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Effectiveness of CO_2 - Sorbent Coated Membrane for Improving Dark Fermentative Hydrogen Production

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ABSTRACT: Dark fermentative hydrogen production ($bioH_2$) could be greatly impaired by the build-up of $bioH_2$ in the reactor headspace, as well as, its re-dissolution in the culture medium. This is because carbon dioxide (CO_2) and reduced nicotinamide adenine dinucleotide in the medium could be used for succinate and fumarate production, which could impact negatively on the $bioH_2$ production. Hence, prompt removal of headspace CO_2 could prevent its re-dissolution in the culture medium and thereby creating potential for improved $bioH_2$ yields. Therefore, this study investigated the $bioH_2$ production effect of removing CO_2 in the reactor headspace using calcium oxide (CaO) sorbent. The results showed that reactors with membrane impregnated with 1 M CaO produced 15.6% and 11.6 % hydrogen yields higher than non-impregnated membranes, and membranes impregnated with 2 M CaO, respectively. Besides, CO_2 yield and loss in membrane storage modulus of 74.5 ml/ g VS and 40 %, respectively, were measured for reactors with 1 M CaO-impregnated membranes while CO_2 yield and loss in membrane storage modulus of 79.9ml/ g VS and 28%, respectively, were measured for reactors with 2 M CaO-impregnated membranes. The results indicated that 1 M CaO-impregnated membranes were more efficient for CO_2 adsorption than 2 M CaO-impregnated membranes. The improved yield using CaO-impregnated membranes justified the effectiveness of the membrane for headspace CO_2 capture and the possible commercial application of the technique if improved upon. The research findings could contribute to the development of hydrogen energy technology.

KEYWORDS: Biohydrogen production, membrane impregnation, CO_2-sorbent, membrane stability, dark fermentation

I. INTRODUCTION

The search for renewable and environmentally-friendly energy sources that could potentially replace fossil fuels has led to a great deal of research work over the last decades on biological hydrogen ($bioH_2$) production from biomass during dark fermentation process. Application of $bioH_2$ as energy is associated with numerous benefits including the non-polluting, non-poisonous, efficient conversion and high energy content qualities of the gas [1-2]. However, sustainable $bioH_2$ depends on the availability of the biomass for its production. Banana is an example of biomass that could be used for continuous $bioH_2$ production since as a staple food widely consumed in most part of the world, especially in developing countries; vast amount of waste is generated from the banana processing and consumption processes. Meanwhile, production of $bioH_2$ during dark fermentation process is often associated with low yield which makes its commercial production from biomass uneconomical when compared to fossil fuels. In an effort to improve $bioH_2$ yield from dark fermentative process, many researchers have used different techniques including low pH, short hydraulic retention time (HRT) and deactivation of H_2 consuming microorganism by chemical, heat, acid or alkaline pretreatments [3-6]. Sometimes, the pretreatment methods convert portion of the feedstock to compounds such as furfural, hydroxymethylfurfural (HMF), syringic acid, p-hydrobenzene acid and vanilline which are inhibitory to the metabolism of anaerobic bacteria [7-9]. Moreover, pretreatment methods seem to have short-term effects on $bioH_2$ yield as the effects disappear over long continuous operation. Therefore, increasing $bioH_2$ yield through other means such as preventing carbon dioxide (CO_2) accumulation in the culture medium might be attractive since dark fermentative hydrogen production is associated with production of CO_2.

Previous research work on improving the yield of fermentative $bioH_2$ production focused on displacement of CO_2 from culture medium by gas sparging [10] which consequently resulted in H_2 yield improvement. However, the displacement of CO_2 into the reactor headspace may not completely prevent its accumulation in the culture medium since the high density and solubility of CO_2 in water favour its re-dissolution in the culture medium. The high polarity and solubility of CO_2 in water could make it to hydrate and dissociate in the aqueous phase (Eq. 1) even under normal pressure of anaerobic H_2 and CO_2 culture, which could vary from 0.6 to 2.5 atm [11].

