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Performance Evaluation of Biogas upgrading by amine scrubbing using activated MDEA

APARNA A M[1]*, Dr. R . BASKARAN[2]

Department of Chemical Engineering, Government Engineering College Kozhikode, India
Department of Chemical Engineering, Agni College of Technology, Chennai
*aparnaam@geckkd.ac.in

Abstract

Biogas upgrading to produce biomethane is emerging as one of the distinguished solutions to the current energy crisis and environmental challenges. Biogas upgraded biomethane is gaining importance as fuel source and can be injected into the natural gas grid. This necessitates the need for energy efficient upgrading technologies. Among the upgrading technologies available, amine scrubbing is considered as a promising method due to low operating pressure, high methane recovery rates and low power consumptions. This paper presents an evaluation of amine scrubbing for biogas upgrading using aqueous solution formulations of piperazine activated methyl diethanolamine (MDEA) in Unisim software. The objective of this study was to coin optimal operating conditions for biomethane production from raw biogas by considering the technical, environmental and economic aspects. The performance of the process was evaluated in terms of mole fraction of methane in biomethane, recovery rate of methane and energy consumption by varying the operating parameters like absorber operating pressure, number of stages of the absorber, flowrate of the solvent and piperazine concentration in aqueous MDEA.

Keywords: Biogas upgrading; Biomethane; amine scrubbing; MDEA; Piperazine.

1. Introduction

The energy demand of the world is drastically increasing and is anticipated to increase by threefold in next thirty years. In the context of current energy crisis and rising energy demand the need for technologies to produce and exploit renewable energy is increasing. [1] Biogas and biomethane is one such promising choice of sustainable energy. Biogas is produced by anaerobic decomposition of organic matter like manure, sludge, sewage, agricultural, municipal and industrial waste. [2] Biogas mainly consist of methane, carbon dioxide and several trace gases. The composition of these gases varies based on the organic sources used for producing biogas [1]. Commercial biogas production in world has increased as it can be used as a fuel or energy source for combined heat and power cycle and is expected to be doubled in coming years. Biogas production is estimated to increase from 14.5 GW (2012) to 29.5 GW (2022) [3].

Apart from Methane, all other components present in biogas are considered to be unwanted and treated as impurities. Hence before deploying biogas as a fuel or introducing biogas to the energy grid these unwanted impurities need to be removed as well the calorific value of biogas need to be upgraded [4]. The Lower Calorific Value (LCV) of CH_4 is 50.4 MJ/kg at standard condition [5]. The calorific value of biogas can be increased by increasing the methane content of biogas. Biogas treatment process involves two major steps, first is the removal of unwanted impurities and the second is upgrading of biogas. Upgrading is the process of removal of CO_2 content from biogas and increasing the calorific value of biogas. The product obtained by upgrading is Biomethane and is composed of CH_4 (95-99 %) and CO_2 (1-5%), with no traces of other impurities [3]. The dominant technologies for biogas upgrading by CO_2 removal can be broadly categorized as sorption and separation process. The sorption process mainly involves

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physical absorption by water scrubbing, organic solvents, chemical absorption by amine solution, Pressure swing adsorption. Various process employed for biogas upgrading via separation are membrane separation and cryogenic separation process [5]. Most of these methods require removal of impurities especially H_2S [4].

Another technology that is being investigated is gas hydrate-based upgrading, Clathrate hydrate technology is a feasible and promising alternative for biogas upgrading [6]. Gas hydrates-based system suffers from high energy demand and high greenhouse emissions. Further research and testing are to be done before successful implementation of this technology [7]. Recently, biogas upgrading based on bio electrochemical system (BES), hydrogen mediated exsitu and insitu CH_4 enhancement are also being explored [8]. Use of microbial electrochemical separation cell that upgrades biogas as well as treat waste water were also reported [9]. More exploration in terms of enhancing mass transfer, developing a suitable reactor configuration and microbial dynamics is required [10]. Cryogenic carbon capture is another emerging technology that is offering high CO_2 recovery and high purity of both methane.[11]. Drawback of cryogenic technology is high energy consumption and more research focusing on this aspect is being carried out. Also, possibility of combining the cryogenic technology with other technology like adsorption. Absorption, membrane and hydrate system are also being explored. Among these combinations membrane technology shows promising results with reduced energy consumption and methane purity [12].

