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Carbon dioxide conversion to fuels and chemicals using a hybrid green process

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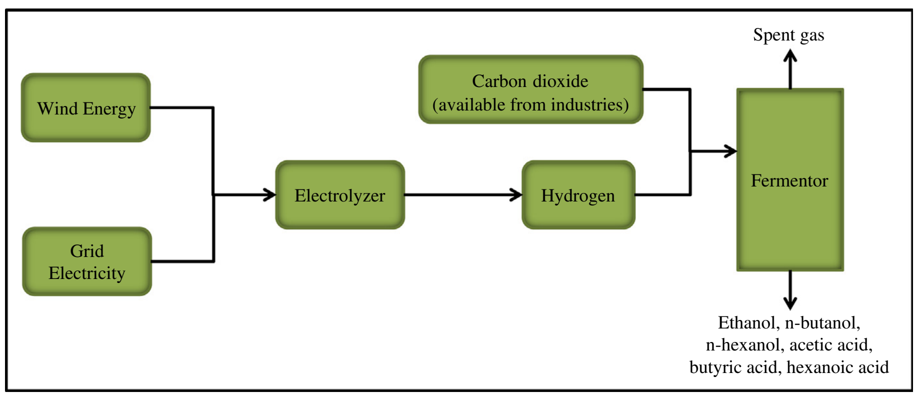
HIGHLIGHTS

- A unique CO_2 conversion technology using microorganisms was demonstrated.
- Corn steep liquor medium enhanced production of n-butanol and n-hexanol.
- Cotton seed extract (CSE) medium promoted ethanol formation.
- CSE medium without morpholinoethanesulfonic acid buffer reduced the cost by 99%.

GRAPHICAL ABSTRACT



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ABSTRACT

A unique hybrid technology that uses renewable hydrogen (H_2) and carbon dioxide (CO_2) sequestered from large point sources, to produce fuels and chemicals has been proposed and tested. The primary objective of this research was to determine the feasibility of using two acetogenic bacteria to metabolize H_2 and CO_2 for the production of ethanol. Three experiments were conducted in small scale reactors to select a bacterium, feed gas composition and nutrient medium source to produce ethanol. The results indicated that *Clostridium carboxidivorans* produced 33% more ethanol and 66% less acetic acid compared to *Clostridium ragsdalei*, making *C. carboxidivorans* the better candidate for ethanol production. Furthermore, the removal of morpholinoethanesulfonic acid (MES) buffer from cotton seed extract (CSE) medium offered a low-cost medium for fermentations. Additionally, we observed that corn steep liquor (CSL) in the medium diversified the product range with both bacteria. Maximum concentrations of ethanol, n-butanol, n-hexanol, acetic acid, butyric acid, and hexanoic acid from different fermentation treatments were 2.78 g L^{-1}, 0.70 g L^{-1}, 0.52 g L^{-1}, 4.06 g L^{-1}, 0.13 g L^{-1} and 0.42 g L^{-1}, respectively. This study highlights the important role that acetogenic microbes can offer for CO_2 conversion into valuable fuels and chemicals.

1. Introduction

The key to ensuring a sustainable and secure energy supply will depend on development of production technologies that leave a minimal carbon footprint. Most of the energy that is produced

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today comes from non-renewable sources such as coal, natural gas and crude oil. However, increasing awareness of environmental issues, climate change and sustainability will allow room for development and incorporation of different renewable energy technologies. A new renewable fuel standard has been established with a legislative target of 2.5 billion gallons of undifferentiated advanced biofuels per year by 2015 and 5 billion gallons per year by 2022 [1]. However, there is no current production of advanced biofuels in the US.

While biofuels will play a crucial role as transportation fuel, wind and solar energy are expected to play a large role in providing renewable electricity in the near future. Optimistic estimates by the US Department of Energy (DOE) show that wind energy generation has a potential to reach 305 GW by the year 2030 from 2008 production levels of 11.6 GW, supplying 20% of the US total electricity demand [2]. On the other hand, a conservative estimate on solar photovoltaic energy production by the US Energy Information Administration (EIA) shows a potential to increase to 25 GW by 2035 [3]. In spite of this, there are two important technological challenges with the development of wind and solar energy systems. First, the locations of renewable sources of energy are far from energy consumption sites. Second, renewable energy generation is uncertain and variable [4]. Unless energy generation and utilization sectors are integrated throughout the US by Smart Grids, most of the renewable energy sources will be underutilized. Energy storage is already considered a huge challenge with the growth of the renewable electricity sector. Although there are proposed options for transmission level and distribution level energy storage, these technologies are still under development [4].

