Chinese Journal of Chemical Engineering 24 (2016) 693–702

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Review

A review of chemical absorption of carbon dioxide for biogas upgrading

Fouad R.H. Abdeen [1,*], Maizirwan Mel [1], Mohammed Saedi Jami [1], Sany Izan Ihsan [2], Ahmad Faris Ismail [2]

[1] *Department of Biotechnology Engineering, International Islamic University Malaysia, Kuala Lumpur 50728, Malaysia*
[2] *Department of Mechanical Engineering, International Islamic University Malaysia, Kuala Lumpur 50728, Malaysia*

ARTICLE INFO

Article history:
Received 3 October 2015
Received in revised form 4 March 2016
Accepted 5 April 2016
Available online 16 May 2016

Keywords:
Biogas upgrading
Biofuel
CO_2 capture
Absorption
Amine scrubbing
Caustic scrubbing

ABSTRACT

Significant attention has been given to biogas production, purification and upgrading as a renewable and clean fuel supplement. Biogas is a product of an anaerobic digestion process comprising methane, carbon dioxide, and trace amounts of other gases. Biogas purification removes trace gases in biogas for safe utilisation. Biogas upgrading produces methane-rich biogas by removing bulk carbon dioxide from the gas mixture. Several carbon dioxide removal techniques can be applied for biogas upgrading. However, chemical absorption of carbon dioxide for biogas upgrading is of special significance due to its operation at ambient or near ambient temperature and pressure, thus reducing energy consumption. This paper reviews the chemical absorption of carbon dioxide using amine scrubbing, caustic solvent scrubbing, and amino acid salt solution scrubbing. Each of these techniques for biogas upgrading is discussed. The paper concludes that an optimised implementation of the chemical absorption techniques for biogas upgrading requires further research.

1. Introduction

Fossil fuel depletion, rapidly growing energy demands, combined with greenhouse gas emissions encourage the development of renewable, sustainable, and environmentally friendly sources of energy [1]. For this, the production of fuel methane from biogas produced *via* anaerobic digestion (AD) interests researchers and environmentalists [2]. Biogas is a mixture of methane (CH_4), carbon dioxide (CO_2), and traces of hydrogen sulphide (H_2S), ammonia (NH_3), nitrogen (N_2), hydrogen (H_2), water vapour and other volatile compounds [3]. The methane content in the produced biogas decides its heat value when converted to energy [4]. The presence of H_2S may damage the equipment and engines used in the conversion process due to its corrosive nature. Therefore, removing H_2S is an important step for biogas cleaning prior to its utilisation [5]. This process of purification has been discussed in several published works [5–9].

Since CO_2 is considered as an inert gas in terms of combustion, it should be removed from biogas to increase its heat value. Removing CO_2 from biogas, usually termed as biogas upgrading/enriching, is necessary when the targeted utilisation requires a high methane content [10].

The standard composition of purified and upgraded biogas depends on its target application and the country policy [11]. The main biogas utilisation options include power generation in the combined heat and power (CHP) unit, injection to natural gas pipelines and converting it to vehicle fuel. When used as a vehicle fuel, biogas has a unique advantage of producing low greenhouse gas (GHG) emissions [12].

A major requirement for injecting biogas to natural gas grid or the transformation of biogas to a vehicle fuel is the upgrading to have more than 95% CH_4 content [13,14]. Moreover, comparing the low heat value (LHV) between biogas and methane, biogas of 60 vol% CH_4 and 40 vol% CO_2 has a LHV of 17,717 ($kJ\cdot kg^{-1}$), while a 100% CH_4 gas has a LHV of 50200 ($kJ\cdot kg^{-1}$) [15]. Hence, biogas upgrading is performed not only to enable its usage in wider applications but also to increase its heat value by the removal of non-combustible CO_2.

CO_2 removal from gases has been performed for many years using techniques such as chemical and physical absorption, membrane separations, pressure swing adsorption (PSA), and cryogenic separation processes. Even though there are numerous experimental data available in literature discussing the CO_2 absorption, there is little published work discussing the implementation of these techniques for biogas upgrading [16].

This paper reviews the published works on CO_2 capture using chemical absorption processes with special attention given to data from biogas upgrading experiments. It highlights the potential chemical absorption of CO_2 in upgrading biogas. Data, important findings, and recommendations from each of the reviewed techniques are integrated, tabulated, and made easy for researchers to estimate the suitability of each technique.

2. Overview of CO_2 Chemical Absorption

2.1. Background

Absorption is a process of transferring a component from its gas phase into a liquid provided that the gas is soluble in that liquid [17].

* Corresponding author.
E-mail address: fouadabdeen@gmail.com (F.R.H. Abdeen).

http://dx.doi.org/10.1016/j.cjche.2016.05.006

In the case of CO_2, the solubility of the gas is dependent on the solvent physical and chemical properties. When the gaseous molecules of CO_2 are attached to liquid molecules with weak intermolecular forces, the absorption is described as physical absorption. Therefore, the physical absorption process is usually operated at high pressure and low temperature to increase the CO_2 solubility in the absorbing liquid. The chemical absorption process is performed *via* absorbing CO_2 from biogas by covalently bonding it into the molecules of the absorbing liquid [18]. The strong covalent bonds between the chemical solvent molecules and the CO_2 molecules make the chemical absorption process more efficient in absorbing CO_2 even at ambient temperature and pressure.

2.2. Process

The chemical absorption process for CO_2 removal from biogas, performed in a packed column like any other chemical scrubbing of any gas, can be optimised by selecting the best solvent, best contactor (tray or packing with respect to process conditions), best gas and liquid flow rates, and best stripping conditions [17,19].