Out of all these technologies, upgrading biogas by scrubbing with amine is the most used method. Selection of solvent is one of the most important steps in amine absorption of CO_2 and solvent selection is finalized by the difference in solubility between methane and CO_2 in that particular solvent. The commonly used amines for CO_2 scrubbing are monoethanolamine (MEA), methyl diethanolamine (MDEA), diethanolamine (DEA), diglycolamine (DGA), piperazine (PZ) and triethanolamine (TEA) [13]. Scrubbing of biogas with diglycolamine can generate biomethane with 91% methane and 99% CO_2 removal from biogas. It is also reported that by using biomethane from diglycolamine scrubbing as fuel a 95 % reduction in emissions can be achieved [14]. A modified absorption scheme using water and diethanolamine (DEA) shows better performance compared to conventional process [15]. Pellegrini et al. studied how the upgrading cost is influenced by biogas from different sources and also compared the performance of water scrubbing and MDEA scrubbing for the same. MDEA scrubbing was found to be more profitable compared to water scrubbing. All the feedstocks studied gave positive profitability and biogas from landfill which had lesser amount of CO_2 showed better performance [16].

The efficiency of different amines and their aqueous blends in biogas upgrading were also investigated by various researchers. Aqueous MDEA was found to be economical and efficient compared to MDEA/MEA blends. The regeneration energy of MDEA was found to be 0.94 $kJ/Nm^3_{BM}/h$ compared to MDEA/MEA blend which had a regeneration energy of 1.43 $kJ/Nm^3_{BM}/h$ [17] Sepulveda et al. investigated the applicability of MEA (primary amine), DEA (secondary amine) and MDEA (tertiary amine) for upgrading the biogas generated by landfill. The results highlight that amines can produce significant enrichment of biogas. The methane content was found to increase from 57.3% to 90% and MEA was found to produce the largest increase in methane concentration of 90.37 % [18]. A comparative study of performance of AMP and MEA for simulated biogas showed larger absorption capacity for AMP when compared to MEA and the regeneration energy was 80% lesser for AMP when compared to MEA [19]. Study on effectiveness of EDA and piperazine dissolved in ethanol for biogas upgrading reports that the regeneration energy for EDA piperazine mixture was found to be less than MEA solution by 25.6 % and 20.5 % respectively. The CO_2 absorption rate of diamine ethanol solution was

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doubled compared to EDA water solution and absorption rate of piperazine ethanol was only slightly enhanced [20].

Though MDEA has very low reaction rate for CO_2 it is known for lesser rate of degradation and corrosion. The reaction rate of piperazine is very high with CO_2. So, by blending piperazine to MDEA. Blends of MDEA and piperazine is reported to have very high absorption capacity compared to MEA or MDEA [21]. As per the reports of Khan etal MDEA/PZ ratio of 35/15 wt % is considered as the most suitable amine ratio to attain maximum separation at minimum energy consumption. A reboiler duty of 3.235 MJ/kgCO_2 was reported for etal MDEA/PZ ratio of 35/15 wt %. They have also investigated different process modifications like cold solvent split, rich vapour compression and combination of both for energy minimization. [22]. The objective of this paper is to evaluate the performance of MDEA piperazine absorption system in terms of mole fraction of methane in biomethane, recovery rate of methane and energy consumption by varying the operating parameters like absorber pressure, flowrate of the solvent, number of stages in the absorber and piperazine concentration in aqueous MDEA. The operating conditions were evaluated considering 95% methane purity and methane recovery over 96%. The absorption process was modelled and simulated in Unisim Design Suite R480.

2. Methodology

2.1 Biogas Source and Absorbent

Biogas obtained from swine manure is used as feed for the process. The composition of the biogas is given in Table 1 [15]. The absorbents used here is aqueous solution of piperazine activated MDEA.