The atmospheric carbon dioxide (CO_2) concentration recorded in August 2012 was 390 ppm compared to 280 ppm recorded in 1960 [5]. The increasing level of CO_2 has been cited as one of the critical reasons for changing climate patterns and global warming [6]. Among the numerous technologies under development for CO_2 utilization, such as adsorption, absorption, mineralization and gas membrane separation [7], biological processes to produce fuels and chemicals will be the most sustainable. Algal systems offer a promising source for CO_2 sequestration and conversion, but they are constrained by large land, water and sunlight requirements [8–10]. Acetogenic bacteria offer parallel opportunities for CO_2 sequestration and conversion into fuels and chemicals.

The use of acetogenic microorganisms for biofuel production from syngas (a mixture of carbon monoxide (CO), CO_2 and hydrogen (H_2)) has received a lot of attention in recent years [11–14]. Unlike this study, most studies previously carried out with acetogenic microbes used a substrate made of model syngas and producer gas or real producer gas generated from gasification of biomass [15–18]. The present study uses acetogenic bacteria to utilize CO_2 and H_2 to produce alcohols and organic acids that can be used as fuels or in the chemical industry. In practice CO_2 for the studied process could come from large point sources such as power plants, refineries and fermentation plants. H_2 required for this process can potentially be produced by electrolysis of water using off-peak electricity generated by renewable sources, which would provide a means of energy storage. Recent advances in commercial scale solar panel technology and electrolyzers may allow development of commercial CO_2 sequestrations close to large point sources of CO_2 [19,20]. Although burning fuels and chemicals produced using the studied process will release more CO_2 than directly burning H_2, safety issues associated with H_2 such as its low electro-conductivity rating impediments the advantages of H_2. Additionally, issues such as high transportation costs and the development of country scale infrastructure are challenges that still need to be addressed with the use of H_2 as a transportation fuel [21]. A schematic of the process used in this study is shown in Fig. 1.

Acetogenic bacteria such as *Clostridium carboxidivorans* and *Clostridium ragsdalei* can metabolize syngas components to produce ethanol and acetic acid [16,22,23]. However, the stoichiometric reactions governing the conversion of syngas to biofuels in literature are different from the current study and mainly focused on CO and H_2. The production of alcohols requires H_2 and CO_2 in a molar ratio of 3:1 as shown in Eq. (1) for ethanol [22].

$$6H_2 + 2CO_2 \rightarrow C_2H_5OH + 3H_2O \quad (1)$$

To define and design a feasible process, a series of experiments were performed to determine the effect of feed gas composition, media supplements and buffer on production of ethanol, n-butanol, n-hexanol and acetic acid from CO_2 and H_2. Two microorganisms, *C. ragsdalei* and *C. carboxidivorans*, were also compared in terms of ethanol, n-butanol, n-hexanol and acetic acid production.

2. Materials and methods

2.1. Culture propagation and maintenance

C. ragsdalei (ATCC PTA-7826) and *C. carboxidivorans* (ATCC PTA-7827) were sub-cultured and maintained under anaerobic conditions in 500 mL serum bottles with 100 mL working volume. A semi-defined medium containing the following components was used as the fermentation medium (per L): 30 mL mineral stock solution, 10 mL trace metal solution, 10 mL vitamin solution, 10 g corn steep liquor (CSL), 10 g morpholinoethanesulfonic acid (MES), 10 mL of 4% cysteine sulfide solution, and 0.1 mL of 1%

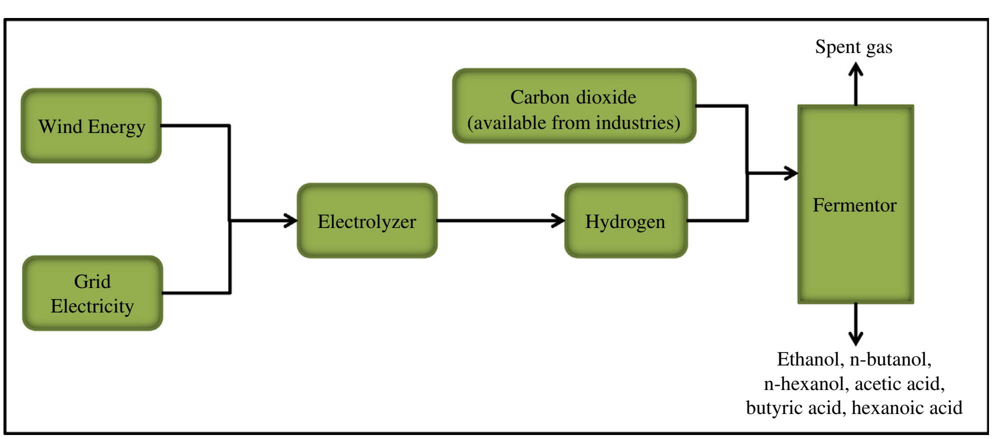

Fig. 1. Schematic of proposed concept showing the biochemical production of ethanol and other value added chemicals using CO_2 and H_2 as the feedstocks.