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Mathematical Modeling, Parametric Estimation, and Operational Control for Natural Gas Sweetening Processes

K. Karthigai Selvan[1], Rames C. Panda[2],*

Abstract

As a result of the increased energy demand and the required environmental compliance, purification of natural gas (NG) need to be processed through more efficient technologies. Most the NG sources contain H_2S and CO_2 as acidic contaminants causing corrosion, reduction in the calorific value of the fuel, and toxicity. Removal of these gases (gas sweetening) is mostly performed in a reactive absorber followed by a stripper for solvents regeneration. Amine solvents are very suitable due to their natural affinity towards the acid gases. In the setting-up of newer plants or retrofitting of old units in existing plants to improve the efficiency of the sweetening process, modeling, optimization, and safer operational control of the process have drawn the attention of many researchers. The development of better models must take into account the synthesis and implementation of proper control strategies. Rate-based, equilibrium, and kinetic models supported by thermodynamic properties of the components have been discussed here and experiments carried out to identify new process models have also been presented.

Keywords: Amine treatment, Gas sweetening, Modeling, Sour gas

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1 Introduction

Natural gas (NG) predominantly consists of methane. Other quantities are paraffinic hydrocarbons such as ethane propane and butanes. Some natural gases contain nitrogen as well as carbon dioxide and sulfur. Trace quantities of argon, helium, and hydrogen may also be present. Natural gas and liquefied petroleum gas (LPG) are energy sources widely used by process industry and civil/domestic bodies. NG is used as fuel in power plants, feed stock for production of ammonia and urea, fuel in furnaces and heating application, for heating of spaces and water for cooking, non-polluting fuel as well as raw material for a variety of chemical products. Various forms of NG are liquefied natural gas (LNG), raw liquefied natural gas (RLNG), and compressed natural gas (CNG). Increasing energy expenditures and a growing demand for NG due to rapid industrialization have urged research on the processing of acid gas. To address the growing energy demand, apart from oil and coal, natural gas is one of the promising fossil fuels that has high energy content and is eco-friendly. To bridge the gap in demand, industries have to process higher amounts of gas with output quality specifications for a clean environment.

About 40 % of the gas reserve contains acid gas. In-spite of the growing field of natural gas, the quality of the gases obtained from reservoirs/oil fields is not rich due to the presence of acid gases that act as impurities. When these impurities increase, the profit after producing the pipeline gases decreases. Sometimes these contaminants include heavy hydrocarbon, mercaptan, heavy metals, moisture, H_2S, and CO_2. Hydrogen sulfide is highly toxic and in the presence of water forms corrosive acids. Higher concentrations in the atmosphere lead to death. Other sulfur species are carbon disulfide (CS_2), mercaptans, and sulfides (R-S-R) in addition to elemental sulfur. If CO_2 is present, the gas may contain trace amounts of carbonyl sulfide. Like H_2S, it forms weak corrosive acids in the presence of water. Processing natural gas in the presence of sulfur compounds and CO_2 causes corrosion to the equipment and affects the environment.

Conditioning these pipeline gases requires the removal of these contaminants. Moreover, emission regulations to resist global warming also require the removal of sulfur and to adhere to tight specifications. For LNG, the amount of CO_2 can only be 3 to 4 mol %. Fig. 1 a shows conventional ways of treating NG through gas sweetening. In this figure, the unit process

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[1] K. Karthigai Selvan
Department of Chemical Engineering, AC Tech Campus, Anna University, Sardar Patel Road, Guindy, Chennai, Tamil Nadu 600025, India.

[2] Dr. Rames C. Panda (corresponding author)
Department of Chemical Engineering, CSIR-CLRI, Sardar Patel Road, Adyar, Chennai 600020, India.
E-Mail: panda@clri.res.in

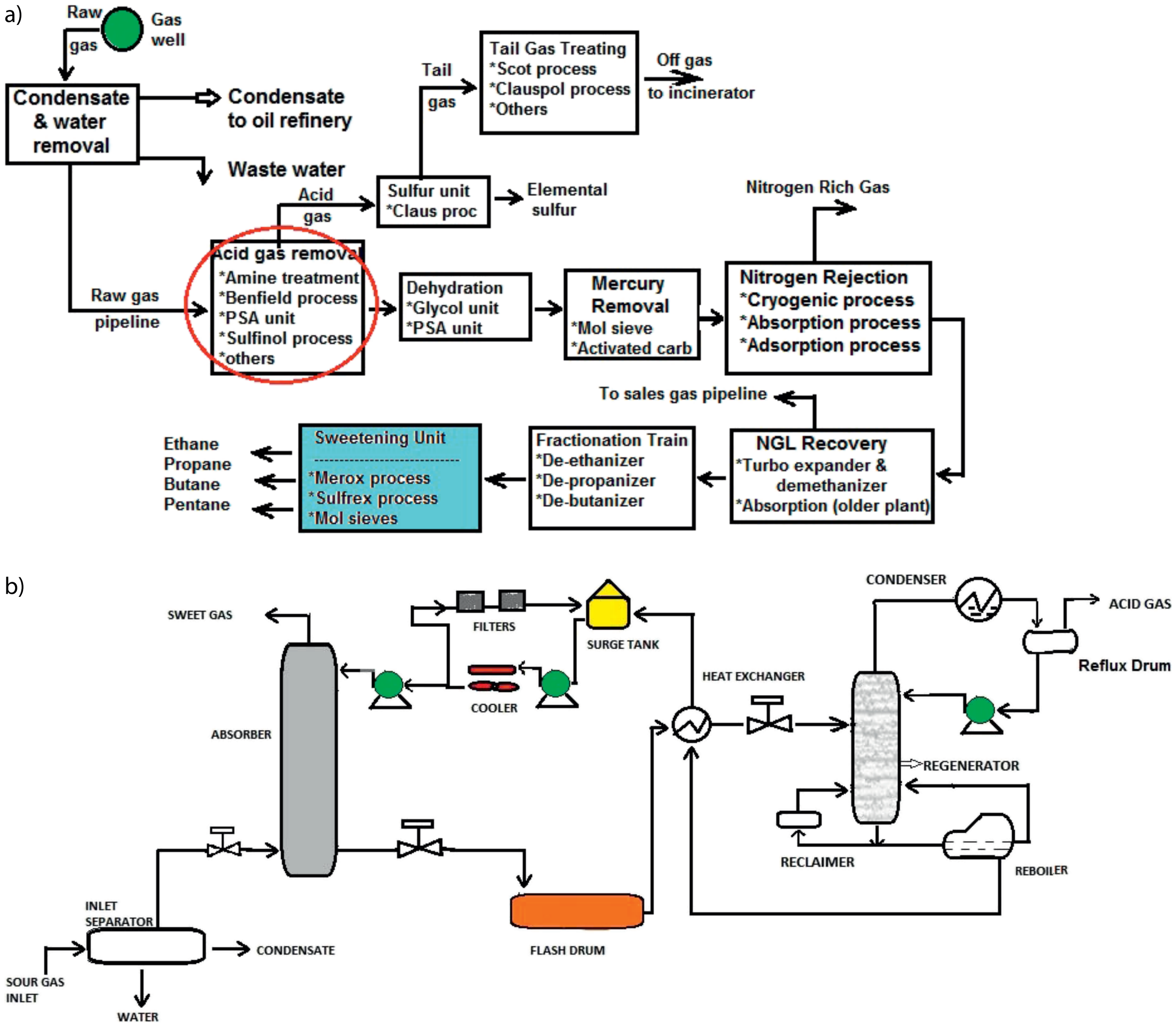

Figure 1. (a) Natural gas sweetening process; (b) Natural gas sweetening process (alkanolamine solvents).

to be considered in the present article is marked by red-circles. Acid gas can be treated by four methods: (i) chemical or (ii) physical absorption, (iii) hybrid processes, and (iv) membrane separation. In the first process, acid gases chemically react in an absorption column with a solvent forming soluble chemical compounds. Later on, the solvent is recovered in a separate stripper column using heat unit operations. The most commonly used solvents are alkanolamines. In the 2nd method, acid gases are absorbed in an organic solvent using physical absorption due to the high solubility of the gas in that solvent. Solubility is favored at low temperatures and higher pressure which may raise the operating cost comparatively.

Separation of H_2S and CO_2 using physical techniques is widely applied. The presence of S and CO_2 induces rusting, while the presence of H_2S, whose removal requires alkanolamines, increases toxicity. Fu et al. [1] proposed that design, simulation, and optimization of gas treating operations requires accurate prediction of phase and equilibrium, which in turn require thermodynamic properties of the system to be known.

1.1 The Solvent Absorption Process

Sulfur can be removed through absorption, solid adsorption, membrane separation, direct conversion, and cryogenic fractionation. Solvent absorption can be done by chemical, physical, or hybrid methods. The chemical method involves the use of amines or alkali salts. Generally, monoethanolamine (MEA), methyl diethanolamine (MDEA), or diglycolamine (DGA) are used to remove H_2S and CO_2. The main advantage of these chemical solvents is their relative insensitivity towards the solute and the ability to reduce the solute to ppm levels. The limitations or disadvantages are the requirement of high energy for the recovery of solvent, the non-selectivity towards solutes, and that the separated solute leads to the aqueous solvent solution reaching saturation levels. The physical method, on the other hand, only requires low energy for the regeneration of the solvent and is selective for certain solutes, namely, H_2S and CO_2. The disadvantages include the difficulty to meet H_2S specification limits and sensitivity to changes in partial pressure of the acid gas. Finally, the membrane separation method has become popular due to its simple and easy operation, no use of chemicals, low capital investment costs, and the modular nature of the system allowing it to attain a high turn-down ratio. Disadvantages of this method are the requirement of a pretreated feed to remove particulate and liquid matters, the loss of higher hydrocarbons from the system (besides solvent), and the difficulty to address almost similar permeation rates of different solutes.