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \quad (1)$$

Besides, the solubility of CO_2 will increase with increase in the pressure of the gas above the surface of the solution according to Henry's law [12]. The dissolution of CO_2 in culture medium could significantly alter the pH of medium and consequently inhibit the fermentation metabolism and activity [13]. Also, CO_2 in the medium could be used along with nicotinamide adenine dinucleotide (NADH) for succinate and fumarate production, thereby, reducing the amount of NADH available for H_2 production.

The effect of CO_2 removal using metal oxides such as calcium oxide (CaO) on hydrogen production from biomass gasification have been studied extensively [14 -16] where it was confirmed that the presence of sorbent in the system increased hydrogen yield. The chemical, CaO, was chosen as the preferred sorbent in most of the studies because of its suitability and cost-effectiveness [17]. However, there was a challenge of physical deterioration and decay in reactivity of CaO through several cycles of CO_2 adsorption and desorption. Therefore, it was suggested that effective adsorption capacity of CaO during biomass gasification would be promoted by decreasing temperature (within range of 450 to 750°C) at a constant total pressure or increasing the total pressure at a constant temperature. The importance of CO_2 removal during fermentation process has made membrane–based CO_2 capture technique to gain increasing attention due to its low footprint, low costs, easy scale-up, high area-to-volume ratio and high energy efficiency [18 - 20]. Hence, CO_2-based membrane adsorption could be an alternative technique to pretreatment methods for improving dark fermentative hydrogen yield. However, effectiveness of membrane-based CO_2 capture depends on process conditions, gas stream composition and properties, which influence the stability, gas permeability and selectivity of the membrane. Polymeric membranes, especially, polyvinylidene fluoride (PVDF) are often used in gas separation processes owing to their gas separation efficiency, good mechanical properties and modification adaptability when compared to other membrane materials such as ceramic and metallic membranes [21 – 24]. However, polymeric membranes could be plasticized when used in an environment filled with high-pressure gas causing the membrane to lose their performance and gas selectivity [25 -27]. As high concentration of carbon dioxide can be built-up in a reactor during dark fermentation processes, the measurement of stability of membrane used for CO_2 capture is necessary to determine the efficiency of the process.

In view of the foregoing and coupled with the fact that little work has been done on application of membrane-based CO_2 adsorption for improvement of bioH_2 production from organic feedstock, the aim of this study was to investigate the potential of improving bioH_2 yield during dark fermentation by employing CaO-impregnated membrane for the adsorption of CO_2 present in the reactor headspace. The efficiency of the process was estimated by measurement of H_2 and CO_2 yields and storage modulus of the membranes.

2.1 Materials Preparation

2.1.1 Seed inoculums, Feedstock and Nutrient

The anaerobic digester sludge used as inoculum was obtained from an active municipal waste digester operating at 55°C. Before its usage in the experiment, the inoculum was screened using a sieve with mesh size of 1mm to remove dirt, and later incubated at 55°C for 3 days to activate the inoculum and make it free from residual carbon source. Banana fruit without the peels was used as the feedstock for the digestion process. The banana fruit, which was obtained from a local supermarket, was ground. using a kitchen blender (Waring Commercial, USA). The fruit slurry obtained was stored in the cold room (5°C) to reduce their deterioration prior to the fermentation process. The basic medium nutrient used for the digestion process was prepared as recommended by Angelidaki and Sanders [28] except with non-inclusion of some vitamins such as cyanocobalamine, nicotinic acid, P-aminobenzoic acid, lipoic acid and DL-pantothenic acid. Before the start of the digestion process, the seed inoculum and the banana were characterized by determining their total solids (TS) and volatile solids (VS). The TS and VS of the inoculums were 1.83 ± 0.02 and 0.95± 0.01%, respectively, while the TS and VS of banana were 22.44 ± 0.49 %and 18.02 ± 0.29 %, respectively.

