Applied Energy 216 (2018) 751–760

Contents lists available at ScienceDirect

Applied Energy

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

Kinetics, multivariate statistical modelling, and physiology of CO_2-based biological methane production

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HIGHLIGHTS

- Gas-to-gas conversion processes are analyzed with respect to bioenergy production.
- CO_2-BMP modeling is performed and model validity is discussed.
- Multivariate data analysis and biological gas conversion mechanistic is integrated.
- Gas limitation and liquid limitation in pure culture biological CH_4 production are highlighted.
- Continuous culture CH_4 bioprocessing from H_2/CO_2 is discussed.

ARTICLE INFO

Keywords:
Archaea
Methanogens
Bioprocess
Biotechnology
Biofuel
Power-to-gas

ABSTRACT

Conversion of surplus electricity to chemical energy is increasingly attracting attention. Thereof, biological energy conversion and storage technologies are one of several viable options. In this work, the inherent challenges faced in analyzing the CO_2-based biological methane production (CO_2-BMP) process for energy conversion and storage are discussed. A comprehensive assessment of key process parameters on several CO_2-BMP process variables was conducted. It was found that literature data often misses important information and/or the required accuracy for resolution of the underlying mechanistic effects, especially when modelling reactor dependent variables. Multivariate dependencies inherently attributable to gas-to-gas conversion bioprocesses are particularly illustrated with respect to CO_2-BMP. It is concluded that CO_2-BMP process modelling requires the application of process analytical technology. The understanding of the CO_2-BMP mechanistic process is discussed to assist with the analysis and modelling of other gas-to-gas conversion processes. The findings presented in this work could aid in establishing a biotechnology-based energy to gas conversion and storage landscape.

1. Introduction

Converting surplus electricity to chemical energy is increasingly attracting attention [1]. In this frame, chemical or biological energy conversion and storage technologies for the power-to-gas concept are one of several viable options [2,3]. Due to decreasing reserves of fossil fuels and growing awareness for global warming, carbon dioxide (CO_2) utilization has become a topic of industrial relevance [4]. An effective reduction of CO_2 emissions will be achieved in the long term if renewable energy production can be linked with power conversion and storage technologies. Furthermore, the production of renewable energy is significantly more carbon neutral when compared to fossil fuel-based energy production [5,6]. Therein, a renewable energy production scenario that consumes CO_2 and produces biofuels could become an integral part of a biorefinery scenario for reducing CO_2 emissions [7]. However, the environmental impact of biofuels production, utilization, and surplus (or excess) energy conversion systems still needs to be evaluated and re-assessed.

Production of 1st generation biofuels would currently be able to compete with fossil fuels in the case where certain energy crops (e.g. *Saccharum officinalis*) are employed in bioethanol production [5]. 2nd generation biofuel production from e.g. lignocellulose could also become competitive to fossil fuels and are already applied on industrial scale for energy production [5,6]. Biofuel production systems of the 3rd and 4th generations have only reached pilot and pre-industrial scales concerning biodiesel production from algae and photo-fermentation of

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https://doi.org/10.1016/j.apenergy.2018.01.075
Received 16 October 2017; Received in revised form 20 January 2018; Accepted 24 January 2018

molecular hydrogen (H_2) respectively [7]. Recent advances in bioprocess technology [2,3,8,9] and the development of biorefinery concepts favored the development of 5th generation biofuels, which employ microorganisms to convert gaseous substrate(s) to gaseous end products. 5th generation biofuels encompass CO_2-based biological methane (CH_4) production (CO_2-BMP) and H_2 production from C_1 compounds [9,10]. CO_2-BMP and H_2 production from C_1 compounds are known to be the only gaseous biofuel production technologies that have no immediate requirement for photosynthesis. Thus, integrating surplus renewable power conversion with CO_2 capture and storage can be performed by applying the CO_2-BMP process.

The CO_2-BMP process is characterized by utilizing hydrogenotrophic methanogenic archaea (methanogens) for CH_4 production [9]. Because CO_2-BMP is a bioprocess, it encompasses distinct and emergent advantages compared to its chemical counterpart – the Sabatier process. One such advantage is the autocatalytic regeneration of methanogens accompanied by CH_4 production [9,11–14]. In this process, methanogens exhale CH_4 as a metabolic end product of their energy conserving metabolism while fixing a variable part of CO_2 in the form of biomass [14–16]. Therefore, the production of CH_4 is essential for the survival of the organisms. The CO_2-BMP process can be carried out by an enrichment culture [17–23] or pure culture of methanogens [9,24] and benefits from its ability to convert CO_2 and H_2 to CH_4 at very high volumetric methane evolution rates (MERs) while in continuous culture [25,26]. An additional advantage is the mild bioprocessing conditions (e.g. temperatures from approx. 0 °C to 122 °C) that can be applied during CO_2-BMP [27,28].