Cryogenic fractionation is a widely used method to separate liquid mixtures. Separating CO_2 and H_2S from natural gas seems to work well due to their different vapor pressures. However, there are problems associated with the separation of CO_2 from methane, CO_2 from ethane, and CO_2 from H_2S: the liquid CO_2 phase freezes when it becomes concentrated and the practical maximum concentration of methane is only 85 to 90 mol %. Also, CO_2 and ethane form an azeotrope at approximately 0.6 mol % of CO_2 which cannot be separated by simple distillation. Separation is difficult because the mixture forms a pinch at higher concentration. Thus, the selection of the sweetening method depends basically on the volume of gas to be separated, its type and concentration, the temperature and pressure of acid gas (high partial pressure favors the physical solvent while low partial pressure suggests amine solvents), the required selectivity for acid gas removal, the specification of the outlet gas, the environmental regulations of hazardous chemical disposal, and the economics of the method.

Acid gas containing CO_2, H_2S, mercaptans, and other sour gases, is fed into an amine-separating tower or absorber (Fig. 1 b). The concentration of CO_2 or H_2S differ up to 50 mol % depending on the source of the NG. The general requirements for treated gas are H_2S concentrations of less than 4 ppm and CO_2 concentrations of less than 50 ppm [2]. The feed gas (natural gas) enters at the bottom of the absorber column while lean amine solution enters from the top. As the amine solution trickles down the absorber column, the acid gases in the gas stream react with the amine upon contact. Thereby, the amine solution becomes loaded with acid gases and leaves the bottom of the absorber as rich amine. The treated gas leaves the top of absorber column and proceeds to other sections for further processing. The rich amine solution then enters one or two flush drums where dissolved hydrocarbons are removed. The recovered hydrocarbons are usually used as plant fuel. The rich amine solution is preheated by exchanging heat with the lean solvent stream in the heat exchanger and then fed at the top into the stripper column. As the rich amine solution flows down the stripper column to the reboiler, acid gases are driven out of the solution and the solution is regenerated. The reboiler at the bottom of the stripper column provides the heat required to strip acid gases from the solution. The lean amine solution exits from the bottom of the stripper (reboiler) unit and proceeds to the filtering/skimming section where the particles and heavy liquid hydrocarbons are separated. It is then passed through a heat exchanger for cooling where rich amine flows in counter-current. The lean-amine stream is further cooled down and allowed to enter the absorber column from the top. The stripped gas stream is cooled to recover the water and is then further processed for recovery of sulfur.

The absorber is typically a packed bed or tray where the operating temperature (about 40 °C) is determined by the tray capacity, kinetics, and its ability to cool the lean amine stream using cooling water downstream. Absorption capacity decreases at higher temperature while the rate of reaction slows down at lower temperatures. This makes the process infeasible at operating temperatures above 40 °C. In case of NG, the gas enters the absorber at about 70 bar [3]. The strippers work at about 120 °C. The increasing temperature of the solvent inside the stripper removes acid gases from the solvent. As the reaction between acid gases and aqueous amine is exothermic, the increase in temperature will move the reaction to the reactant side, which will revert back the reactants (equilibrium shifts to backward side). The operating pressure in the stripper ranges from 1–2 bar. In case of NG richer in CO_2, the separation of sour gases is depicted in Fig. 2. Different types of solvents are in use for the removal of sour gases. Fig. 3 a explains the

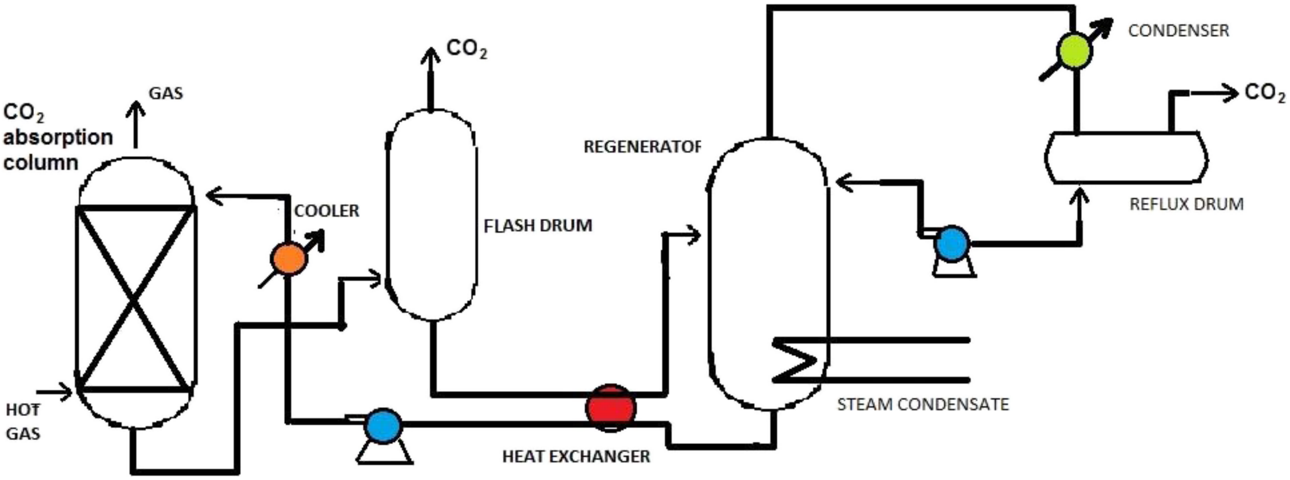

Figure 2. Removal of acid gases from natural gas streams enriched with CO_2.

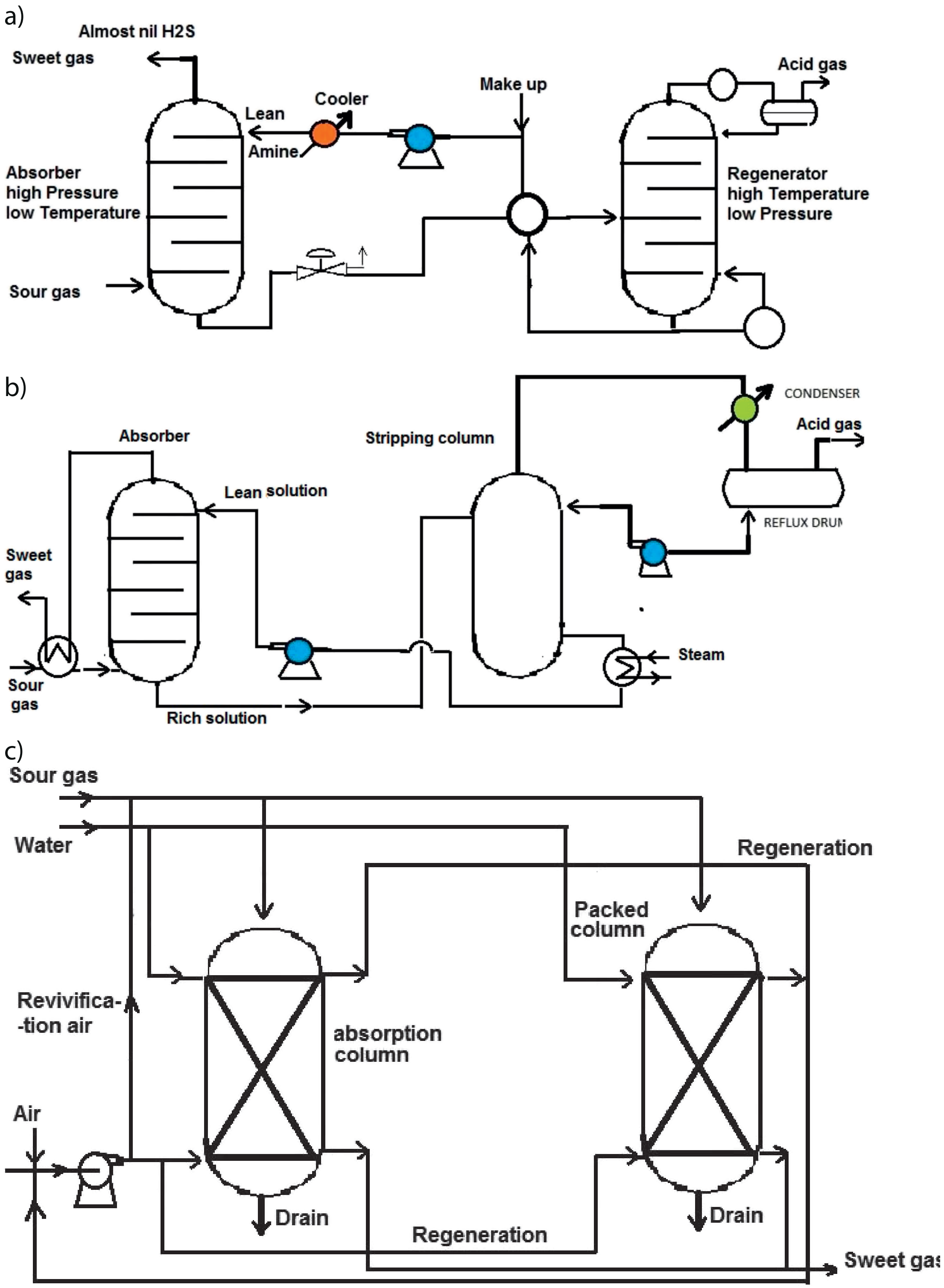

Figure 3. (a) Removal of acid gases from natural gas streams; (b) separation of acid gases from NG using hot potassium carbonate solvent; (c) removal of acid gases using iron oxide process.

removal using alkanol-amine solvent, Fig. 3 b describes the separation using hot potassium carbonate, and Fig 3 c shows a process flow scheme using iron oxide as absorber (in packed towers) of sour gases.