2.1.2 Membrane Material

The membranes used for the experiment were hydrophilic polyvinylidene fluoride (PVDF) membrane from Durapore® membrane filters (Merck Millipore, Carrigtwohill, Co. Cork IRL). The pore size, thickness and porosity and air flow rate characteristics of the membrane were 0.1 µm, 125 µm, 70 % and 0.15 L $min^{-1}cm^{-2}$ respectively. The membranes were cut and folded into rectangular dimension (3 by 6 cm), and then heat sealed using a sealing maker (HPL 450 AS, Hawo, Germany). The membranes were impregnated with two different concentrations (1 M and 2 M) of calcium oxide (CaO) solutions by immersing them in the solution for 24 hrs. after which they were air-dried for 2 hrs. before the membranes were characterized and used in the digestion process.

2.2 Experimental procedure

The semi-continuous mode experiment was conducted using Automatic Methane Potential Test System (AMPTS) (Bioprocess Control AB, Sweden). The AMPTS was made up of thermostatic water bath which served as incubator for maintaining nine reactor glass bottles at 55±1C°; gas volume measuring device/data acquisition unit containing flow cells that work by liquid displacement; and a computer that collected, analysed, and displayed the digital pulse from the gas measuring device. All the nine reactors with each having an active volume of 400 ml were seeded with the same amount of inocula (350ml), nutrient (30ml), water and substrate (20 ml). The culture was thoroughly mixed and the

initial pH of the mixture was measured as 7.8 ± 0.01 without any adjustment. The experiment was carried out in triplicate with three of the reactors containing suspended CaO-coated (1 M) membranes each, another three reactors contained suspended CaO-coated (2 M) membranes while the last three reactors were used as control without any membrane. All the reactors were then fitted with rubber stoppers with three metal tubing for feeding, effluent withdrawal and gas outlet. Before the experiment started, each of the reactors was purged with nitrogen to create anaerobic condition. The experiment was initiated with organic loading (OLR) of 4.2 g VS $l^{-1}d^{-1}$, which was later increased to 5.6 and 6.3 g VS l^{-1} d^{-1}, consecutively. The reactors, which were manually mixed by shaking and swirling once a day, were fed once in 24 hrs. with each organic loading rate maintained for three days (Table 1), and the experiment was left to run for 10 days before it was stopped.

Table 1. Process parameters for the dark hydrogen fermentative production using CO2 –sorbent coated membrane

Organic loading rate (OLR) (VS l^{-1} d^{-1})	Active volume of reactor (ml)	Feeding rate of feedstock (ml /day)	HRT (d)
4.2	400	100	4.0
5.6	400	150	2.7
6.3	400	200	2.0

2.3Analytical method

The compositions of the gases (H_2, CH_4, and CO_2) produced during the digestion process was daily monitored and measured using a gas chromatograph (Auto system, Perkin Elmer, USA) equipped with a packed column (Perkin-Elmer, 6' x 1.8" OD, 80/100, Mesh, USA) and a thermal conductivity detector (PerkinElmer, USA) set at 200 °C. The temperatures of the oven and injector were set at 75 and 150 °C respectively, and nitrogen gas at a flow rate, temperature and pressure of 20 mL/min, 60 °C and 1 bar respectively; was used as the carrier gas. The measured gas volume was adjusted to the volume at standard temperature (0 °C) and pressure (1 atm). Meanwhile, volatile fatty acids (VFA) in the effluent samples withdrawn daily were analysed using the gas chromatograph (Auto system, Perkin-Elmer, USA) but equipped with a capillary column (Zebron ZB-WAX plus, polyethylene glycol or PEG, 30m x 0.25mm x 0.25µm, USA) and a flame ionized detector (Perkin-Elmer, USA) with an injection and detection temperatures of 250 °C and 300 °C, respectively. Nitrogen at a flow rate of 2 ml/min and pressure of 20 psi was used as the carrier gas.