Table 1. Biogas Composition [15]

Components	Values in Mole fraction
Methane	0.6
Carbon Dioxide	0.24
Hydrogen Sulfide	3000 ppm
Water	0.056
Nitrogen	0.02
Oxygen	0.001

2.2 Process Description and Modelling

This study is developed in Unisim process simulation software. The flowsheet of activated MDEA based process is given in Fig 1. It consists of mainly two columns- absorber and stripper, pumps, compressors, heat exchangers and flash vessels. The biogas stream after single stage compression and cooling enters the absorption column from bottom of the absorber. The absorbent solution enters the absorption column at the top. Methane rich product (BIOMETHANE) leaves the absorber column from the top. The CO_2 absorbed solvent (SOLVENT OUT) leaving the absorber at the bottom of the column is then directed to a flash separator for separating the solvent and released gas (RBIOGAS). The rich solvent (SOLVENT F) is then directed to a pump where the pressure is raised. The solvent is preheated before entering the stripping column. This is mainly done to reduce the external energy dependency. In the stripper, CO_2 and other impurities are stripped off from the solvent and the lean solvent (LEAN AMINE) leaving the stripper is redirected to enter the absorption column.

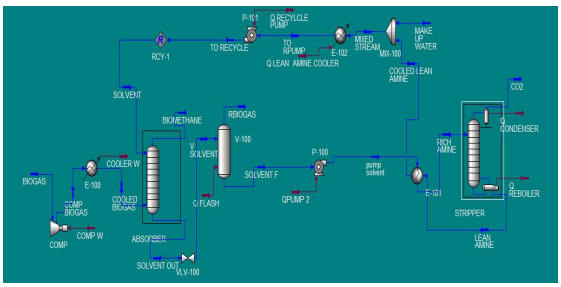

Fig.1. Process Flowsheet for activated MDEA based process developed in UNISIM platform

The thermodynamics property estimation is governed by the DBR amine package available in Unisim Design Suite [21]. A base model was developed to simulate the process of absorption and stripping process using specified set of solution composition and operating condition. Conditions of operation of the base model are summarised in Table 2. More than 100 simulations at different operating conditions where performed to arrive at the base model conditions. Further,

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these parameters were varied to study the effect of various parameter on CH_4 mole fraction in biomethane. Methane recovery (equation 1) and reboiler duty.

Methane Recovery

$$\text{Methane Recovery} = \frac{B_{CH_4}}{F_{CH_4}} \times 100\ \% \qquad (1)$$

Where

$\dot{b}_{.q\dot{p}_5}$ (kmol/hr - flowrate (molar) of methane in biomethane stream

$P_{\dot{q}\dot{p}_5}$ (kmol/hr) - flowrate (molar) of methane in biogas stream[15].

Table 2. Operating Conditions for Base model simulation [15]

Stream/ Equipment	Process Parameters
Biogas	Flow rate: 1000 kmol/h Temperature: 30^{0}C Pressure : 100 kPa
Solvent	Flow rate: 16,000 kmol/h MDEA concentration: 35 wt % Piperazine concentration : 5 wt% Pressure: 200 kPa Temperature: 35^0_C
Absorber	Pressure: 190 kPa No. of stages :15
Stripper	Condenser Pressure: 186 kPa Reboiler Pressure: 210 kPa No. of stages :15

3.Results and Discussions

This section illustrates and discusses the results obtained by simulating the model at varied operating condition.

3.1 Influence of absorber pressure

The effect of absorber pressure on methane recovery, mole fraction of methane and reboiler duty was studied by varying the absorber pressure from 100 kpa to 200 kpa using 5% piperazine and 35% MDEA solution. The solvent flowrate and biogas flowrate were maintained at 16000 kmole/hr and 1000 kmole/hr respectively. The results of methane mole fraction and reboiler heat duty are illustrated in Fig. 2.

