

A Review of Biogas Purification through Chemical Absorption

Ireen Maile and Edison Muzenda

Abstract—Biogas is an alternative source of energy which is produced by anaerobic digestion (AD) of waste materials. Biogas contains 50 -70% methane and 30-50% carbon dioxide as well as small amounts of other gases with a calorific value of about 21-24 MJ/m³. These trace components limit the usage of the biogas as they lower the calorific value of the gas and limit its commercialization. Hence, there is a need for purification and upgrading to meet specified application standards. The purification and upgrading processes can be classified into four major techniques which are absorption, adsorption, membrane separation and cryogenic separation. This review is focused on biogas enrichment through chemical absorption. This process involves amine washing with mono-, di- or tri-ethanolamine solutions, alkali washing with calcium oxide, calcium, potassium and sodium hydroxides, and synthesised ionic solutions of halide imidazolium ionic liquids. The regeneration of the spent chemicals for re-use will also be studied.

Keywords—absorption, anaerobic digestion, enrichment, purification, regeneration

I. INTRODUCTION

Biogas is a source of energy supply that is produced by digesting biodegradable organic matter in the absence of oxygen/air. It's a clean form of energy that can be used for heat, electricity, combined heat and power (CHP) generation and fuel for vehicles. For it to be utilized effectively, purification is required to remove contaminants which reduces its calorific value. Typical raw biogas consists of about 55–65% methane (CH₄), 30–45% carbon dioxide (CO₂), traces of hydrogen sulfide (H₂S), fractions of water vapours and other contaminant gases [1-2].

Petrol, diesel, ethanol, biodiesel and methane are examples of fuels used in motor vehicles [3]. Biomethane has become the most preferred alternative fuel to replace of fossil derived fuels for vehicular use. The market price of upgraded biogas is nearly 20-30% lower than that of petrol. However, its use is limited since it requires vehicles to be dual-fuel which is expensive when compared to conventional ones. In addition, benefits of reducing the tax when using dual-fuel cars

Ireen Maile is with the department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg, South Africa, 2028 (ireenmaile@yahoo.com).

Edison Muzenda is a Professor of Chemical Engineering. Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Doornfontein, P O Box 17011, 2028, South Africa (Email: emuzenda@uj.ac.za).

compared to conventional passenger cars exist [4].

Purification of biogas is influenced by the intended application. The composition of the raw biogas varies with feedstock and the variation in purification techniques required. Generally the purification techniques applied in the upgrading of biogas can be classified into: absorption (physical/chemical), adsorption, membrane separation and cryogenic separation [5-6].

The objective of this study is to explore the purification of biogas to match the standard of natural gas that can be used as vehicular fuel by chemical absorption. The study will focus on (i) amine washing using mono-, di- or tri-ethanolamine solutions (ii) alkali washing with calcium oxide, calcium, potassium and sodium hydroxides, (iii) synthesised ionic solutions of halide imidazolium ionic liquids. The regeneration of the spent chemical for commercial use for the economic viability of the processes will also be studied.

II. ABSORBENTS

Chemical absorbents are used in biogas upgrading to remove the contaminant gases. They can be used together with the other upgrading technologies to enhance the efficiency of the process. However, the disadvantage with the absorption process is the need for regenerating the spent solvent for application in the next batch. Fig. 1 shows a general picture of a chemical absorption process.

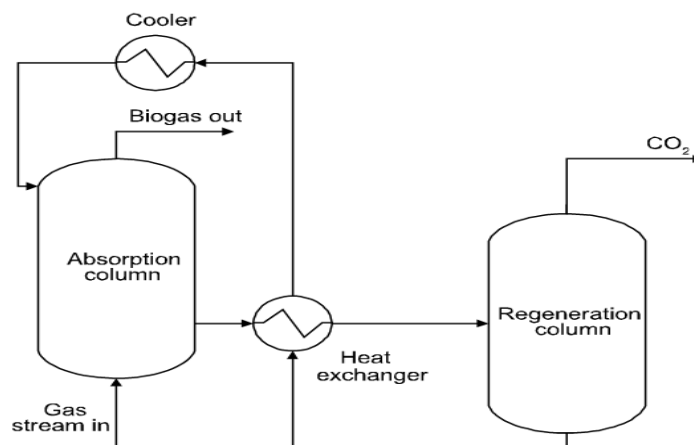


Fig. 1: Typical chemical absorption unit [7].