The column in which chemical absorption process is performed can be represented with an ideal plug flow reactor where there is mixing only in the radial direction and not in the axial direction [20]. Fig. 1 shows the flow diagram of a typical gas absorption process. The detailed designs of the absorber, stripper, and solvent selection are governed by the composition of the feed gas and the required composition of the scrubbed (treated) gas.

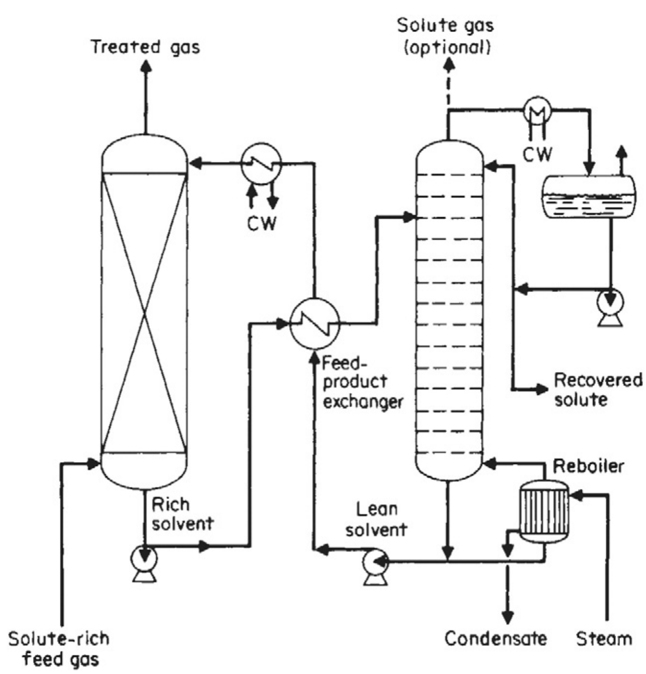

Fig. 1. Gas absorber using a solvent regenerated by stripping [19].

When using a packed column for absorbing CO_2 from biogas, a water solution is usually prepared from the selected absorbent and is fed into the top of the packed column while the raw gas is fed from bottom in a counter current flow. The estimation of the column height and diameter are dependent on other factors such as gas and liquid flow [21].

2.3. Solvent selection

Solvent selection is the most important step in the biogas upgrading process. The suitability of a solvent to be used for absorbing CO_2 from biogas is decided by the difference in solubility between CO_2 and methane in that solvent. Water can be used to selectively absorb CO_2 from biogas by a pure physical process [22]. The solubility of main biogas components NH_3, H_2S, CO_2 and CH_4, in water at 25 °C and 0.1 MPa partial pressure of diluted gas, is 280000, 1020, 340, and 13.2 $mmol\cdot kg^{-1}\cdot MPa^{-1}$, respectively, as reported by [10]. In addition to solubility gradient between CO_2 and CH_4, the solvent has to comply with other requirements of being available, cheap, environmental friendly, having a high CO_2 load, easy to regenerate, and having low viscosity [10].

To upgrade biogas to a vehicle fuel, several chemical absorption techniques have been used. Few liquids have been used for upgrading biogas including amines, caustic/alkaline solvents, and amino acid salts.

3. Chemical Absorption Techniques for Biogas Upgrading

Since solvent selection is the most important step in the chemical absorption of a gas, the techniques discussed in this section are categorised based on the solvent used. For each of the amine scrubbing, caustic solvent scrubbing, and amino acid salt scrubbing techniques, the theory, the early work, and the most recent improvements are discussed. The following review includes the process applied for CO_2 absorption with special attention to solvents and techniques performed for biogas upgrading.

3.1. Amine scrubbing

3.1.1. Theory and background

Amine scrubbing of CO_2 is where CO_2 is absorbed by an amine-based solution. The absorption is a chemical absorption process since covalent bonds are formed between the amine and CO_2. The most common amines used for CO_2 removal are monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), and piperazine (PZ) [10,18]. MEA is the most used amine for absorbing CO_2 as a scrubbing agent. Eqs. (1) and (2) summarise the possible reactions using MEA mentioned by many researchers [23–25].

$$2RNH_2 + CO_2 \rightleftharpoons RNH_3^{+} + RNHCOO^{-} \qquad \text{(Carbamate route)} \qquad (1)$$

$$RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3^{+} + HCO_3^{-} \qquad \text{(Bicarbonate route)} \qquad (2)$$

The amine solution absorbs CO_2 both physically to the liquid and chemically. However, the mass transfer of CO_2 from the gaseous phase to the liquid phase is increased by the chemical reaction between CO_2 and the amine. The chemical reaction consumes CO_2 in the liquid phase to maintain the concentration gradient of CO_2 in the two phases [26]. One recommendation while performing amine scrubbing is to keep the molar flow of amine at a rate of at least four times of the molar flow rate of CO_2 [18]. More about the mass transfer and the thermodynamic of the process is discussed by [23,27].

An early use of amine scrubbing for CO_2 removal was reported in 1930 by [28]. The amines recommended for the CO_2 scrubbing were primary, secondary, and tertiary and may contain a carboxyl group [28]. Other early studies examining amine-based CO_2 scrubbing used monoethanolamine, triethanolamine, and diaminoisopropanol [29], di- and tri-ethanol amine [30], ethylaminoethanol [31], methyldiethanolamine [32], piperidine methanol/ethanol/propanol/butanol or pentanol [33], and hydroxyethyl piperazine [34]. One early study claimed that the effectiveness of monoethanolamine and diaminoisopropanol is twice that of triethanolamine [29].

More recent works emphasised the use of the sterically hindered amines for CO_2 removal from the mixture of gases [35–37]. It was claimed that steric hindrance gives amines higher thermodynamic capacity and faster absorption rates when CO_2 concentration is high [37]. Nevertheless, it was later claimed that hindrance of amines