High purity H_2 and CO_2 can be employed as substrates for the CO_2-BMP process [9,12,26]. It has also been shown that the CO_2 by-product of the anaerobic digestion process can be microbiologically transformed to CH_4 at different conversion efficiencies and MERs [13,21,24,29]. However, it has been noticed that the technology readiness level (TRL) of the different microbiological biogas converting technologies can vary tremendously [24]. Although direct microbiological biogas conversion in anaerobic digesters was shown to be possible, the MER and CH_4 concentration in the offgas remained negligible [20,24]. On the contrary, microbiological biogas conversion by using pure [13] or enrichment cultures [21,23] of methanogens was shown to be efficient. Drawbacks of using enrichment cultures for microbiological biogas conversion are the ambiguous adaptation procedures, the time it takes for the culture to adapt to certain conditions, and unintended side reactions that occur within the enrichment [24,30]. Eventually, pure cultures of methanogens were not only applied in microbiological biogas upgrading [13,31], but were also utilized for conversion of CO_2 from industrial flue gases [13]. While pure cultures have been used for the conversion of chemical species, it should be noted that the CO_2-BMP process results in a different product formation kinetic [32,33] when compared to liquid-based continuous culture bioprocessing [6,34]. Therefore, many challenges in the analysis of production kinetics, physiology, scale-up, and modelling of the CO_2-BMP process have emerged [8].

The first aim of this study was to comprehensively assess the effects of key process parameters (KPP) on several CO_2-BMP process variables, which were obtained from literature, on continuous culture bioprocessing. Second, this study discusses the multivariate dependencies inherently attributable to CO_2-BMP gas-to-gas conversion bioprocesses. Third, it is shown that the presented models possess limits that prevent a simple analysis of the CO_2-BMP process. Fourth, the application of multivariate data analysis and modelling CO_2-BMP process is thoroughly discussed. It was of great interest to review and refine the understanding of the kinetic aspects involved in gas converting bioprocess technologies and to better control and avoid undesired or uncontrolled limitations of the CO_2-BMP kinetics.

The novelty of this contribution goes beyond bioprocess modelling. Here, a critical analysis of literature on CO_2-BMP in pure culture was performed. It is shown that both liquid and gas limitations need to be carefully considered when attempting CO_2-BMP bioprocessing. Examples on how to model the CO_2-BMP processes are given and it is shown that wrong conclusions have often been drawn due to an application of erroneous results. It is discussed that during CO_2-BMP modelling an in depth understanding of the biology and the process is required and that the physiology of the target organism must be carefully considered to cope with the multivariate nature of this process. Finally, it is shown that biological gas-to-gas conversion and energy storage processes must be scaled by linking kinetics, modelling, and physiology.

2. Material and methods

First, the existing literature of pure culture CO_2-BMP, independent of bioreactor conditions and scale, was reviewed with an in depth examination of methanogenic strains, bioprocess setup, and growth conditions. Second, pure culture CO_2-BMP data was extracted from literature [11,12,25,26,32,35–44]. Third, the data was applied for qualitative and quantitative assessment and subsequent modelling. A list of comprehensively extracted results from literature is provided in Supplementary Material 1. From all literature reports on pure culture CO_2-BMP, only the data on continuous culture experiments were analyzed as the stability of process variables in steady state allowed for a precise quantification. Closed batch and fed-batch CO_2-BMP experiments were not considered.

2.1. Definition of parameters and units

The following variables and KPPs were extracted or calculated based on the information provided in literature: the gassing rate per working volume per minute (vvm [$L\,L^{-1}\,min^{-1}$]), temperature [°C], the pH, oxidation reduction potential (ORP [mV]), agitation [rpm], sulphide dilution rate (DS [d^{-1}]), trace element concentration (TE), medium dilution rate (D [h^{-1}]), the gassing ratio, and the reactor pressure [barg]. Additionally, the following variables relating to production and/or yield were extracted from literature: methane evolution rate (MER [$mmol\,L^{-1}h^{-1}$]), the specific CH_4 evolution rate (qCH_4 [$mmol\,g^{-1}$ (gram cell dry weight) h^{-1}]), the CH_4 offgas concentration [Vol.-%], biomass concentration (x [g (gram cell dry weight) L^{-1}]), the specific growth rate (μ [h^{-1}]), and the growth yield (Y_{CH4} [g (gram cell dry weight) mol^{-1}]), or, where attainable, the growth to product yield ($Y_{(x/CH4)}$ [C-mol mol^{-1}]). $Y_{(x/CH4)}$ was used to assess the flux of the carbon into biomass and into CH_4 on a C-molar level for all the cultivations performed with *Methanothermobacter marburgensis* [11,12,26]. Although the analysis of $Y_{(x/CH4)}$ was possible for experiments reported before [11,12,26,35], $Y_{(x/CH4)}$ could not be retrieved or calculated from all of the experiments presented in Supplementary Material 1 because C-molar biomass productivity ($r_{(x)}$) [C-mmol $L^{-1}\,h^{-1}$] had not been reported. However, Y_{CH4} that was defined as the quotient of μ to qCH_4 [15] could be retrieved from literature. Most KPPs and variables could be directly extracted from literature without the necessity to convert results [11,12,26,35]. In some cases the conversion of extracted literature data into aforementioned molar units was performed.

2.2. Data validation procedure

Data was curated according to the degree of reduction balance (DoR-balance) and carbon balance (C-balance) by applying manual data quality control steps. These mass balance curation steps could only be performed were the relevant information was provided in literature. The relevant bioprocess and physiological parameters were then presented after a data quality assessment based on published methodologies [9,45]. Data curation also involved a thorough qualitative selection procedure where an assessment step analyzing the data by using the MER/MER_{max} concept was implemented. The MER/MER_{max} ratio presented is the dimensionless quotient of MER to the maximum possible