Del Valle-Zermeño [4] used alkaline solvents to desulfurize flue gas. According to Bishnoi and Rochelle [5, 6], most widely used solvents for separation of sour gas are aqueous solutions of MEA or MDEA. Their mixtures also reduce operating cost

[7] and it has been observed that the advantage of using MDEA over other amines is attributed to its selective removal of H_2S from its mixture with CO_2 and its higher rate of reaction with H_2S than with CO_2 [8]. The mechanism of reaction states that the release of a proton from H_2S to MDEA is very fast and induces spontaneous reaction. Moreover, MDEA is more stable, less volatile, less corrosive, and has lower heat of reaction compared to other amines, which leads to higher absorption capacity.

Literature has revealed that either aqueous MEA at a concentration of 20–30 ma % or 6–11 mol % or aqueous MDEA at a concentration of 30–50 ma % or 6–13 mol % is used in industrial practices. Many technologies have been suggested for the recovery of solvent section depending on the energy requirements for the recovery. This energy is a function of heat of reaction between the acid gas and amine solvent. The energy is also spent for the pumps to circulate the regenerated solvent around the unit which further depends on the concentration and capacity. For better economy in energy, an increase in concentration with a decrease in circulation rate is advised [9]. However, this is needs to be limited to avoid corrosion. Besides H_2S and CO_2, the presence of sulfur or its compounds also creates problems.

In order to study start-up and shut-down operations, scaling up, optimization and parametric sensitivity, a theoretical model is necessary. The objective of this article is to present the state of the art on modeling, identification of process parameters, and process control and optimization of gas sweetening. Thus, the remainder of the paper is organized as follows: Sect. 2 presents a survey on experimental findings and identification of model parameters of the process, Sect. 3 discusses advances in process modeling for the natural gas sweetening process, with models using first principle, non-linear and heuristic bases (neural nets, fuzzy-logic, etc.). Sect. 4 describes parametric sensitivity and optimization studies relating to the NG sweetening process. Sect. 5 explains the progress on research on process control for safe operation of the process. Conventional and model based controls with single-loop and multi-loop structures are explained here. A conclusion has been drawn at the end.

2 Experimental Studies for Kinetics of Absorption

The main purpose of this section is to survey experimentation, parametric identifications carried out in absorption of sour gases using amine and other solvents.

Fu et al. [1] have performed their experimental study to investigate the mechanism behind mass transfer and related prediction using artificial neural networks. In that work, the overall mass transfer coefficient for CO_2 absorption into aqueous diethylenetriamine (DETA) was experimentally determined in an absorption column over a temperature of 50–60 °C and at atmospheric pressure. The influence of the main operating parameters on the mass transfer coefficient was investigated. In addition to that, an artificial neural network (ANN) model was developed and employed to evaluate mass transfer performance. The input parameters were operational and physical parameters and the output parameter was the mass transfer coefficient. A comparative study between predicted values from the ANN model and experimental data showed that the ANN model was suitable for predicting the performance of the absorption column. Performance of a mini channel reactor used for CO_2 capture was investigated by Bangerth et al. [10]. The objective of their study was to study mass transfer and fluid flow characteristics of CO_2 mixed with N_2 absorption through MEA in a mini channel reactor. The flow patterns observed during the absorption process was visualized through high-speed imaging technique. The performance of reactor was studied with the help of absorption efficiency, pressure drop, mass transfer coefficient, interfacial area, enhancement factor and Sherwood number. The performance study shows that the reaction can reach close to 100 % absorption efficiency under certain specified operating conditions with a mass transfer coefficient 2–4 orders of magnitude higher than for conventional reactors.

The performance of a conventional gas sweetening process was investigated by Tavan and Hosseini [11]. They tried to remove CO_2 in presence of azeotrope. This study involved the simulation of the CO_2 separation from ethane using amine solutions. Four parameters, namely, lean amine solution, lean amine flow rate, column reflux ratio, and feed location, were examined and estimated. This amine process employs less equipment, and leads to high CO_2 reduction and high CO_2 removal efficiency compared to other conventional extraction processes [12]. The estimated parameters may be useful in designing automatic controllers for the process. Azizkhani et al. [13] have designed an ensemble neural network to improve the identification performance of a gas sweetening plant using negative correlation learning (NCL) and genetic algorithm (GA). The authors have trained the component neural networks (CNN) of ensemble neural networks (ENN) simultaneously. CNN negatively correlated through the penalty term in their objective functions. The weighted average of outputs of CNNs was used to predict output. The results followed the experimental data and this method is better than other neural network ensemble techniques. Blauwhoff [14] discussed reaction and equilibrium processes for absorption using MDEA and suggested guidelines for design. Dissolution kinetics of flue gas in the sorption process was studied and reported by Koech et al. [15]. Many researchers have reported experimental studies; however, their objectives were either modeling, parametric sensitivity, or closed-loop control. Hence, those contributions are discussed in relative places as follows.

3 Process Modeling

Process modeling of this particular field includes three phenomena: mass transfer, reaction kinetics, and hydrodynamics. Mass transfer of contaminant gas occurs through diffusion through bulk liquid or solvent in two steps: absorption of gas into amine solution followed by diffusion and reaction of gas with solvent. Mathematical models are comprised of rate-based models and equilibrium-based approaches. Based on the reaction kinetics, either homogeneous or heterogeneous systems need to be considered. Models concerning the hydro-dynamics are based on plug flow non-ideal flow. By considering a homogeneous system, the models are concerned with film and bulk reactions, which finally lead to a chemical equilibrium. Amines are bases and the important reaction in gas processing is the ability of the amine to form salts with the weak acids formed by H_2S and CO_2 in an aqueous solution. The reaction is highly exothermic.

$$R_3N + H_2S \rightleftharpoons R_3NH^+ + HS^- \tag{1}$$

The reaction between amine and CO_2 is more complex. When dissolved in water, CO_2 hydrolyzes to form carbonic acid, which dissociates into bicarbonate. The bicarbonate then undergoes an acid-base reaction with the amine to yield the overall reaction as follows:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{2}$$

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \tag{3}$$

$$R_3N + H^+ \rightleftharpoons R_3NH^+ \tag{4}$$

$$R_3N + H_2O + CO_2 \rightleftharpoons R_3NH^+ + HCO_3^- \tag{5}$$

These above reactions are not as rapid as is the case for H_2S, since the carbonic acid dissociation to bicarbonate is relatively slow. The acid-base reaction between MDEA and CO_2 is slower than of MDEA with H_2S, which makes MDEA selective to H_2S. Primary and secondary amines react at the same time with H_2S and CO_2 which impedes selective removal of the acid gases. This is not the case with tertiary amines. In order to overcome the slow reaction rate of MDEA with CO_2, small amounts of primary/secondary amines are mixed with MDEA. As these reactions are exothermic, based on Le'Chateliers' principle, an increases concentration of acid gas or a decrease in reaction temperature shifts the reaction to right or forward side.

Some models account for external and internal resistances to mass transfer and then slowly proceed to chemical equilibrium. In order to maximize the removal of CO_2 and H_2S (by slipping of CO_2 followed by absorption of H_2S) from the gas treatment process of an amine plant, a mathematical model for the amine process is required that needs to be validated against actual operating data. However, CO_2 absorption is not just influenced by the ratio of amine to CO_2, but also by mass transfer of the CO_2 to the amine. This suggests increasing the length of contact time between the CO_2 and solvent molecules. In order to solve the material balance equation to obtain prediction profiles of the process variables, property packages are required that use equations on activity coefficients. Distribution of gas in two phases has been studied by many researchers. This survey reveals that of the research concerned with the removal of CO_2, some involve removal of H_2S and others consider separation of both. A model is required to scale up/down, to optimize and to study characteristic behavior or sensitivity of parameters.

The selection of the proper amine solution depends on operating conditions, partial pressures, and the purity of the gases. The major advantages of MEA are high reactivity, low cost, and low capacity for absorption of hydrocarbons. The main disadvantages are the high corrosiveness, which is enhanced by temperature, high heat of reaction with CO_2 and H_2S, resulting in high energy requirements for the solvent regeneration and consequently, increased total costs of the process, as well as the relatively high vapor pressure, which brings about notable amine losses via vaporization. Though MDEA is more expensive, the industry prefers it over MEA due to the selective absorption of H_2S from mixtures with CO_2, low heat of reaction of acid gases with MDEA, resulting in notably lower regeneration energy compared to MEA, significantly lower vapor pressure reducing amine loss by evaporation, higher absorption capacity, very low corrosion rate and high thermal and chemical stability [16].

The amine solvents used can be compared with regards to various aspects such as solvent cost, loss of solvent, selectivity towards acidic gases, thermal stability, corrosion on equipment, regeneration of solvents, etc. MDEA has the highest costs as compared to other amines (MEA, DEA, DGA). Considering the solvent loss as criteria for the separation by different solvents, it can be found that in case of amines, low vapor pressure favors lower solvent loss. Critical comparison of solvent selectivity revealed that MDEA is suitable for complete removal of H_2S over CO_2 (in case of mixed gas) and it removes carbonyl sulphide (COS) and CS_2 minimally. DGA, DEA, MEA have less potential as solvent for the selective removal of acid gas in mixed gas system. To achieve a specific concentration of H_2S, MDEA requires the lowest steam rate compared to MEA and DEA. The study has found that MEA has the highest reactivity while MDEA has the highest selectivity. MDEA selectively removes H_2S, but allows CO_2 to slip through. It has also been found that MDEA has the lowest circulation for regeneration compared to the other two amines, due to which MDEA requires the lowest pump power and lowest heat exchanger duty. Moreover, MDEA has the highest acid gas loading compared to MEA and DEA. As far as the vaporization loss is concerned, MEA has highest and DEA the lowest, while MDEA lies in between. A further critical study on the operating vapor pressure of amine solvents on the separation suggests that amine concentration for acid gas absorption is based on operating experience.