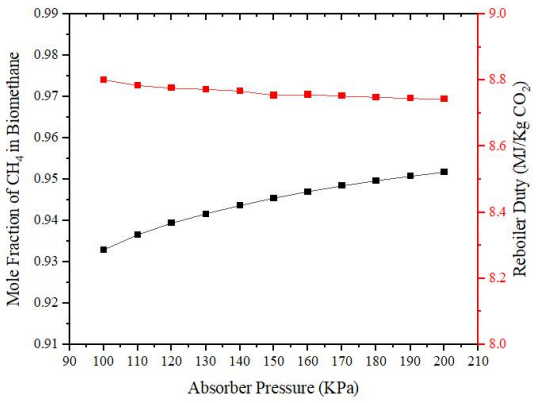

Fig. 2 Influence of Absorber Pressure on mole fraction of CH_4 in biomethane and Reboiler duty

It can be noted that the methane content of biomethane increased as the pressure of the absorber is increased. This happens as the amount of absorbed CO_2 in the solvent solution increases at higher pressures which makes the mole fraction of methane in biomethane high as per Henry's Law. Effect of absorber pressure on methane recovery and CO_2 removal efficiency is illustrated in Fig 3. The removal efficiency of CO_2 is increases as the pressure is increased and hence increasing the methane content in biomethane. Recovery of methane is not much effected by the increase in pressure. The value decreased from 99.96 % to 99.92. Reboiler duty was also not much effected by increase in pressure.

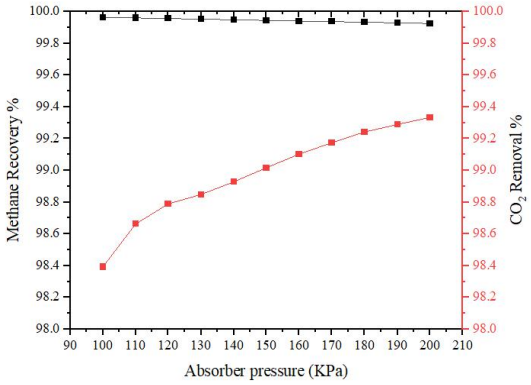

Fig.3. Influence of absorber pressure on Methane recovery and CO_2 removal efficiency

3.2 Influence of solvent circulation rate

The solvent circulation rate was varied from 10,000 kmol/hr to 20,000 kmol/hr to study the influence of solvent circulation rate on mole fraction of methane in biomethane, methane recovery rate and reboiler heat duty. An

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absorber pressure of 190 kPa was maintained and the solvent concentration was maintained as 5% piperazine and 35% MDEA solution. Biogas flowrate was maintained at 1000 kmol/hr The results obtained is illustrated in Fig 4.

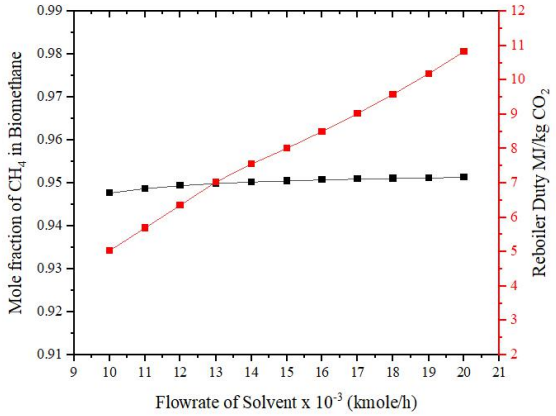

Fig 4. Influence of Solvent flowrate on mole fraction of CH_4 in biomethane and Reboiler duty

There was very slight increase in the mole fraction of methane from 0.947 to 0.951 as the flowrate was varied from 10,000 kmol/hr to 20,000 kmol/hr. Whereas the reboiler duty increased drastically from 5 MJ/ kg CO_2 to 10.82 MJ/ kg CO_2. As the flowrate increases the CO_2 absorption increases as can be seen from Fig 5. And hence the methane content in the biomethane is increasing. Due to the increase in circulation rate of solvent, quantity of solvent to be handled by the stripper is increasing which increases the regeneration energy requirement and thus the reboiler duty is increased. There is not much variation in methane recovery %. It decreased from 99.95 to 99.90 %, this can be attributed to the fact that as the solvent quantity is increased there is chance that some methane is getting dissolved in the solvent.