A. Amine washing

The amines that are normally used for biogas upgrading include mono-, di-, and tri-ethanolamine [1]. The amines widely used in industry for gas purification are primary monoethanolamine (MEA) and tertiary N-methyldiethanolamine (MDEA) [8]. These alkanolamine solvents are effective in removing acidic components such as CO₂ and H₂S normally found in natural or industrial gases. Their reaction with CO₂ is exothermic and reversible [9]. The reaction mechanism between amine and CO₂ follows the mechanism depicted in Fig. 2 [10].

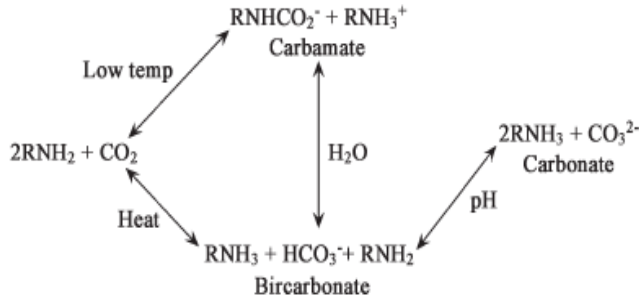


Fig. 2 Proposed reaction sequence for the capture of carbon dioxide by liquid amine-based systems [10].

Higher concentrations of amines have higher CO₂ absorption capacity and that MEA is a better CO₂ absorbent than DEA [11 -14].

TABLE I

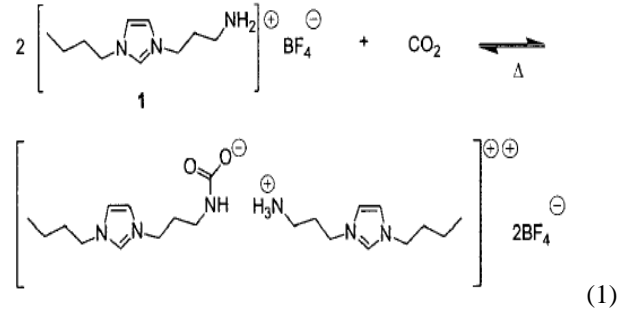
ADVANTAGES AND DISADVANTAGES OF AMINE WASHING

Advantages	Disadvantages
Has potential to completely remove H ₂ S	Loss of CO ₂ -remotion performance
High efficiency and reaction rates compared to water scrubbing	Toxicological impacts for fugitive emissions
The process can operate at low pressure	Possible equipment corrosion
High efficiency (>99% CH ₄)	High enthalpy of reaction
Cheap operation	Regeneration process is high energy-intensive
Regenerative	Make up chemical inputs needed
More CO ₂ dissolved per unit of volume (compared to water)	Expensive investment
Very low CH ₄ losses (<0.1%)	Decomposition and poisoning of the amines by O ₂ or other chemicals
	Precipitation of salts
	Foaming is possible

B. Ionic solutions

Ionic solutions can be synthesised from commercially readily available chemicals at room temperature [11]. They are non-volatile and reversible absorbents [15] and can be

classified as room temperature ionic liquids (RTIL) and task-specific ionic liquids (TSIL). Synthesis is usually done by a two-step procedure, the cation is synthesised in the first step followed by anion exchange reaction [16]. Equation (1) shows the reaction mechanism between TSIL and CO₂ [11, 15, 17]. Ionic liquids are non-volatile and hence they can be considered for “green synthesis” and gaseous separation [18].



Classifications of the ionic liquids

Imidazolium-based ionic liquids are the widely used class of ionic liquids in CO₂ capture/ absorption and they are further classified into conventional ionic liquids (FIL), functionalized ionic liquids (FIL), supported ionic membranes (SIM), polymerized ionic liquids (PIL), and mixtures of ionic and solvent liquids.

Conventional ionic liquids (CIL)

Conventional ionic liquids have been tested and found to have low CO₂ absorption capacity [15,19].The ionic liquids that form part of CIL include; 1-butyl-3-methyl-imidazolium hexafluoro-phosphate [C₄mim][PF₆], 1-*n*-octyl-3-methylimidazoliumhexafluorophosphate ([C₈mim][PF₆]), 1-*n*-octyl-3-methylimidazoliumtetrafluoroborate ([C₈mim][BF₄]), 1-*n*-butyl-3-methylimidazoliumnitrate ([C₄mim][NO₃]), 1-ethyl-3-methylimidazolium ethyl sulphate ([C₂mim] [EtSO₄]), and *N*-butylpyridiniumtetrafluoroborate ([*N*-bupy][BF₄]) [19].