Generally, increased amine concentration will result in a reduced circulation rate and plant operating costs. However, this effect does not give enough benefit as expected, because at higher amine concentrations and equivalent acid-gas/amine mole ratios, the acid-gas vapor pressure is higher over concentrated solutions. When a smaller volume of amine solution is used to absorb the same quantity of acid gas, the temperature increases due to the reaction heat ,which consequently increased the acid gas vapor pressure above the solution. Hence, optimum amine strength can be chosen based on feed characteristics. Temperature also plays a significant role in the process and for the efficiency of separation. The bulk of the absorption occurs near the bottom of the column. A significant amount of heat is released in the liquid phase, raising the liquid temperature and causing further heat transfer to the gas. A temperature bulge is absorbed near the bottom of the column for absorption of CO_2 and H_2S in alkanolamines. In general, lower temperature favor the absorption of lower molecular weight components based on the vapor-liquid equilibrium. If the process is kinetically limited, it will be difficult to predict the effect of temperature on the absorption,e.g., reactive absorption of CO_2 into amines is kinetically limited in certain situations.

The overall efficiency of an amine plant is affected by the lean amine temperature. Multiple parameters are required to determine the lean amine temperature that ensures a proper balance between acid gas removal and efficient operation. Lower temperatures reduce the solvent circulation rate and hydrate formation in most of the cases. Parameters such as CO_2 and H_2S content of the sweet gas, solvent pumping requirements, and sweet gas water vapor content, are necessary to determine the effect of the lean amine temperature on both processing equipment and effectiveness of sweetening process. As a rule of thumb, a differential temperature of 5 °C between incoming acid gas and lean amine feed is maintained to avoid condensation of hydrocarbons in the absorber. Performance of the absorber can be increased by decreasing temperature. Lower temperatures are suitable for primary and secondary amines with little kinetic involvement. In the case of MDEA, lower temperatures favor the absorption of only H_2S and not CO_2. If the absorber temperature is reduced below 5 °C differential temperature, the condensed hydrocarbon phase creates problems such as foaming, shortening the life of carbon filters and leading to loss of product. In addition to this, extra operating precautions are taken to keep the outlet temperature of the lean/rich heat exchanger at a constant value. A set point of 99 °C is the desired temperature for major cases to avoid acid gas break out. If acid gas break out occurs, the heat exchangers and stripper line are prone to corrosion/erosion.

3.1 Mathematical Modeling

Mass transfer supported by thermodynamics and kinetic models is of prime importance. The gradient of material transfer in both liquid and gas phases drives the transport. Besides the bulk phases, there is an interstitial gas phase as is assumed in modeling. There are two types of mathematical modeling the separation of sour gas from natural gas: (i) equilibrium models and (ii) rate-based models.

3.1.1 Equilibrium Models

The equilibrium models generally consider diffusion of one or more acidic components from the bulk gas phase to the gas-liquid interface (by absorption), followed by transport of reactants from the interface to the bulk liquid phase, reaction between dissolved gas and liquid along with mass transfer, and dissemination of reaction products into the bulk liquid phase due to concentration gradients. It is necessary to determine the concentrations of the various dissolved molecular and ionic species which are in equilibrium. Humbul et al. [17] presented an extensive review on available thermodynamic models and their selection using alkanolamines in treatment of NG. However, in this article, equilibrium models relating to separation of acid/sour gas components from NG are discussed to show the state-of-art application of thermodynamic properties of different solvents in the separation system (absorber). Sadegh et al. [18] studied solubilities of the H_2S system in alkanolamines under high pressure. Thermodynamic modeling as developed for absorption of CO_2 in aqueous N-methyl-ethanolamine using the extended UNIQUAC model for the CO_2-MDEA-H_2O system. In that work, the authors had presented different types of experimental data consisting of pure MDEA vapor pressure, vapor-liquid equilibrium, freezing point depression, excess enthalpy, heat capacity, and heat of absorption. Brinkmann et al. [19] have presented a hydrodynamic analogy-based approach for modeling reactive systems. In that work, non-reactive and reactive separation process models were developed for columns filled with structured packings. Ammonia in water (physical adsorption), SO_2 and CO_2 in sodium hydroxide solutions (chemical absorption) were systems of interest for modeling reactive absorption processes. Turbulent conditions favor the diffusion of ammonia and SO_2 while the absorption of CO_2 took place under laminar condition. The simulation of the above processes shows that the experimental values were incompatible with simulation results. Reactive absorption taking place in-column with structured packing was well explained by hydrodynamic analogy model.

Absorption of H_2S by a hollow fiber membrane from natural gas at high pressure was investigated by [20]. Experimental behavior was validated using the developed model taking into account the influence of pressure on H_2S gas concentration, diffusion coefficient and gas flow rates. The model predictions showed good compatibility with experimental data at low pressure conditions. At higher pressure, the predictions from the model were higher than the experimental values. The influence of gas, liquid, membrane diffusion and solubility coefficients of H_2S at high pressure was studied through sensitivity analysis. The modeling result showed the parameters were insensitive to changes in solubility coefficients. High pressure membrane wetting phenomena were also studied. Absorption of H_2S at higher pressures below 3 % membrane wetting has been well predicted using model.

A modified sulfur recovery process from natural gas to reduce the carbon footprint in the atmosphere was proposed by [21]. The conventional amine sweetening process is energy intensive because of its high requirement of heating and cooling. In order to reduce the energy consumption and operating costs, the authors have proposed a modification to the existing plant considering the lean amine circulation flow rate, temperature, and concentration. In their article, the authors have compared conventional split loops and modified split loops through simulation and sensitivity analysis done by Aspen Hysys v7.3. A comparison among them reveals that conventional split loops saves up to 50 % of the current operating expenses, increase capital investment by £175 000, and leave only 1 ppm of H_2S in the sweet gas. Finally, the authors have suggested two modifications to conventional sulfur recovery process though it is not economically profitable. Posey et al. [22] developed a model for predicting acid gas solubilities (H_2S and CO_2) in alkanolamines. The model consisted of parameters obtained by regression of vapor liquid equilibrium (VLE) data. The model was validated for total gas loadings from 0.003 to 0.8 % and over a wide range of temperatures, amine concentrations, and partial pressures. Predictions were compatible with a more complex model over seven orders of pressure magnitude. The model developed was consistent and it could be applied to other simple alkanolamine systems too.

The solubility of acidic gases (CO_2 and H_2S) in the ionic liquid (IL) 1-ethyl-3-methylimidazolium tris(triflurophospate) ([C_2mim][eFap]) was reported by Jalili et al. [23] at a temperature range of 303–353 K and pressures up to 2.0 MPa. The experimental results showed that H_2S is more soluble than CO_2 in the IL mentioned above. The authors have used experimental data to determine thermodynamic functions via Henry's law constants. The experimental results were correlated to extended Henry's law-Pitzer's virial expansion for Gibbs free energy as well as the generic Redlich-Kwong equation of state (RK-EoS) for IL systems. RK EoS was used to calculate CO_2 and H_2S selectivity of [C_2mim][eFap] at various temperatures, pressures, and CO_2/H_2S feed ratios and compared to results of selectivity of other IL. Safavi et al. [24] have studied the solubility of CO_2 and H_2S and their mixture in the ionic liquid 1-octyl-3-methylimidazolium hexaflurophospate ([C_8mim][PF_6]) at temperature ranges from 303.15–353.15 K and pressures up to 2 MPa. The solubility of H_2S was higher than of CO_2 and solubility of CO_2 and H_2S were increased with increasing pressure and decreased with increasing temperature. The experimental results were also correlated to Henry's law-Pitzer virial expansion and generic RK-EoS for ionic liquid systems. Binary systems including CO_2/IL and H_2S/IL had good consistency with above mentioned models within experimental uncertainties. A ternary system consisting of CO_2/H_2S/IL was very consistent with the RK model. The solubility of this system was compared to [C_8mim][TF_2N]. CO_2 and H_2S are better soluble in ILs with $[TF_2N]^-$ as anion. In another report, the authors [25] presented vapor-liquid equilibrium (VLE) data for H_2S/CO_2 systems at isothermal conditions at temperature from 258 K to 313 K in the pressure range of 1.0 to 5.5 MPa. The static analytic method was used for this experimental work. The phase behavior of H_2S-CO_2 systems were described through Peng-Robinson equation of state or the Soave-Redlich-Kwong equation of state combined with classical mixing rule and appropriate binary interaction parameters.

Using the extension of the cubic-two state equation of state (eCTS-EoS), Medeiros and Arredondo [26] modeled CO_2 and H_2S solubilities in aqueous alkanolamine solutions. This equation was used for chemical and phase equilibrium systems including acid gases (H_2S and CO_2), alkanol-amines (monoethanolamine, diethanol-amine, and methyl diethanolamine) and water. Pure and binary parameters of the model were estimated through measurement of saturation pressures, liquid densities, binary and ternary VLE. Pure, binary, and ternary systems showed low deviation from experimental data. Finally, eCTS-EoS was employed for quaternary data for CO_2-H_2S-alkanolamine blends over a broad range of temperatures and alkanolamine concentrations. The equation prediction was good for quaternary system.

