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Biogas upgrading technologies: Energetic analysis and environmental impact assessment☆

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ABSTRACT

Biogas upgrading for removing CO_2 and other trace components from raw biogas is a necessary step before the biogas to be used as a vehicle fuel or supplied to the natural gas grid. In this work, three technologies for biogas upgrading, *i.e.*, pressured water scrubbing (PWS), monoethanolamine aqueous scrubbing (MAS) and ionic liquid scrubbing (ILS), are studied and assessed in terms of their energy consumption and environmental impacts with the process simulation and green degree method. A non-random-two-liquid and Henry's law property method for a CO_2 separation system with ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) is established and verified with experimental data. The assessment results indicate that the specific energy consumption of ILS and PWS is almost the same and much less than that of MAS. High purity CO_2 product can be obtained by MAS and ILS methods, whereas no pure CO_2 is recovered with the PWS. For the environmental aspect, ILS has the highest green degree production value, while MAS and PWS produce serious environmental impacts.

1. Introduction

Biogas produced by biomass fermentation is regarded as a supplement even substitute for natural gas [1] and green energy due to its renewability. However, besides methane (CH_4), carbon dioxide (CO_2) is also the main component in the raw biogas from anaerobic digestion, which accounts for 30%–47 % (by volume) [2], lowering the calorific value of biogas and increasing energy demand for its compression and transportation. Therefore, raw biogas cannot be used directly as vehicle fuel or supplied to the natural gas grid before removal of CO_2 component.

Currently, the technologies of biogas upgrading include pressure swing adsorption, pressured water scrubbing (PWS), chemical scrubbing, membrane separation and cryogenic method [2–4]. Among them, absorption is one of the most widely used technologies; for example, PWS and chemical scrubbing are employed with 40% and 25% share, respectively, among more than 200 bio-methane plants in European region [5]. Generally, PWS is one of the cheapest and simplest technologies [3]. Besides its high efficiency and low CH_4 loss, hydrogen sulfide (H_2S) can be removed as well [2,3,6]. However, the drawbacks of clogging from bacterial growth and low flexibility toward variation of input gas cannot be avoided [6]. Additionally, water consumption is huge and waste water is discharged inevitably. Another prevailing absorption technology is amine scrubbing widely used in commercial CO_2 capture processes due to its relatively high absorption capacity and rate [7–9]. However, the drawbacks are high energy consumption for solvent regeneration, corrosion to equipment, and significant solvent degradation and losses [8].

Ionic liquids (ILs), as promising gas absorbents, have received increasing attentions because of their unique physical properties, including negligible vapor pressure, high thermal stability, non-flammability, high CO_2 solubility and designability by adjusting the combinations of anions and cations [10–15], especially for removing CO_2 from mixed gases [16–19]. Karadas *et al.* [20] reviewed the use of ILs as alternative fluids for natural gas sweetening. Aparicio and Atilhan [21] used the molecular dynamics method to infer the interaction mechanism of ILs in natural gas sweetening. Raeissi and Peters [22] measured the solubility of CO_2 in [bmim][Tf_2N] in pressure and temperature ranges of (0.5 to 14) MPa and (310 to 450) K. Ali *et al.* [23] determined the cost effective operating conditions for 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) to capture CO_2 by simulation method. Raeissi and Peters [24] measured the solubility of CH_4 in [bmim][Tf_2N] in pressure and temperature ranges of 1–16 MPa and 300–450 K. According to these studies, anions of ILs play a dominant role in CO_2 solubility [16]. For example, with cation of $[bmim]^+$, the solubility of CO_2 increases in the following anion order: [NO_3] < [DCA] < [BF_4] < [PF_6] < [TfO] < [Tf_2N] < [methide] at 25 °C [25]. [bmim][Tf_2N] shows higher CO_2 absorption capacity among these ILs,

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better thermodynamics stability [13], and lower viscosity [26]. In this work, [bmim][Tf_2N] is selected as a physical solvent to remove CO_2 from raw biogas.

For a biogas upgrading technology, both energy consumption and environmental impact are critical screening criterion. Compared to energetic analysis [2,9], the environmental impact assessment for biogas upgrading process is relatively fewer [27,28]. Starr *et al.* [27] evaluated three biogas upgrading technologies, *i.e.*, PWS, alkaline with regeneration and bottom ash upgrading, and showed that the bottom ash upgrading process has the least environmental impact even compared to the pressure swing adsorption and chemical scrubbing method. Cozma *et al.* [28] assessed the environmental impact of PWS process with the life cycle assessment (LCA) tool and showed that the main impact categories are the global warming, human toxicity and acidification potentials, mainly caused by the exhaust gas from desorption column and energy consumption. LCA method is comprehensive but complicated, as an alternative, green degree (GD) method proposed by Zhang *et al.* can quantitatively assess the environmental impacts based on nine environmental impact categories, such as substances, streams, units and systems [29,30]. However, for ionic liquid scrubbing method, to the best of our knowledge, there is a little systematic study on the energetic analysis and environmental impact assessment for biogas upgrading processes.

In this work, three biogas upgrading technologies, *i.e.*, PWS, monoethanolamine aqueous scrubbing (MAS) and ionic liquid scrubbing (ILS) are studied in terms of their energy consumption and green degree production. Firstly, rigorous thermodynamic models are established for CO_2 capture system with [bmim][Tf_2N] ionic liquid by fitting available experimental data [22,24]. Secondly, the three biogas upgrading processes are simulated and the key parameters affecting the energy consumption are analyzed and optimized. Finally, circulating solvent, energy consumption, energy efficiency and environmental impact of each technology are evaluated and compared.