Functionalized ionic liquids (FIL)

According to literature functionalized ionic liquids have a faster CO₂ absorption rate and a higher CO₂ absorption capacity [15, 19]. Conversely, they have a setback because of their high viscosity which hinders CO₂ absorption [19]. Functionalized ionic liquids can be synthesised through functionalizing the anion with alkaline group-NH₂ and attaching the functional group to the anion [15].

Supported ionic liquids membranes (SILM)

Supported ionic liquid membrane is made of an ionic liquid used as a liquid phase of the membrane [15, 20]. Since the ionic liquid is viscous and non-volatile, it helps lengthen the life of the supported ionic liquid membrane without lessening the separation ability and selectivity. The supported ionic liquids membranes can either be based on conventional or functional ionic liquids [15]. Some of the ionic liquids used in supported ionic liquid membranes that can be synthesised

include 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C₄mim][Tf₂N], N-aminopropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₃NH₂mim][Tf₂N] and N-aminopropyl-3-methylimidazolium trifluoromethanesulfone [C₃NH₂mim][CF₃SO₃].

Polymerized ionic liquids (PIL)

Polymeric ionic liquids were synthesised to address the shortfall of SILM when the pressure drop exceeds the liquid stabilizing forces [15]. It also reduces the absorption and desorption times. Zhao et al [15] synthesized polymers of tetraalkylammonium-based IL (poly[*p*-vinylbenzyltrimethylammonium tetrafluoroborate][P[VBTMA][BF₄]) and reported their higher CO₂ sorption capacity compared to conventional ionic liquids. Bara et al [21] reported that the sorption/desorption of poly-CIL is entirely reversible in their solubility, permeability and diffusion of CO₂, CH₄ and N₂ measurements. CO₂ sorption capacities of PIL's were found to decrease in the following order: ammonium > pyridinium > phosphonium > imidazolium, and the PILs with different anions were in the sequence of BF₄⁻ > PF₆⁻ > Tf₂N [22-26].

Mixture solvent of ionic liquids and molecular solvents

The absorbent is synthesised by mixing ionic liquids with organic solvent or water. The combinations that were studied in literature include: (i) ionic liquid with water or methanol, (ii) ionic liquid with alkanolamines, and (iii) ionic liquid with super-base or other organic solvents.

TABLE II

ADVANTAGES AND DISADVANTAGES OF IONIC LIQUIDS

Advantages	Disadvantages
Contributes to process economy	Increase in viscosity as CO ₂ is absorbed.
Contributes to process sustainability	Solvent losses during regeneration.
Lowers solvent inventory	Corrosion problems in valves due to re-circulation difficulty
Reduces the discharge of volatile chemicals to the atmosphere	
The solvent can be regenerated using low energy requirements	
Reasonable thermal stability	
Strong dissolubility	
Wide liquid range	
Tunability of structure and property	

C. Alkali washing

Aqueous solutions of alkaline salts can be used for biogas upgrading. They are often employed in CO₂ removal. The salts that have been studied include CaO, Ca(OH)₂, NH₄OH, KOH and NaOH. The absorption process is influenced by agitation, turbulence in the liquid, gas – liquid contact time and solution concentration [27]. Figs. 3a and 3b are typical examples of bench scale setups for biogas upgrading using chemical absorbents [27]. Typical chemical absorption reactions are shown in (2) to (5).

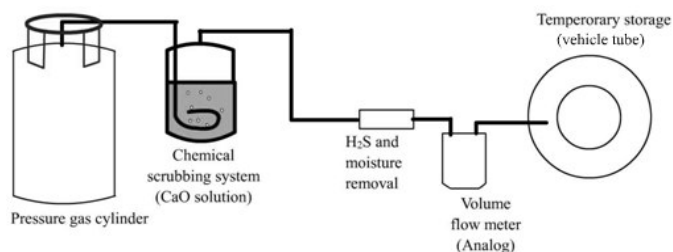
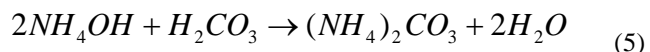
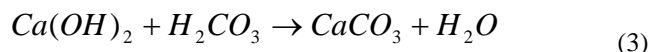
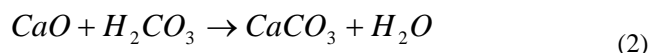


Fig. 3a Chemical purification setup line diagram [27].