Comparison of performances of sulfinol solvent with amine solvents in removing sulfur compounds and acid gases from natural acid gas was presented by Ghanbarabadi and Khoshandam [27] through simulations. This study involves the removal of acid gases (CO_2 and H_2S) and sulfur compounds (methyl and ethyl mercaptans, dimethyl sulfide, COS) using the mixed solvent sulfinol (sulfolane+MDEA+H_2O) and DGA, MDEA+AMP (adenosine monophosphate) solvents to compare the performance with MDEA. The objective of this study was to establish the sulfinol-M solvent to replace the aqueous amine solvent in the gas sweetening unit of the Ilam (Iran) gas refinery due to the lack of a merox unit. The simulation results show that more than 30–40 % of mercaptans along with acid gas are absorbed with sulfinol-M solvent at lower flow rate. The process requires only 10–25 % less energy to regenerate the solvent compared to MDEA. In addition to that, the process has little waste of solvent compared to amine solvents (MDEA+AMP, DGA, MDEA). The new solvent process results in easily controllable process parameters, better economy, and energy saving.

The performance of physical and chemical solvents to remove acidic gases from natural gas was discussed by Angaji et al. [28]. They investigated various concentrations of sulfolane in the sulfinol-M compared to the conventional MDEA solvent. Increased concentrations of sulfolane and high partial pressures favor the adsorption of acidic gases. This process requires significant amounts of physical solvent because of the limited stoichiometric reaction. Compared to other amine solvents, the sulfinol-based process has better performance, economics as well as reduced energy, investment and solvent costs. Removal of acid gases using membranes has also been reported. Gilani et al. [29] have investigated the separation of H_2S from H_2S/CH_4 mixtures using functionalized and non-functionalized vertically aligned carbon nanotube membranes. For this, two non-functionalized tubular carbon nanotube (CNT)/anodic aluminum oxide (AAO) membranes were fabricated with CNT inner diameters of 23 nm and 8 nm. The experiments showed that the smaller-diameter membrane was dependent on the H_2S feed pressure and the upstream feed pressure, but had higher selectivity than large-diameter CNT. Dodecylamine was used to functionalize the CNT/AAO membrane with high selectivity to enhance the separation of H_2S. The amido-functionalized membrane had increased H_2S permeability and selectivity than the non-functionalized membrane. Ghiasi and Mohammadi [30] have developed a machine learning system for rigorous modeling of the CO_2 equilibrium absorption in MEA, DEA, and TEA (triethylamine) aqueous solutions at various concentrations and different levels of temperatures over a wide range of CO_2 partial pressures. The equilibrium data was obtained from literature for the systems H_2O+MEA+CO_2, H_2O+DEA+CO_2, and H_2O+TEA+CO_2. The data were modeled using the least square support vector machine (LSSVM). Optimum parameters were obtained by coupled simulating annealing (CSA). The developed models were superior due to their simplicity and predictions were in satisfactory agreement.

Changes occurring in density and viscosity of single sulfolane loaded with CO_2 and H_2S gases simultaneously over a temperature and pressure range were investigated by Jalili et al. [31]. The experimental results show that density and viscosity of mixtures decrease with increasing temperature and acid gas solubility in sulfolane. Henry's law constants and partial molar volumes at infinite dilution for dissolution of CO_2 and H_2S gases in the liquid sulfolane at the temperature were obtained using measured solubility and density data. Henry's law constants were used to determine partial molar thermodynamic properties. A model incorporated with extended Henry's law and virial expansion was formed using the measured solubility data.

3.1.2 Rate-based Models

Rate-based models are developed to find strategies of safe operations. These models are formulated based on the first principle modeling technique. These models incorporate inputs, outputs, as well as accumulation and reaction terms and are helpful in finding the dynamics, optimal operating points etc. Rate-based models have been developed for two types of processes, one with acid gas separation and the other with sour gas. This section contains models based on separation in an absorption tower with conventional solvent, ionic liquid, and membranes.

Separation of acid gas components was modeled for the absorption column by many researchers. Mohebi et al. [32] have developed a theoretical model for a hybrid separation process to remove acidic gases from a $CO_2/H_2S/CH_4$ mixture. The authors have used hollow fiber membrane contactors and amine solution for the separation of CO_2 and H_2S from natural gas. The reaction mechanism and equations for three phases of gas, liquid, and membrane were required to model this system. The simulation results showed that the concentrations of CO_2 and H_2S were reduced. Increased liquid (amine) velocity and increased gas pressure also had a positive effect on the separation of CO_2 and H_2S. Kazemi et al. [33] have presented a case study on feasibility, simulation, and economic evaluation of natural gas sweetening at a low-capacity plant in Iran. This study involves the selection of a suitable alkanolamine solution for the sweetening process and the analysis of the process by simulation. Based on the selection of the amine, three processes were simulated, namely, the sulfinol-M process, the chelated iron (LO-CAT) process, and the mixed amine (Shell) process. These processes were analyzed with regard to the economics using the simulation tool ASPEN process economic analyzer. As far as the removal of acid gas (H_2S, CO_2) is concerned, LO-CAT is the best process to save capital and operating costs.

Sadegh et al. [34] have developed a static analytic method to measure H_2S solubility in MDEA in the presence of methane used as make up gas. The authors have investigated the solubility at various ranges of total pressure and H_2S partial pressure. The experimental data were compared to predictions using the extended UNIQUAC model. The result showed that H_2S solubility in MDEA is affected by the total pressure. Fouad and Berrouk [35] studied mixed tertiary amines for gas sweetening energy reduction. In their study, they discussed the use of amine solvents consisting of the two tertiary amines methylethanolamine and triethanolamine. The process simulation of the above process revealed that a reduction in unit running costs of up to 3.0 % was obtained using mixed solvents (40 wt % MDEA + 5 wt % TEA). At the same time, the specifications of the sweet gas in terms of H_2S and CO_2 were met. The mixed solvent was compared to a standardized solvent (45 wt % MDEA), primary/tertiary and secondary/tertiary amine mixtures. The mixed solvent with the above mentioned specifications reduced the costs of raw materials, regenerator, and trim cooler energy requirements. Gutierrez [36] discussed methods of reduction of greenhouse gases in the treatment of NG processing with energy optimization techniques.

Rate-based models for the separation of sour gas were also developed and simulated by many researchers. Liu et al. [37] modeled a chemical absorption process by computational mass transfer (CMT) that could predict the concentration and temperature as well as velocity distribution along the column without assuming the turbulent Schmidt number. This model consisted of a differential mass transfer equation with its auxiliary equations and the accompanied formulation of computational fluid dynamics (CFD) and CMT. The model was validated through a pilot-scale randomly packed chemical absorption column packed with ceramic berl saddles and an industrial-scale absorption column packed with stainless steel pall rings for CO_2 removal from a gas mixture and natural gas by aqueous MEA solutions. The simulated results were compared with published experimental data. Both concentration and temperature were found in compatible with experimental data.

Mudhasakul et al. [38] have developed a model for CO_2 absorption using MDEA as a solvent and piperazine as an activator. This process was simulated using Aspen Plus equipped with a physical property package for the MDEA system. The model was validated using actual data from a natural gas processing plant. The data fitted the model developed. Sensitivity analysis revealed that piperazine had a significant impact on the process performance and increased piperazine weight enhanced CO_2 absorption. A dynamic model of reactive absorption was presented by Kenig et al. [39] using the rate-based approach while several model optimization issues were also discussed. However, specific optimization issues are discussed in next section. The authors suggest that modeling of an absorption process requires fundamental understanding of the physics and chemistry governing the process. The model describing the absorption process should be simple and elegant and it should facilitate reliable and fast process simulations. The absorption rate of CO_2 was studied by Zeng et al. [40] using aqueous ammonia in a packed column. The objective of their experimental work was to study the overall absorption rate as well as the overall mass transfer coefficient. The experimental results showed that overall absorption rate is a function of manipulated temperature, gas flow rate, liquid flow rate, aqueous ammonia concentrations, and CO_2 inlet concentration. As the gas flow rate increases, the rate of absorption also increases and the rate of absorption was found to be proportional to the bulk gas partial pressure. The overall mass transfer coefficient was determined by plotting the absorption rate against the bulk gas partial pressure at different concentrations. The overall mass transfer coefficient increases when ammonia concentration increases.

Han et al. [41] have reviewed the current status and challenges of the ammonia-based CO_2 capture technologies with regard to commercialization. Most of the ammonia-based CO_2 recovery processes are technically feasible, lead to significant CO_2 recovery, and need low regeneration energy. The authors suggested looking in to the following factors to be considered for pilot stage to commercialization: economic plausibility, prevention of ammonia vaporization, use of ammonia vapor for production of salts, and regeneration using pressure. Current challenges in the removal of CO_2 from natural gas using membranes were presented by Adewole et al. [42]. The authors present fundamentals of gas separation in polymeric membranes as well as some major hurdles, i.e., trade-off between membrane selectivity and perm-selectivity, CO_2-induced plasticization, conditioning and physical aging. Various polymeric membranes have been investigated for plasticization property and maximum plasticization pressure for commercial separation. Following the investigation, the authors suggest techniques for improving the separation performance of polymeric membranes and better membrane fabrication methods to suppress plasticization.

A mathematical model was developed and simulated for aqueous ammonia-based post carbon capture process by Qi et al. [43]. The developed model was based on the rate sep module in Aspen plus that used available kinetics, thermodynamics, and transport property models for the NH_3-CO_2-H_2O system to predict the performance of CO_2 capture. The model was validated using pilot plant data. The model showed good compatibility with pilot plant results. The detailed analysis of the absorption process revealed the absorption mechanism. The conditions required minimizing NH_3 loss. Tan et al. [44] have investigated the absorption of high-pressure and high-concentration CO_2 by a 20 wt % MEA aqueous solution, a MEA hybrid solution consisting of 20 % MEA with 40 wt % N-methyl pyrrolidone and 40 wt % water, and pure water in a countercurrent packed column. They observed that high pressure significantly increases the absorption of CO_2 into the solvents water, MEA hybrid solution, and MEA aqueous solution. Water has the lowest absorption capacity among these three solvents.

