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Thermodynamic efficiency of carbon capture and utilisation in anaerobic batch digestion process

Sung T. Oh[a,*], Alastair Martin[b]

[a] School of Science, Engineering and Technology, University of Abertay Dundee, DD1 1HG, United Kingdom
[b] Department of Engineering, Lancaster University, Bailrigg, Lancaster, LA1 4YR, United Kingdom

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ABSTRACT

Carbon capture and storage (CCS) in the oil and water industries is becoming common and a significant consumer of energy typically requiring 150–450 °C and or several hundred bar pressure [1] particularly in geological deposition. A biological carbon capture and conversion has been considered in conventional anaerobic digestion processes. The process has been utilised in biological mixed culture, where *acetoclastic bacteria* and *hydrogenophilic methanogens* play a major key role in the utilisation of carbon dioxide. However, the bio catalytic microorganisms, *hydrogenophilic methanogens* are reported to be unstable with *acetoclastic bacteria*. In this work the biochemical thermodynamic efficiency was investigated for the stabilisation of the microbial process in carbon capture and utilisation. The authors observed that a thermodynamic efficiency of biological carbon capture and utilisation (BCCU) had 32% of overall reduction in yield of carbon dioxide with complimentary increase of 30% in yield of methane, while the process was overall endothermic. Total consumption of energy (≈0.33 MJ l^{-1}) was estimated for the carbonate solubility (0.1 mol l^{-1}) in batched BCCU. This has a major influence on microbial composition in the bioreactor. This thermodynamic study is an essential tool to aid the understanding of the interactions between operating parameters and the mixed microbial culture.

1. Introduction

The UK emission of greenhouse gases has been slowly decreasing year by year; was estimated to be 569.9 million tonnes carbon dioxide equivalent (MtCO2e) annually [2] in 2013 whereas it was 777.12 MtCO2e [2] in 1990. The UK strategy of the greenhouse gas emissions seems to be almost achievable, which will reach by at least 80% reduction (from the 1990 baseline) by 2050 [3]. However the UK water and waste industry has produced approximately 6 MtCO2e [4] annually; of which 56% is in the result of wastewater treatment processes including sludge management: in particular activated sludge process [5]. In case of the Thames Water Plc. in London consumes 7.7 TWh [6] (≈2.5 MtCO2e by conversion factor of industrial coal) for wastewater treatment annually, which is approximately 2–5% of the whole UK national consumption of primary fuel. This is a disappointing result regardless of high efficiency of 'low-carbon' technologies to compete internationally and generate economic growth.

As a direct in-door capture followed by storage technology, such as geological carbon capture and storage (CCS) or oceanic reservoirs, has been widely introduced for the UK water industry but it still has many difficulties to adapt the technology: long term operating and monitoring costs [7], significant risk of site-leaking [8], effective carbon capture and transport [9] from conventional activated sludge process. A biological carbon capture and conversion has been considered in existing and conventional anaerobic digestion process in water industry. Fernandez, et al. [10] utilised anaerobic batched digestion process to observe maximum BCCU capacity and limitation/inhibition in range of the process capacity, which overall CO_2 reductions are 3–34% in anaerobic batched digestion process and CH_4 yields are increased in range of 13–138%. Salomoni et al. [11] also observed an extra 25–30% of methane (CH_4) yield in continuous two-stage anaerobic digestion of sewage sludge. These results seem to be a promising technology in CH_4 conversion from biological carbon capture and utilisation whilst, Oh et al. [6] reported very low energy efficiency (5–15%) of anaerobic digestion process itself and the biogas yield is less than 50% of carbonaceous feedstocks [6,12] in heterogeneous domestic or municipal wastes. Moreover, Alimahmoodi and Mulligan [13] reported a 69–86% efficiency of *only aqueous* CO_2 *uptake* in an upflow anaerobic sludge blanket (UASB) reactor of food wastes.

* Corresponding author.
E-mail addresses: s.oh@abertay.ac.uk (S.T. Oh), a.martin1@lancaster.ac.uk (A. Martin).

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These observations directly tell us that biological carbon capture and utilisation (BCCU) is strongly limited by *hydrogenophilic methanogens* with a range of CO_2 solubility, which is less than 1300 mg l^{-1} of CO_2 in diluted aqueous solution.

Biological CO_2 capture is dependent on reversible or backward reaction by *acetoclastic bacteria* [14] under strong dissociation of CO_2, meanwhile the utilisation relies on the microbial activity of *hydrogenophilic methanogens*. The two simultaneous reactions, both are thermodynamically spontaneous, competitive and exothermic, but rely on 'H_2 partial pressure'. Moreover the utilisation is indirectly correlated to microbial relationship between *acetoclastic methanogens* and *syntrophic acetogenic bacteria* followed by *fermentative bacteria.* Oh and Martin [15] reported that the *activity of acetoclastic methanogens* is thermodynamically spontaneous ($\Delta G < 0$) but entirely endothermic process. The *syntrophic acetogenic bacteria* converting fermentation products into acetate and 'molecular H_2' are not generally thermodynamically feasible biological reactions ($\Delta G >> 0$), only becoming feasible at very low 'H_2 partial pressure' [16] in absence of acetoclastic conversions. The metabolic efficiency and the growth yield of the *syntrophic acetogenic bacteria*, depend strongly on the removal rate of the 'molecular H_2' by a consuming species [17,18].