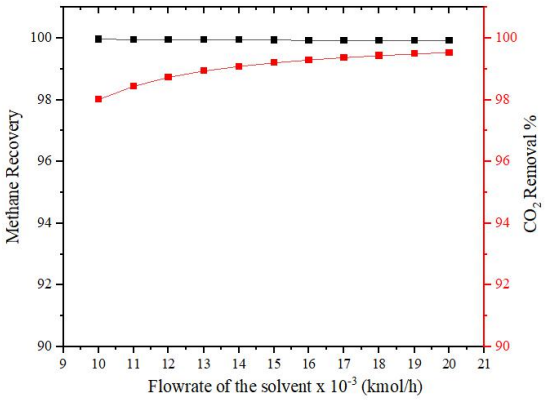

Fig 5. Influence of solvent flowrate on Methane recovery and CO_2 removal efficiency

3.3 Influence of piperazine concentration

The piperazine concentration was varied from 1% to 7%, maintaining the amine and water weight % of the solvent at 40 % and 60 % respectively. The absorber was maintained at a pressure of 190 kPa, solvent and biogas flowrate at 16,000 kmol/hr and 1000 kmol/hr respectively. The influence of methane content in biomethane and reboiler duty is illustrated in Fig 6. The mole fraction of methane in biomethane increased from 0.932 to 0.952 when the piperazine concentration was varied from 0.01 to 0.07. This is because piperazine has very high absorption for CO_2 and on increasing the concentration of piperazine the CO_2 absorption increases (Fig 7) and hence the methane content in biomethane. From 0.01 to 0.05 there is a drastic increase in methane mole fraction from 0.92 to 0.95 after that the increase is not much pronounced.

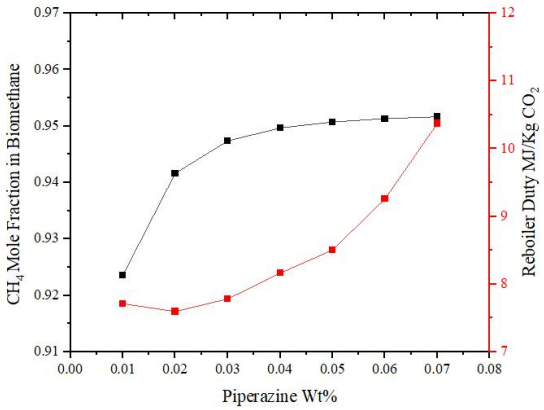

Fig .6. Influence of piperazine concentration on mole fraction of CH_4 in biomethane and Reboiler duty

The reboiler duty increases from 7.71 MJ/kg CO_2 to 10.37 MJ/kg CO_2. Pure

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MDEA requires less heat for regeneration, when piperazine is added more CO_2 is absorbed (Fig 8) and more heat is required to regenerate the solvent. Piperazine concentration has almost no effect on methane recovery. It remains constant at 99.93 % throughout and CO_2 removal increases drastically from 87.74 % to 99.67 % as piperazine has very high absorption rates for CO_2.

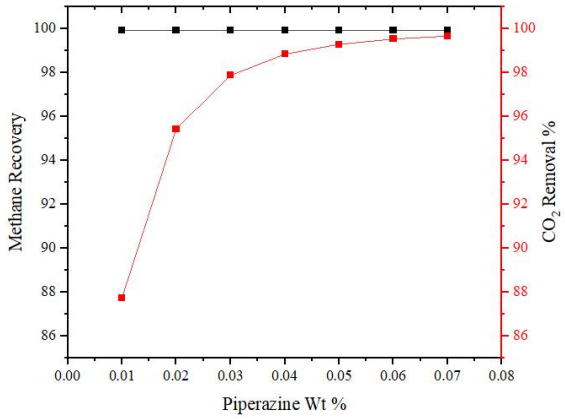

Fig 7. Influence of piperazine concentration on Methane recovery and CO_2 removal efficiency

3.4 Influence of number of stages in absorber

To study the influence of increase in number of stages in the absorber on methane content of biomethane, methane recovery and reboiler duty. The number of stages in absorber was varied from 7 to 15. The absorber was maintained at a pressure of 190 kPa, flowrate of the solvent was maintained at 16,000 kmol/hr and the solvent concentration was kept at 5% piperazine and 35% MDEA solution. The results obtained at illustrated in Fig 8.