Li et al. [45] have presented a rate-based model using MEA for post-carbon capture (PCC) application. The process was simulated and validated. Four different packings on four different scales were tested in a pilot-scale plant. The model was comprised of gas solubility and mass transfer data. The simulation study indicates that ta consistent data set for model validation is important to obtain a reliable mass transfer correlation. The present model can predict the majority of pilot plant results mostly within the uncertainty of the experimental data. The study of this reactive absorption process can be utilized for the removal of sour gas from CO_2, and the removal of CO_2 using other aqueous amine solvents in PCC. In another pioneering work, Sanchez and Oliveira Jr. [46] have studied the exergy analysis of offshore petroleum processing plants with two configurations CO_2 and without CO_2 systems and its influence on plant efficiency and environmental conditions. The ASPEN HYSYS process simulator was used to identify a suitable potential process. The exergy analysis revealed that petroleum heating in the separation process has a noticeable influence on the whole plant irreversibility.

A paper on high pressure measurement and thermodynamic modeling of CO_2 solubility in a mixture of N-methyl diethanolamine and 1-butyl-3-imidazolium acetate ([bmim]Ac) was presented by Hagtalab and Shojaeian [47]. The partial pressure of CO_2 against its molality and mole fraction of CO_2 as well as the solution enthalpy of CO_2 have been calculated. A combined equation of state (Peng-Robinson-Equation of State, PR-TS-EoS) for nonspecific energy contribution and two state association models for association energy contribution were used for thermodynamic modeling. In addition to that, PR-TS-EoS was applied to correlate the new experimental data. PR-TS-Eos parameters were adjusted for pure components. Binary molecular interaction parameters for the sub system (CO_2/[bmim]Ac) were optimized. The results showed that aqueous MDEA solution with [bmim]Ac can significantly reduce the solution enthalpy of CO_2 in the solvent.

Ganapathy et al. [48] have investigated the chemical absorption of CO_2 into aqueous DEA in a microreactor. The authors have studied mass transfer and hydrodynamic performance of the microreactor. An empirical model of the Sherwood number was developed and compared against experimental data. It was observed that absorption efficiency close to 100 % was possible under certain operating conditions. This process shows high process intensification due to a higher magnitude order of mass transfer coefficient compared to other conventional absorption processes. Kale et al. [49] have developed a rate-based model considering multicomponent mass transfer for the capture of CO_2 using MEA. The model consists of multi component mass transfer, chemical reactions in the film and in the bulk phase, non-ideal phases behavior, fluid mechanics, and heat transfer. The model was validated using published pilot scale data of the absorption of CO_2 by aqueous MEA in a structured packing column. The influence of input parameters on the performance of the absorption column was studied through sensitivity analysis to optimize the process. The model can predict given experimental results without fixing any parameters of the absorption plant. Ionic liquids can be used to enhance the separation of unwanted components.

In another paradigm of enhancing separation by employing ionic liquids as solvents, Kumar et al. [50] have reviewed the use of IL-amine blends and CO_2-BOLs (binding organic liquids) for the application in natural gas sweetening and PCC. They have comparatively discussed IL, amine solvents, and BOLs with regard to physico-chemical properties, energy intensity, regeneration cost, corrosiveness, etc. CO_2 can effectively be captured by a blend of IL and amine solvents. In addition to that, the use of BOLs was also reviewed. The authors have concluded with the expectation of using the above blended solvents for natural gas and PCC-based CO_2 removal applications. Althuth et al. [51] have investigated the natural gas purification by supported IL membranes (1-ethyl-3-methyllimidazolium tris-trifluorophosphate impregnated in the γ-alumina layer of tubular porous asymmetric membranes). The authors have investigated the permeability of various components of natural gas (CO_2/CH_4/C_2H_6/C_3H_8) through the IL membrane. The new technique is not very suitable for the removal of CO_2 from natural gas due to low perm selectivity of CO_2/CH_4.

A comparative study of CO_2 absorption in a packed column using imidazolium-based ILs and MEA solution was reported by Krupiczka et al. [52]. The investigation was performed for post combustion at low pressure in an absorption column filled with Raschig rings. The removal efficiency was investigated through initial CO_2 concentration, absorption temperature, gas and liquid flow direction. The resistance in the series model of the absorption process in a packed column together with the enhancement factor of the reaction between CO_2 and the investigated liquids was used to compare experimental results. The experimental investigation reveals that ILs have comparable CO_2 absorption capacities to MEA, but take long time to absorb it from the gas mixture. The authors concluded that the lower viscosity and price may be of advantage in using ILs in CO_2 removal. Lee and Lin [53] have developed a method to screen ILs to capture CO_2 from various processes. Henry's law constant for solubility is predicted by the activity coefficient determined from the COSMO-SAC model and fugacity of gas in liquid state. Limited data of vapor pressure were used to determine the model parameters and/or solubility of gas in some systems. The interaction between CO_2 and IL is described by screening charges on the molecular surface obtained through quantum mechanical calculations. In this method, Henrys law constant is quantitatively predicted for a variety of systems and temperature conditions with an accuracy of about 17 %. Quantum mechanical calculations facilitate the screening process of ionic liquids for CO_2 capture. The COSMO-SAC model is an efficient tool for screening and/or designing new IL candidates.

Enhancing separation was not restricted to ionic liquids. Researchers also tested membrane separation. A CFD model based on finite element analysis was formulated Ghadiri et al. [54] to simulate the flow and concentration in a polymeric membrane contactor for CO_2 stripping at high operating temperature. The model was developed using 2-D Navier stokes equations as well as mass conservation equations for steady state conditions. The model forecasted the velocity fields and the concentration of CO_2 along the membrane under laminar flow regime. The proposed model was validated using experimental data and the data showed compatibility with the model. Zhang and Wang [55] reviewed the CO_2 separation technology using membranes available for natural gas, bio gas, and enhanced oil recovery, etc. in the recent past. The main features of membranes, i.e., high energy efficiency, simplicity in design, construction of membrane modules, environmental compatibility, and cost effectiveness, were discussed. Various types of polymeric gas membranes used for CO_2-selective facilitated transport, such as hollow-fiber gas-liquid membrane contactors, inorganic membranes and mixed matrix membranes, as well as their advantages and disadvantages for specific separation applications were also discussed.

Saedi et al. [56] have prepared asymmetric gas separation membranes of polyethersulfone (PES) and polyethersulfone (PES)/ polyurethane (PU) with different blend compositions for the separation of CO_2 from methane. X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), discrete Fourier transform (DFT) were used to study the effect of PU on the microstructure, miscibility of PU/PES blend composition, thermal properties of PES and PES/PU, morphology of membrane as well as the relative affinity of CO_2, CH_4, and H_2O for PES and PU. Mixed gas experiments were carried out in PES and PES/PU membranes. The observation results showed that the CO_2/CH_4 selectivity is enhanced by the presence of PU and PU increases the plasticization pressure of PES membranes. Lock et al. [57] have presented modeling, simulation, and economic analysis of CO_2 from natural gas using co-current, countercurrent, and radial cross-flow hollow fiber membranes. The study involved the separation performance with parameter sensitivity of typical membrane selectivity, CO_2 feed composition in industrial application, and process economics of different flow and optimization. The study found that the counter-current flow exhibits better performance than the radial cross-flow while both were superior to the co-current flow. A trade-off needs to be made between the most effective separation performance of the process and its economy. The authors suggest finding an optimal flow configuration to remove CO_2 under different operating conditions based on the trade-off analysis. Hoff and Svendsen [58] have presented membrane contactors for CO_2 absorption, including application, modelling, and mass transfer effects. The objective of study was to develop a model based on enhancement factors and liquid phase hydrodynamics for CO_2 membrane absorption units. The model was validated using experimental data for both MEA and MDEA solvents. Mass transfer enhancement through liquid mixing has also been investigated. This membrane separation process has significantly improved diffusion and absorption enhancement phenomena for a contact period of less than 1 s.

Baghban et al. [59] have developed a multi-layer perception artificial neural network (MLP-ANN) and an adaptive neuro-fuzzy interference system (ANFIS) to estimate CO_2 solubility in the presence of various ionic liquids over a wide range of temperatures, pressures, and concentrations. A regression analysis was conducted to verify the proposed models with experimental and predicted solubilities of CO_2 in IL. A comparative study was conducted between experimental and predicted values of CO_2 solubility by thermodynamic models. From that study, the authors concluded that the ability and performance of MLP-ANN is more accurate than alternative models. Norouzbahari et al. [60] have modeled CO_2 loading from natural gas in an aqueous solution of piperazine (PZ) over an extensive range of operational conditions, i.e., temperature, pressure, PZ concentration, and CO_2 partial pressure. To investigate different operating conditions, the authors had to develop a feed forward back propagation multilayer perception artificial neural network (FFANN) and test it by employing the Levenburg-Marquardt training algorithm, enhanced through combination of Bayesian and regularization technique. The result revealed that the developed neural network had high prediction ability and robustness. Adib et al. [61] have developed support vector machine (SVM) modeling to estimate the process output of an industrial natural gas sweetening plant that included an absorption column and an amine regenerator column. The model was evaluated using data obtained from a refinery in Iran. The same data set was used to compare the SVM model to the ANN model. SVM showed better performance than ANN in terms of accuracy. This study revealed that SVM can be used as a reliable accurate modeling method for absorption columns. Muhammad et al. [62] have reviewed the role of process simulators in front end engineering design (FEED), particularly in natural gas sweetening units. The authors have elaborately elucidated the role of computer-aided process simulation tools in determining the optimum operating conditions with a minimum of time and effort as well as merits and demerits of various types of thermodynamic and kinetic models used in process simulators. The authors emphasized the importance of accurate modeling and simulation of natural gas sweetening units. They suggested exploring novel solvents for sweetening through computational chemistry and absorber capacity enhancement through improved solvent, solute-solvent interaction, or both. Finally, the authors state the need improved sweetening units by studying these novel solvents on the macro and micro scale, improving thermodynamic and kinetic properties to accurately predict solvent properties, modifying process schemes to reduce regeneration energy, optimizing the operating conditions on a steady state and dynamic basis, and economically studying the natural gas sweetening units.