Practically the 'molecular hydrogen' having very low solubility (Henry's law coefficient 8.58×10^{-4} mol atm^{-1} l^{-1}) is spontaneously transferred into 'gas phase' and the 'partial pressure' is maintained in very low range of values (i.e. $10^{-6} < H_2\,(atm) < 10^{-4}$) [17,18]. The hydrogen transport between functional anaerobic microorganisms is almost impossible as a result of the hydrogen diffusion coefficient (4.50×10^{-9} m^2 s^{-1}) [16], while 'transport of electrons and protons' has a feasibility to link metabolic pathway between functional anaerobic microorganisms. In case of anaerobic biofloc, microbial oxidising bacteria are continuously producing electrons and protons while microbial reductive bacteria are consuming them through hydrogen bonding structure in water [15,16]. In intrinsic distance between functional microorganisms such as fixed biofilm, the microorganisms produce biochemical mediators (i.e. NAD^+/NADH) for electrochemical salt bridge between functional microorganisms to electrical conduction of electrons and protons. This suggests that the electron/proton transport between functional microorganisms can occur independently of the conventional biochemical carriers but the success of the biological carbon capture and utilisation (BCCU) might be attributable to the efficiency of the proton/electron transport in microbial processes.

On this basis this work established the catabolic reactions completely linked between the microorganisms through proton/electron pairs, in terms of a couple of inter cellular mediator (NAD^+/NADH). The overall process was thus assumed to be at the electrochemical equilibrium state whilst there is a quasi-steady state of microbial growth. The authors thermodynamically investigated the efficiency and the limitation of the BCCU in anaerobic digestion process. The resulting model is used to only investigate a magnitude of the thermodynamic driving force (i.e. ΔG,ΔH and ΔS) but overcome thermodynamic limitations leading to practical operation of biological carbon capture and utilisation (BCCU).

2. Model development

The biological carbon capture and utilisation (BCCU) is modelled and simulated in an isothermal and isobaric condition (298.15 K and 1 atm) of anaerobic batch digester. The anaerobic digester is assumed to contain a 'fully acclimatised' *fermentative bacteria*, *syntrophic acetogenic bacteria*, *acetoclastic bacteria* and methanogenic consortium with *anaerobic ammonium oxidising bacteria*. A two-phase digester is assumed: gas and solution.

In this case, the authors propose the addition of carbon dioxide into the two-phase digester for a BCCU and then an intensive biogas. The initial substrate is the aqueous form of carbon dioxide (aqueous CO_2) in the constant moles of glucose (0.1, 1 and 10 m mol). Initial moles (10 m mol) of glycerol ($C_3H_8O_3$) and ethanol (C_2H_6O) are also constantly injected, where 10 m mol of aqueous ammonia (NH_3) is assumed in approximately range 10 250 m mol l^{-1} as mixed sewage sludge [19,20]. 1 m mol l of NADH is considered as a biochemical hydrogen mediator to trade-off hydrogen molecule between micro-organisms. The authors consequently investigate sensitive changes (ΔE, ΔH and ΔS) in electrochemical equilibrium state (ΔG = zero) at conserved system mass (one kilogram). As the initial mole fraction of aqueous carbon dioxide ($x = CO_2/(H_2O + CO_2 + NH_3 + C_2H_6O + C_6H_{12}O_6 + TNADH)$) is increased, the moles of solvent water (H_2O) is reduced. This is based on the mass conservation of system (one kilogram). In regarding different conditions (i.e. feeding concentration of CO_2), it is also investigated how the deviation has an influence on the sensitive changes (ΔE, ΔH and ΔS) and then how they can affect BCCU. Although the authors theoretically investigate in the whole range of initial CO_2 mole fraction ($0 < x < 0.93$) in the conserved mass (1 kg of three phased batch reactor), where the high range of initial CO_2 mole fraction ($x > 0.0005$) has practically been operated [10,11]. Furthermore, the low range of initial CO_2 mole fraction ($x < 0.0005$) is also included in the case of an sequencing injection as a solid or gaseous forms of CO_2.

The thermodynamic model comprises three parts of equilibrium state (phase transition, dissociation and electrochemical reaction) on quasi steady state of growth rate in microorganisms. The first includes equilibrium expressions that relate the relative aqueous activities and vapour fugacities of all chemical species in the two-phased digestion process. The second consists of the dissociation/association that quantifies the relationships between cation activity and anion activity in the liquid phase. The third consists of the reduction and oxidation state that based on the electrochemical potential (V) through NAD+/NADH ratio. The completed model consists of a set of highly non-linear simultaneous equations which was solved using Newton-Raphson Algorithm [15] based on the Jacobian matrix.

2.1. Stoichiometric relationships of carbon capture and utilisation

The stoichiometric expressions are established in the common manner to quantify the feasible relationships between the initial substrate and the products and the intermediates. Table 1 shows the stoichiometric relationship for BCCU in anaerobic sludge digestion. The stoichiometric relationships are categorised by three equilibrium relationships which are electrochemical reaction, two-phase transition and electrolyte ionisation reaction.

2.2. Equilibrium relationships of carbon capture and utilisation

This model from the stoichiometric foundations is developed using the fundamental definition of thermodynamic chemical equilibrium.

$$\sum \nu_i \mu_i = 0 \tag{1}$$

where ν_i is stoichiometric coefficient of component i and the chemical potential μ_i is expressed as the standard chemical potential μ_i° and activity a_i of component i.

$$\mu_i = \mu_i^\circ + RT\ln a_i \tag{2}$$

where R is universal gas constant and T is absolute temperature.