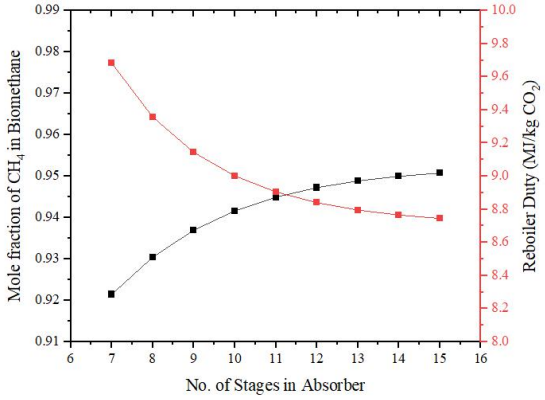

Fig 8. Influence of number of stages on mole fraction of CH_4 in biomethane and Reboiler duty

The mole fraction of methane in biomethane increases from 0.92 to 0.95 and the reboiler heat duty decreased from 9.68 MJ/kg CO_2 to 8.74 MJ/kg CO_2 as the number of stages increases. On increasing stages in absorber the CO_2 absorption increased from 86.93 % to 99.28 % (Fig 9) and hence the mole fraction of methane in biomethane also increases. The recovery of methane remains constant at 99.93% when the number of stages is varied as there is no methane loss with increase in number of stages.

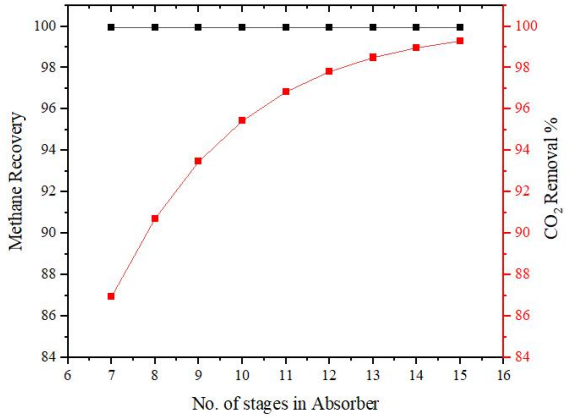

Fig 9. Influence of No. of stages of the absorber on Methane recovery and CO_2 removal efficiency

4. Conclusion

Amine based sorption process is an effective technology to upgrade biogas to biomethane by removal of CO_2 and enhancing the methane content. One of the key challenges encountered in amine-based sorption process is the selection of suitable amine solvent and reducing the energy consumption. In the present study the use of activated MDEA in upgrading the biogas to biomethane is investigated.

Addition of piperazine increases the absorption efficiency from 87.74 % to 99.67 %. When piperazine is added the reaction becomes mass transfer controlled rather than reaction dominated process. The piperazine concentration of 5 wt% was found to be ideal to achieve the methane mole fraction of 0.95, increasing wt % of piperazine beyond 5 % did not produce any pronounced results. Hence, piperazine concentration of 5% was chosen as the optimal. Increasing the pressure of the absorber increased the mole fraction of methane in biomethane from 0.93 to 0.95. The reboiler duty was

found to increased drastically from 5 MJ/ kg CO_2 to 10.82 MJ/ kg CO_2 when the flowrate was increased. The reboiler heat duty decreased from 9.68 MJ/kg CO_2 to 8.74 MJ/kg CO_2 and CO_2 absorption increased from 86.93 % to 99.28 % as the number of stages is varied. It can be concluded that piperazine activated MDEA is promising solvent for biogas upgrading. Further optimisation is to be performed to obtain the optimised operating conditions to achieve maximum enrichment at minimum energy consumption.

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