4 Studies on Sensitivity and Optimization

4.1 Results and Discussion

The separation performance of acid gas-compositions in lean gas depends on the solvent concentration, temperature, flow-rate, steam flow rate, acid gas feed rate, and ratio of acid gas composition H_2S/CO_2. The equilibrium and rate-based models have been considered for this review. These model equations have partial differential equations and algebraic equations taking into account the diffusional interactions in the absorber and regenerator sections. Results reveal that a low concentration and flow-rate of DEA favors maintaining H_2S specifications while contact time and temperature of absorption play an important role in the kinetically controlled CO_2 absorption process. Increase in solvent concentration decreases acid gas compositions in lean gas. Increase in temperature up to a certain limit favors separation, however, above that, the performance of separation decreases. Increasing steam flow rate decreases the acid gas concentration in the sweet gas. Increasing DEA solution flow rate contributes positively to improving acid gas quality. The faster rate of reaction contributes to more efficient removal of CO_2 from rich amine solutions. However, only a slight improvement was observed in case of H_2S removal. Increasing inlet acid gas load would reduce acid gas quality at exit. It has also been reported that the higher to ratio of the H_2S to CO_2 in the feed, the higher the slip in the sweet gas. An increasing number of regenerator equilibrium stages will reduce H_2S composition in the sweet gas.

In general, operating problems in separation rise due to loss in solvent (amine), foaming and solvent corrosion, changes in the concentration of residual gas in the lean solvent, and winterization. Losses in amine can be much higher depending on several factors such as acid gas flow rate, reboiler temperature, high differential temperature between amine solution and the acid gas in the amine absorber, bad mist eliminator on the absorber top, bad filtration system, and foaming. Foaming is usually detected by a sharp rise in the pressure drop across the amine absorber and reduces the tower capacity, resulting in a higher solvent requirement. Acid gases combined with water form acids, which will attack the metal surfaces in contact with the amine solution in the regenerator, amine pumps, heat exchangers, and reboilers. The amount of residual acid gas in the solution depends on the heat used in the stripper reboiler. Increasing the heat reduces the residual acid gas and vice versa. If the concentration of residual gas is low, then more acid gas can be absorbed by the lean amine solution in the absorber. This will also allow a reduction in the circulation rate of the amine solution. If the inlet acid gas rate changes, the amine solution flow rate and the reboiler heat should be changed in the same proportion to match the acid gas changes. As the freezing point of the solvents is affected by temperature, winterization creates a problem in the smooth running of the plant. Abdulrahman and Sebastine [63] have also studied on natural gas sweetening and optimization of a natural gas plant in the Khurmala field in the Iraqi Kurdistan region. The aim of the study was to simulate a sweetening process for the removal of high acid gas contents and to investigate the process optimization, suitable selection of amines, and its economic consideration. The sweetening process using DEA as a solvent was simulated by ASPEN HYSYS V7.3. The process was suitable for reduction of H_2S concentration to 4 ppm. The authors investigated the process with several types of amine and blends of amines. The optimized amine circulation rate was 35 wt % at 400 m^3h^{-1}. Qiu et al. [64] have investigated the impact of the operating conditions on the gas sweetening efficiency and economic benefits through simulation and optimization techniques for a sweetening process using MDEA. The authors suggested a high absorption pressure and many trays to reduce energy and operating costs. The result revealed that rather than minimizing the costs of the process, the treated gas yield should be taken as optimization objective to improve the economic efficiency of gas processing.

Berrouk and Ochieng [65] have discussed the optimization technique based on the Benfield-Hipure process at the Abudhabi Gas Liquefaction Company Limited (ADGAS) to improve revenue and operations and the use of the process simulation tool PROMAX. The simulation study suggests increasing the gas flow rate to the plant with the support of existing pumps and exchangers. Simulation results were compatible with plant operating data. The effect of changes in the process parameters on the ADGAS plant performance were investigated through a simulation model. The simulation study revealed that with the support of existing pumps and exchangers, the gas flow rate to the plant can be increased. This may result in energy reduction as well as profit of the plant. Muhammad and GadelHak [66] have worked on the estimation of additional amine costs resulting from the acid gas load in natural gas. The amine sweetening process was simulated using natural gas with 25 million standard cubic feet per day, 1.7 mol % H_2S, and 4.13 mol % CO_2.This process was scaled up to handle natural gas with 25 mol % CO_2 and 3 mol % H_2S by scaling up amine circulation rate. The capital and operating costs increased linearly with respect to the percentage of acid gases in natural gas loading. Utility requirements of natural gas plant also showed a linear relationship in terms of cost. The economics of the scaled up process were second-order polynomial with respect to various partial pressures of CO_2 and H_2S without any sulfur compounds (assumption).

Tohidi et al. [67] have presented a simulation study of mercaptan removal from natural gas by the efficient cyclic adsorption process. The authors have proposed pressure-vacuum swing adsorption (PVSA) versus the current industrial pressure-temperature swing adsorption (PTSA) process. An enhanced PVSA process consists of a sequences of bed pressurization, adsorption, equalization, blow down, bed regeneration, and by-product purge. The comparison of PTSA vs PVSA revealed that, at the same feed characteristics, the same packed columns, and adsorption operating conditions, the PVSA process can achieve an equal product purity as PTSA, but shows less cycle time, more recovery, more productivity, and reduced operating conditions. Experiments on absorption and solubility measurements of CO_2 in ZnO and SiO_2 nanofluids were performed by Haghtalab et al. [68]. The solubility of CO_2 in nanofluids was enhanced due to the presence of nanoparticles. ZnO nanofluids were more effective than SiO_2 nanofluids at all experimental conditions. The solubility of CO_2 was measured for various wt % of ZnO nanofluid at a specified temperature and pressure condition. It was observed that the absorption was enhanced while the ZnO mass load was increased. The mechanism of CO_2 absorption of nanofluids is discussed and compared with the gas solubility in pure water.

Absorbed acid gases, dissolved hydrocarbons, and some water are stripped from amine in a regenerator column. The operating pressure has an important effect on the regenerator column. The reboiler temperature is directly related to the reboiler pressure. High-pressure operation of stripping columns results in increased reboiler temperature and is suggested for optimum stripping; however, there is a limit to the extent of increase for amine degradation. Increasing the primary and secondary amine concentration is suggested for achieving the desired acid gas loading, but does not lead to corrosion problems in lean and rich heat exchanger and reboiler. The steam ratio is of importance for the stripping unit since the lean amine quality depends on the steam ratio. One of the key advantages of maintaining a lean amine quality is related to the circulation rate, which has a direct impact on the reboiler duty. A steam ratio of 0.12 $kg\,L^{-1}$ is suggested for most cases.

5 Control of Natural Gas Sweetening

There are two major pillars in gas sweetening: reactive absorption and regeneration. Frequent changes due to disturbances in load/feed or environmental fluctuations/conditions drift the process towards new operating points. The control is necessary to run the process at equilibrium or at steady state to achieve set-point or reject disturbances quickly, and to have safer operational controls with optimal inputs. Generally, a typical separation system will have the following controls: a flow controller to regulate the water content by accounting for the water amount exiting the top of the stripper, two pressure controllers, one for each column, acting on the gas streams exiting the top of the columns; a flow controller to regulate the water/solvent recycle stream from the stripper to the absorber, a level controller to manage the bottom holdup of the absorber, and a temperature controller to regulate the top temperature of the stripper by acting on the stripper reboiler duty. In the case of the stripper, there are no level controllers. As it is assumed that there is only a negligible amount of solvent loss due to evaporation from the bottom of the absorber or the top of the stripper, a flow controller performs the required duty. Loss of solvent can be minimized by maintaining the top temperature of the solvent absorber as low as possible, maintaining proper concentrations of solvent, ensuring clean solvent by good filtration, proper re-boiler control to avoid chemical breakdown of solvent and avoid all contamination of solvent and by regularly checking all operating parameters & process variables to maintain steady running condition of the solvent unit. Foaming in the solvent is prevented by checking for overloading in the inlet-separator, by keeping the temperature of the absorber above the due point of component hydrocarbons (to avoid condensation), by applying a corrosion inhibitor, by avoiding oxidation of the solvent (proper control of reboiler), by maintaining charcoal filters that absorb liquid contaminants, or by adding a defoaming agent. The corrosion problem is avoided by maintaining the solvent in clean condition so that trapping of air is minimal. The concentration of the residual gas in lean amine is reduced by maintaining a higher temperature in the reboiler of the stripper. The typical manipulated variables are the DEA solution flow rate, DEA solution temperature, and re-boiler duty. The disturbances are the feed flow rate and the mole fractions in the feed gas while the design parameters are the number of trays in the absorption column and the number of trays in the regeneration column. The control variables are concentration of sour/acid gas compositions in the exit gas.