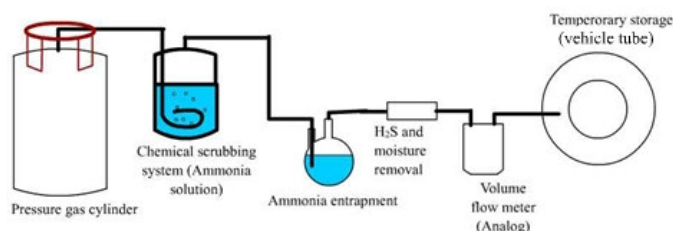


Fig. 3b Line diagram for gas purification system using aqua ammonia [27].

D. Other chemicals used for biogas purification

Chemicals such as FeCl₃, FeCl₂ and FeSO₄ are fed into the digester, react with H₂S to form iron sulphide [28]. Alternatively, Fe₂O₃ and Fe(OH)₃ can be impregnated on a reaction bed that can either be wood chips, pellets or rust steel wool for the absorption of the H₂S [28]. In some situations, absorption solutions such as (i) diluted NaOH which reacts with the H₂S to form Na₂S or NaHS precipitate (ii) FeCl₂ which reacts with H₂S to form insoluble FeS and (iii) Fe(OH)₃ which reacts with H₂S to form Fe₂S₃ [29] maybe used.

TABLE III

ADVANTAGES AND DISADVANTAGES H₂S REMOVAL FROM DIGESTER

Advantages	Disadvantages
It is a cheap investment (storage tank and dosing pump)	Low efficiency (100-150 cm ³ m ⁻³)
Low electricity and heat requirements	Expensive operation (iron salt)
Simple operation and maintenance	Changes in pH/temperature not beneficial for the digestion process
Compact technique	Correct dosing is difficult
H ₂ S not in biogas wire	
No air in biogas	

TABLE IV
ADVANTAGES AND DISADVANTAGES FOR ADSORPTION ON
OXIDES OF IRON

Advantages	Disadvantages
High removal efficiency (>99 % Sensitive for water)	Expensive operation costs
Mercaptanes are also captured	Regeneration is exothermic (risk of ignition of the chips)
Cheap investment	Reaction surface reduced each cycle
Simple process setup	Released dust can be toxic

TABLE V
ADVANTAGES AND DISADVANTAGES OF USING LIQUID
ABSORBENTS

Advantages	Disadvantages
Low electricity requirement	Expensive investment & operation
Smaller volume, less pumping, smaller vessels (compared to absorption in water)	More difficult technique
Low CH ₄ losses	Not regenerative
High removal efficiency: 95-100 %	Difficult technique
Cheap operation	Regeneration through oxygenation (Fe(OH) ₃)
Small volume required	

III. REGENERATION

Chemical absorption is of interest in biogas upgrading due to solvent regeneration. Regeneration potential and re-usability in the next cycle are important considerations in the selection of the chemical absorbent. Ionic liquids can be regenerated by heating at 180 °C for 3 hours [11]. Amines like MEA can be regenerated by boiling for 5 minutes [1]. CaCO₃ can be heated to 825 °C and dissociate to calcium oxide and carbon dioxide. This makes it not a preferable absorbent for commercial use due to its high intensive regeneration energy requirements. Ammonia can be easily regenerated by heating ammonia carbonates and bicarbonates to 60-80 °C for 5-10 minutes or they can be sold as fertilizers [30]. Diluted NaOH and FeCl₂ solutions pose environmental challenges as the resulting sodium salts and FeS are not re-generable and causes disposal challenges. The Fe₂S₃ formed from Fe(OH)₃ solution can be regenerated with oxygen or air in a closed system.

IV. CONCLUSION

Production and utilization of biogas from municipal solid waste and other biodegradable material can significantly contribute to sustainable solid waste management, energy poverty reduction, disposal airspace savings, climate change

mitigation and creation of green jobs. Its application as an energy source can be improved by purification. This paper reviewed the use of chemical absorbents for biogas purification and upgrading. Amines have a huge potential as absorbents since 99% process efficiency can be achieved. Furthermore, biogas amine scrubbing results in low methane losses which is highly desirable in biogas upgrading and can easily be regenerated.

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