The membrane stability was determined by using Q-series dynamic thermal and mechanical analysis (DMTA) equipment, which measured the viscoelastic (storage modulus) property of the membrane. The storage modulus of the membrane, which was measured as a function of temperature over a range between 30 and 65 °C, was determined before and after the end of the experiment (Table 2). The membrane was cut into a test specimen with length, width and thickness of 22.81± 0.06, 8.72± 0.05 and 0.09 ± 0.02 mm, respectively. The test specimen was clamped between the movable and stationary fixtures and then enclosed in the thermal chamber. The analyser applied tensional oscillation (stress) with the frequency of 1 Hz to the test sample and recorded the sample response while slowly moving through the specified temperature range of 30 °C to 65 °C which is the rubbery plateau of the membrane above its glass transition of about -35° C.

Table 2. Comparison of strength (storage modulus) of membranes before and after the experiment

Temper-ature	Membrane impregnated with 1 M CaO (R1)		Membrane impregnated with 2 M CaO (R2)	
	Before the experi-ment	After the exper-iment	Before the exper-iment	After the experi-ment
35°C	326	302	329	252
55°C	270	162	288	207

3. RESULTS AND DISCUSSION

3.1 Gas production

Hydrogen and carbon dioxide were the major components of the gas produced while very little methane production was observed (Figures 1 - 3). A little amount of methane was produced during the first three days when the hydraulic retention time (HRT) was 4 days but the production decreased to nearly zero when the hydraulic retention time was reduced to 2.7 days. The decrease in methane production could be due to the longer doubling times required for the stabilization of methane producing bacteria [29 - 34]. Significant hydrogen productions from all the reactors were observed only after the 2nd day of the experiment. Average hydrogen yields produced daily from control reactors (Control), reactors with membrane coated with 1 M CaO (R1) and reactors with membrane coated with 2 M CaO (R2), were 53.2, 61.5 and 55.1 ml/g VS, respectively. From the hydrogen yields results, there was an increment of 15.6% in daily hydrogen yield when membrane coated with 1 M was included in the reactor headspace when compared with control. However, it seemed

