is to first consider reduction and then capture of these emissions. In this work, a refinery processing 400,000 bbl/day of crude oil is examined which creates almost 775 tonnes/year CO_2 related pollution.

The CO_2 reduction methods surveyed in this work consisted of implementing an intensive energy management policy, efficient process control and careful monitoring of motor driven machinery and process equipment. These methods indicate that the improvement in energy efficiency is a proven cost-effective mitigation strategy capable of reducing 4–5% of CO_2 emissions. Furthermore, the carbon capture and storage (CCS) technology is yet another mitigation procedure commonly used in the oil and gas sector. This technology is however more feasible at larger emission sources such as power plant stacks, fluid catalytic cracker, distillation units, methane steam reformer, etc. The methods also indicate that robust process control systems and strategies could reduce CO_2 emissions by 2–3%. Process heaters are referred in the literature to be the largest contributor of CO_2

emission, which is also the case with the refinery discussed in this article (*Table 1*). It is therefore recommended to improve their design and operation to reduce unduly large emissions.

The capture of CO_2 by absorbing with amine-based solvents was considered in this work. Two amine-based solvents, namely Piperazine/MDEA and sulfolane/MDEA, were chosen for comparison. A flowsheet for a CO_2-amine absorption plant was developed in a process simulator called ASPEN. The process was considered without recycle because only the performance of the solvents was the focal point. The hydrodynamic and reaction parameters were selected from previous studies. Since the re-boiler heat duty is the most uneconomical factor in amine based absorption, a parametric study was conducted to determine the minimum heat requirement at the re-boiler. The re-boiler duty required in the stripper column was found to depend strongly on the stripper feed inlet temperature. It is therefore recommended to improve the design of the heat exchanger that exchanges heat between lean and rich solvent. Based on optimization studies, it is concluded that the PZ-based amine solvent provides more energy savings than sulfolane-based amine solvent.

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