It has been found that control loops for the sweetening of NG are either PID, model-based, or intelligent heuristics. In case of model-based-control, a mathematical model is required. A model for the absorption column was developed by Najim and Ruiz [69] where the concentration of CO_2 in a gas mixture is reduced to a desired value using DEA as solvent. The authors have developed a long-range predictive control algorithm for this column. The model was developed from the first principle incorporating mass balance, transport phenomena, and chemical reactions in the liquid phase. The model consisted of three nonlinear partial differential equations. A low order linear discrete equation was required to develop the control model, with unknown time varying parameters. The least square algorithm was used to develop model parameters in order to achieve a long-range adaptive control. The main objective was to minimize the quadratic criterion function of the input and output tracking errors in feedback control to achieve horizon control policy. The implementation of the control strategy gave the desired performance and was suitable to achieve efficiency of high sensitive absorption column. Attarakih et al. [70] have analyzed a gas absorption column using MATLAB and SIMULINK. A mathematical model was developed for a sieve tray absorption column to remove ethanol from CO_2 in a fermentation process. The simulation software was used to study steady-state and closed loop dynamics of a sieve tray gas absorption column. The authors have analyzed the nonlinearity of the process and the response of a system to changes in the inlet gas flow rate. The closed-loop analysis showed that the outlet gas composition (controlled variable) had a linear dynamics due to step changes in set point. Govindarajan et al. [71] have developed a model-based control process for pressure drop in the packed absorption column. The article acts as a design guide to readers to implement their own model-based controllers on nonlinear SISO processes. The authors have developed a first principle model for control. The objective of this model was to be tested on both servo and regulatory modes. The control scheme consisted of a primary controller to control the pressure drop and a secondary controller to control the flow rate. The developed model can adapt to the following situations: no-integral wind up in a constrained case, bumpless transfer between manual and automatic mode, nonlinearities in pressure drop, tuning of primary and secondary controller, and dynamic adjustment of model to process model.

Intelligent control algorithms based on heuristics have also been reviewed. An ANN model was formulated by Hamzehie et al. [72] to predict solubility of 32 commonly single and mixed amines and ionic liquids over a wide range of conditions. Temperature, partial pressure of acid gases, overall mass concentration, apparent molecular weight, critical temperature and critical pressure of the solution were chosen as input variable. The network was developed using 733 data points and validated through a data set including 169 data points for H_2S solubility. The extra data sets of 114 data points for CO_2 solubility were used to investigate the extrapolation capability. The Levenberg-Marquadt back propagation algorithm was used to optimize the network. The developed ANN model had the ability to predict the solubility of acid gases in different solutions. The optimal control of an amine plant using non-dominated sorting genetic algorithm-II was presented by Behroozsarand and Shafiei [73]. The study focused on optimization of multiple variables that competed with each other. The study explained that, in case of improper value selection of controller-tuning constants, the process leads to instability, deterioration of control system performance. In order to avoid that, the controller parameters were tuned to achieve good controller performance by using appropriate values of tuning constants. In this study, a multi-objective genetic algorithm concept was utilized in conjunction with a PID controller to control the amine plant. The PID controller was tuned through the non-dominated sorting genetic algorithm (NSGA-II).The result showed that optimal control of the plant was achieved through NSGE-II based tuning.

Salooki et al. [74] have developed an ANN model for manipulating the sweetening regenerator column outputs in a gas refinery (Khangiran in Iran). A well-trained and extensively tested ANN was employed and evaluated using experimental data. The developed model was in good agreement with the experimental and simulation data and can be used for prediction of output parameters of regenerator columns. Hafizi et al. [75] considered gas flow rate and pressure as inputs and dirty amine flow rate as output for the construction of an ANN model using training methods through adaptive neuro-fuzzy systems and multi-layer perceptron neural networks with back propagation methodology and found that the former model is superior to the latter.

Chen et al. [76] have presented a paper on optimum conditions for the capture of CO_2 with a bubble column scrubber using NaOH as a solvent. A continuous bubble column was used under a static pH environment to determine the effects of process parameters on absorption efficiency, absorption rate of CO_2, gas liquid flow rate, and overall mass transfer coefficients. The Taguchi (fuzzy-logic) method was employed to find the optimum parameters for the scrubber design. The S/N ratio analysis was used to obtain important parameters. The gas flow rate and pH value were the important parameters while the operating temperature and liquid flow rate exhibited a minor effect on absorption process. This article facilitates the design of a scrubber for absorption processes. ANN was applied by Shahsavand et al. [77] to simulate data collected for CO_2 capture in an absorption packed column. The data for the ANN model was obtained from a column separating CO_2 from air using various concentrations of DEA, MDEA solutions. Back propagation multilayer perceptron (BPMLP) and radial basis functions (RBF) were trained for several sets of experimental data collected from a pilot plant and then compared. Two in-house efficient algorithms were used to train both neural networks. The simulation result showed that RBF could perform better than the MLP networks in filtering the noise and capturing the real trend. Many reports assumed a multivariable control structure for the process. A paper was presented by Sahraei and Ricardez-Sandoval [78] on simultaneous design and control of a MEA absorption process of a CO_2 capture plant. The authors have proposed an optimization framework to minimize the process economics complying with process constraints. The process was complying with process constraints in the unsteady state domain using a decentralized control scheme. The proposed methodology had been validated and compared against the traditional optimal steady-state design approach. The results indicate that the proposed design is dynamically feasible in the presence of oscillatory disturbances in the flue gas flow rate.

The above studies show a comprehensive state of art review of modeling, experimentation, parametric identification, and automatic control for the separation of H_2S and CO_2 acid gases and others from natural gas using amine and other potential solvents.

6 Conclusion

A comprehensive critic on modeling, experimentation and control of gas sweetening has been presented here. The knowledge of thetreatment process is necessary for studying the pretreatment in hydrodesulphurization, steam reforming of hydrocarbons, stripping of sulfur in the Claus process, and removal of CO_2 from flue gas of coal-fired power plants. The sweet gas should contain no more than 0.25 grains of H_2S per 2.268 Nm^3 of gas. The process needs a contractor with 16–20 trays for gas-liquid (counter-current) contact, where acid gas enters from the bottom and solvent trickles down, a heat exchanger (180–220 °F) at the bottom of the absorption column, a regenerator where rich amine is stripped near the top and meeting hot gas from the reboiler to remove acid gases. Primary and secondary amines are very effective in removing the sour/acid gases at a higher rate. Gases with low H_2S concentration can be treated with ethanol-amine solvents at 100 °F and regeneration can be done at 240 °F. If the acid gas composition is higher, hot potassium carbonate solution may be chosen as solvent. The selection of the amine restricts its circulation rate, energy requirement for regeneration of the solvent and selectivity of acid gas components in the reactive absorption process. While MDEA has a higher affinity for H_2S than for

CO_2, allowing traces of CO_2 to slip, DEA can be used in medium to high-pressure treatment. MDEA has highest solvent costs compared to other amines while MEA has the highest reactivity, and MDEA the highest selectivity. The survey reveals that about 15 % MEA can be recommended to reduce the H_2S concentration to below 4 ppm and the CO_2 concentration to below 0.05 % from a NG flow of 1.85 m^3. The overall efficiency of an amine plant is affected by the lean amine temperature. The differential temperature of 5 °C between incoming acid gas and lean amine feed is suggested to avoid condensation of hydrocarbons in the absorber. Though MDEA is chosen for the removal of high or moderate CO_2 concentrations, its use was limited due to improper design-simulations. The chemical equilibrium capacity of MDEA for CO_2 is very high, however, due to low solubility of CO_2 (Henry's Law) in water, absorption is too slow for trays.

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K. Karthigai Selvan received his B.Tech and M.Tech degrees in Petroleum Refining and Petro Chemicals from Anna University, Chennai, India, in 2011 and 2013, respectively. His areas of interest include process modeling, control, chemical engineering thermodynamics, and process optimization. Currently, he is pursuing his research at the A. C. Tech Campus, Anna University, Chennai, India.

Rames C. Panda received his M.Tech. and Ph.D. degrees in Chemical Engineering from the Indian Institute of Technology, Madras, in 1989 and 1994, respectively. In 1993, he joined the Chemical Engineering Department of CLRI, Council of Scientific & Industrial Research, as a scientist. He looks after industrial instrumentation and process control-related works. Presently, he is working as a Principal scientist at the Chemical Engineering Department at CLRI. His research area includes autotuning, PID controllers and analysis of control systems, process modeling, and simulation.

Abbreviations

AAO	anodic aluminum oxide
AMP	adenosine monophosphate
ANFIS	adaptive neuro-fuzzy interference system
ANN	artificial neural network
BPMLP	back-propagation multilayer perceptron
CFD	computational fluid dynamics
CMT	computational mass transfer
CNG	compressed natural gas
CNN	component neural networks
CNT	carbon nanotube
COS	carbonyl sulfide
CSA	coupled simulating annealing
DEA	diethanolamine
DETA	diethylenetriamine
DFT	discrete Fourier transform
DGA	diglycolamine
DSC	differential scanning calorimetry
eCTS-EoS	extension of cubic -two state equation of state
ENN	ensemble neural networks
EoS	equation of state
FEED	front end engineering design
FFANN	feed forward back propagation multilayer perception artificial neural network
GA	genetic algorithm
IL	ionic liquid
LNG	liquefied natural gas
LPG	liquefied petroleum gas
LSSVM	least square support vector machine
MDEA	methyl diethanolamine
MEA	monoethanolamine
MLP-ANN	multi-layer perception artificial neural network
NCL	negative correlation learning
NG	natural gas
PCC	post carbon capture
PES	polyethersulfone
PES	polyethersulfone
PTSA	pressure-temperature swing adsorption
PU	polyurethane
PVSA	pressure-vacuum swing adsorption
RBF	radial basis function
RK	Redlich-Kwong
RLNG	raw liquefied natural gas
SEM	scanning electron microscopy
SVM	support vector machine
TEA	triethylamine
TGA	thermogravimetric analysis
VLE	vapor liquid equilibrium
XRD	X-ray diffraction

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