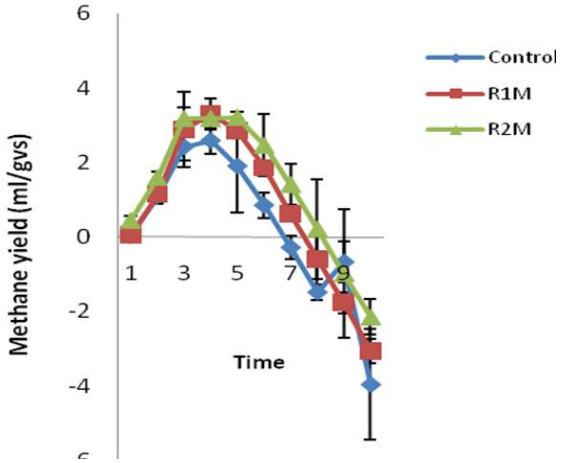

Figure 1. Cumulative methane yield during the dark fermentation process

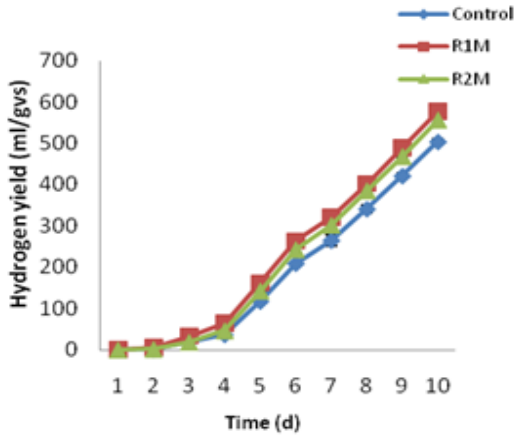

Figure 2. Cumulative hydrogen yield during dark fermentation process

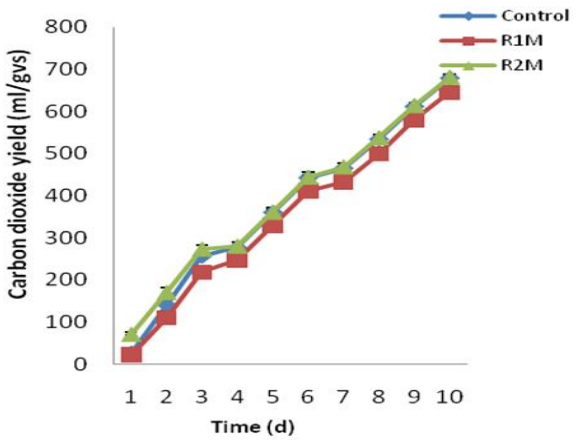

Figure 3. Carbon dioxide yield during the fermentation process

that higher concentration (2 M) of the adsorbent (CaO) could have negative effect on dark fermentative hydrogen production as it produced yield that was lower than when 1 M CaO was used for the membrane impregnation. Throughout the 10 days of the experiment, the cumulative volume of hydrogen produced from total amount of banana added (119.93 g) was 1462, 1673, 1499 ml from control, R1 and R2 respectively, equivalent to 22.7 % (control), 26 % (R1) and 23.3 % (R2) of the theoretical value (assuming that the production was from glucose alone).

3.2. Volatile fatty acid (VFA) production

The composition of the VFA produced during the experiment showed that the VFAs were composed majorly of acetate and butyrate (Figures 4 – 6). The concentrations of acetate