2. Methodology

Thermodynamic models are the core of simulation and design of a process. For PWS and ILS, non-random-two-liquid (NRTL) and Henry's law property methods are employed, which has been proved to be appropriate for such systems [28,31,32]. For MAS, KEMEA thermodynamic package is applied based on the electrolyte non-random-two-liquid model [8]. Lacking of parameters related to the ionic liquid-based system, physical properties of [bmim][Tf_2N] are estimated and thermodynamic models of [bmim][Tf_2N] based system are established. CH_4 recovery ratio, specific energy consumption, energy efficiency, selectivity and GD are calculated as assessment indicators of upgrading performance.

2.1. Thermodynamics of ionic liquid systems

CO_2 solubility in [bmim][Tf_2N] is estimated with NRTL and Henry's law method. The NRTL model is written as

$$\ln\gamma_i = \frac{\sum_{j=1}^{\delta} x_j\tau_{ji}G_{ji}}{\sum_{k=1}^{\delta} x_kG_{ki}} + \sum_{j=1}^{\delta}\left(\frac{x_jG_{ij}}{\sum_{k=1}^{\delta} x_kG_{kj}}\left(\tau_{ij} - \frac{\sum_{m=1}^{\delta} x_m\tau_{mj}G_{mj}}{\sum_{k=1}^{\delta} x_kG_{kj}}\right)\right) \quad (1)$$

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right); \quad \tau_{ij} = \left(g_{ij}-g_{jj}\right)/RT = a_{ij} + b_{ij}/T \quad (2)$$

$$\alpha_{ij} = \alpha_{ji}(i \neq j) \quad (3)$$

where δ represents the number of components, x is the mole fraction, T is the absolute temperature, R is the gas constant, G_{ij} is a dimensionless interaction parameter depending on energy interaction parameter (g_{ij}) and non-randomness factor (α_{ij}), a_{ij}, b_{ij} and α_{ij} are the binary parameters.

The heat capacity (C_p) of [bmim][Tf_2N], which is a necessary parameter to estimate the energy consumption, can be calculated by DIPPR equation, which is taken from the Aspen Plus software.

$$C_{p_i} = 572.739 - 0.568633T + 0.00184545T^2. \quad (4)$$

The binary interaction parameters of CO_2/IL and CH_4/IL shown in Table 1 are regressed based on experimental solubility data in literature [22,24]. The predicted values are in agreement with experimental data as shown in Figs. 1 and 2. The comparison between the experimental [33] and predicted values of C_p is shown in Fig. 3. Other physical properties of ILs, such as critical properties, density, surface tension and thermal conductivity are taken from literature [34].

Table 1
NRTL binary interaction parameters of CO_2/IL and CH_4/IL

Binary interaction parameters	a_{ij}	a_{ji}	b_{ij}	b_{ji}	α_{ij}
CO_2/IL	−38.60	−1.40	19,030.71	233.99	0.30
CH_4/IL	−3.57	7.16	671.06	−1834.32	0.30

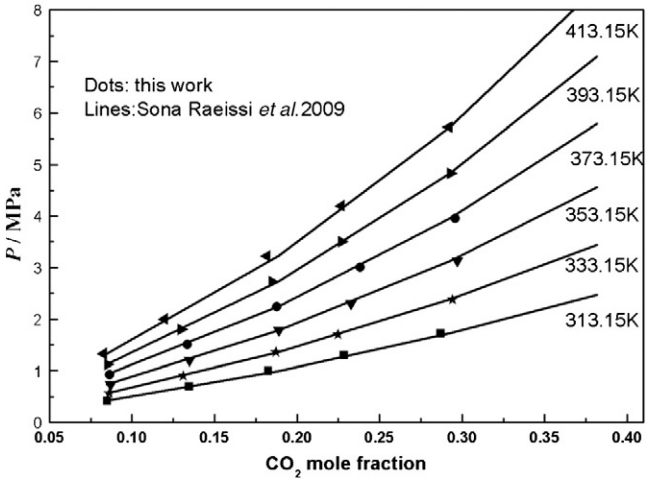

Fig. 1. CO_2 solubility in [bmim][Tf_2N].

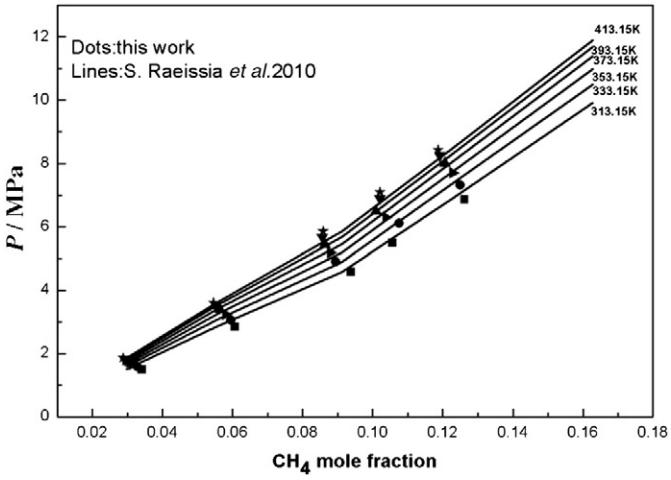

Fig. 2. CH_4 solubility in [bmim][Tf_2N].