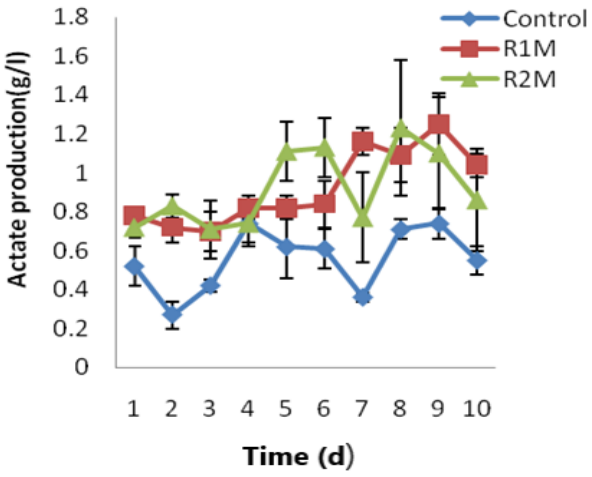

Figure 4. Acetate production during the dark fermentation process

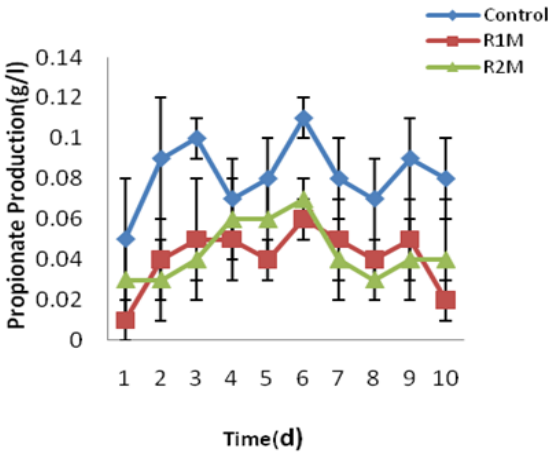

Figure 5. Propionate production during the dark fermentation process

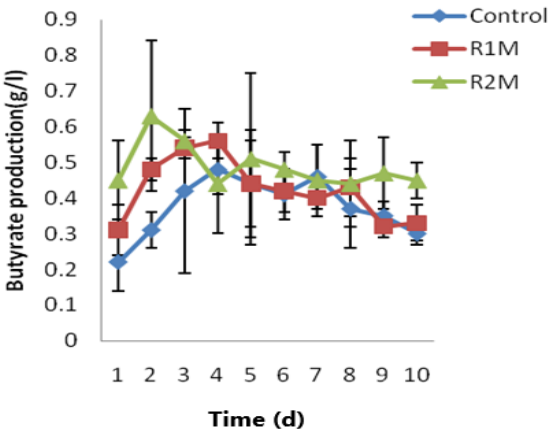

Figure 6. Butyrate production during the dark fermentation process

throughout the experiments were relatively constant with time with average values of 0.5 ± 0.07, 0.84 ± 0.08 and 0.84 ±0.2 g/l from control, R1 and R2 reactors respectively. Similarly, the butyrate concentrations varied around average values of 0.57 ± 0.08, 0.38 ± 0.05 and 0.44 ± 0.11 g/l from control, R1 and R2 reactors respectively. The relative constant values of acetate and butyrate might, in part, might be due to continuous adsorption of CO_2 which prevented the dissolution of CO_2 in the reactor medium, thereby favouring more production of CO_2 and its accompanied VFAs. Meanwhile, during the course of the experiment, the propionate production in all the reactors was not significant; having values that varied around average values of 0.075 ± 0.02, 0.04± 0.02 and 0.04± 0.02 from control, R1 and R2 reactors, respectively. The low propionate concentration might imply a relatively stable dark fermentation process during the experiment since high concentrations of propionate, often caused by organic overload, might be inhibitory to the digestion process [35].

3.4 Effect of CO_2 adsorption on membrane stability

After the end of the experiment, the storage modulus of membrane in R1 at 55 °C, which was the operating temperature, was observed to decrease by 40% while that of R2, at the same temperature, decreased by 28%. The loss in storage modulus, which is a measure of the stiffness of a material, might be due to the adsorption of CO_2 by the membranes since dipolar nature of CO_2 could allow it to have dipolar interaction with polar groups of the membrane polymer. Moreover, exposure of membrane to high CO_2 pressure above its limit of adsorption capacity could cause membrane swelling, plasticization and lost in selectivity of the component of gas streams. The higher loss in storage modulus of membrane in R1 than R2 might indicate that membrane in R1 has higher potential of adsorbing CO_2 than R2 which could be supported by the lower average CO_2 yield measured in R1 (74.5 ml/ g VS) than in R2 (79.9 ml/g VS).

4. CONCLUSION

CO_2 adsorption from reactor headspace could be a technique for improving dark fermentative hydrogen production from biomass. The present study investigated the potential for improving fermentative hydrogen yield using CaO-impregnated membrane to adsorb CO_2 present in the reactor headspace. The findings from the study showed that reactors with 1 M CaO-impregnated membrane (R1) produced hydrogen yields with 15.6% higher than those without the impregnated membranes (control), and 11.6% higher than those with 2M CaO (R2). The higher loss in storage modulus of membranes impregnated with 1M CaO than membranes impregnated with 2M CaO coupled with the lower CO_2 concentration (74.5ml/gVS) present in the reactor with 1 M CaO than the CO_2 concentration (79.9ml/gVS) present in reactors with 2 M CaO, indicated that 1M CaO-impregnated membranes were more efficient in CO_2 adsorption than 2 M CaO-impregnated membranes. Meanwhile, despite the improvement in daily hydrogen yields from reactors with CaO-impregnated membranes compared to those without membranes, the cumulative yields of R1 and R2 in 10 days of the experiment were still lower than the theoretical yields, with R1 and R2 having 26 % and 23.3 %, respectively, of the theoretical yields (assuming that the production was from glucose alone). Hence further research is necessary on membrane physical and chemical modifications to improve its CO_2-sorbent qualities.

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