Clean Production of Bioplastic and Bio-oil from Solar Energy and CO_2

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ABSTRACT

This paper presents a clean technology to convert CO_2 into biomass, bioplastic and bio-oil by using a novel artificial photosynthetic system. In contrast to conventional photosynthetic plants and algae, the artificial system decouples the solar energy capture from CO_2 fixation so that CO_2 can be canptured and converted continuously regardless of the intermittency of insolation. The system consists of a photovoltaic assembly and a water electrolyzer to capture and convert solar energy into H_2 and O_2. An autolithotrophic bacterium is hired to fix CO_2 using H_2 in dark conditions. Because the microbial CO_2 fixation is not restricted by light, a high cell density (> 20 g/L) was conveniently achieved. The specific cell growth rate on CO_2 fixation was about 3 times higher than that of the fastest growing species of microalgae or cyanobacteria. About 50% of cell mass formed from CO_2 was polyester, which contains 50% more energy than starch. The biopolyester can be used either as a bioplastic, or processed into bio-oil or other drop-in chemicals. The overall efficiency from solar energy to biomass ranges from 4 to 8%, which is higher than the efficiency of plants and algae (0.5-2%). Efficiency analysis indicates that the solar electricity has the lowest efficiency (10-17%) compared with dark CO_2 fixation (32-59%) and water electrolysis (70-80%). The system efficiency can therefore be further improved with new photovoltaic technology. This new technology has a potential of high intensity carbon capture for power plants and oil refineries.

Keywords: carbon capture, solar energy, photosynthesis, biopolyester, bio-oil

1 INTRODUCTION

Global energy consumption is projected to increase, even with substantial energy conservation. Although it will be met by fossil resource in the near future, accumulation of greenhouse gases including CO_2 in atmosphere has raised concerns on global warming [1]. Solar energy is the largest renewable resource, providing more energy to the earth in one hour than all of the energy consumed by humans in an entire year [2]. Because of the intermittency of insolation, solar energy must be captured, stored and dispatched on demand. An attractive approach is to store the solar energy in biomass via photosynthetic CO_2 fixation. Indeed, biomass is the primary resource for bio-based fuels, chemicals and materials with reduced carbon footprint. The energy efficiency of conventional photosynthetic systems including plants and algae, however, is quite low (0.5-2%) [1, 2], which may result in land competition with food and feed. In addition, the overall productivity of conventional systems is also quite low because of system idle in dark conditions. Solar energy-based carbon capture is limited by the lack of a high intensity industrial process that can work efficiently on 24/7 mode.

An artificial photosynthetic system suitable for industrial CO_2 fixation is in development at University of Hawaii. Unlike the conventional photosynthetic systems, the artificial system decouples the light capture from CO_2 fixation. The relatively slow biomass formation from CO_2 can therefore be performed in dark conditions, regardless of the intermittency of solar radiation. This paper presents the information on metabolic reactions, products, and kinetics of CO_2 fixation in dark conditions, followed by efficiency analysis of the artificial photosynthetic system.

2 DARK CO_2 FIXATION

2.1 Cell Structure and Metabolic Reactions

Ralstonia eutropha, an autolithotrophic bacterium, fixes CO_2 using the same Calvin cycle in plants and algae [3]. The required NADPH and ATP, however, are generated from H_2 oxidation by using two types of hydrogenase, a membrane bounded hydrogenase (MBH) and a soluble hydrogenase (SH) in cytoplasm [4]. Figure 1 illustrates the primary metabolic reactions of CO_2 conversion with H_2 and the image of a cell under electron microscope. The microbial biomass consists of two major components, (a) polyhydroxybutyrate (PHB) in the form of white granules in Figure 1 (bottom) and (b) the residual cell mass including cell walls, membranes, proteins, nucleic acids and other biological compounds.

2.2 Bioplastic and Bio-oil Formation

The PHB content ranges from 15% to 70% of cell mass, depending on culture conditions, nitrogen nutrients in particular. PHB has a monomeric formula of $C_4H_6O_2$ and is a polyester of big molecular size (500,000 – 1,000,000 Da) [5]. It is formed by the bacterium as energy storage, and the energy content is similar to petroleum-based polyesters,

about 50% higher than the energy content of starch in plants. Purified PHB exhibits the similar thermal mechanical properties of polypropylene (PP), and is a truly biodegradable and biocompatible plastic with low carbon footprint [5]. In supercritical methanol (~240 ^{o}C), the polyester is degraded and liquefied into a bio-oil of methyl ester fractions. Figure 2 is the oil components separated in a biodiesel column and determined with a GC FID against a mixture of fatty acid methyl esters standards (FEMS).

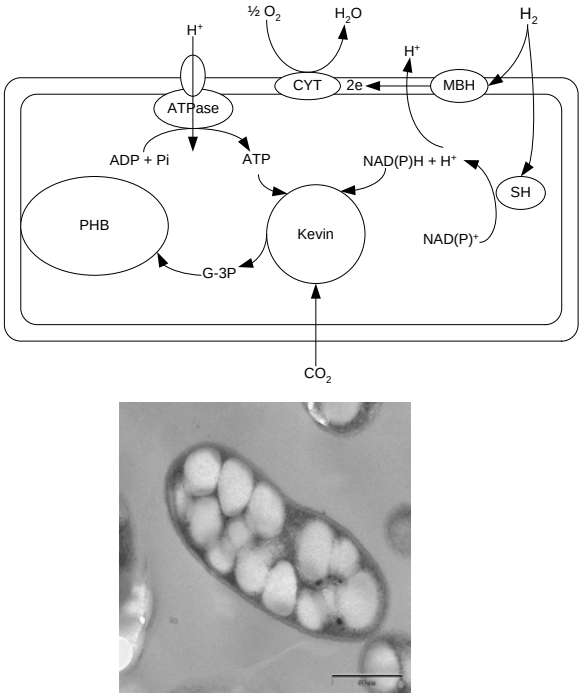

Figure 1. The primary metabolic reactions of CO_2 fixation with H_2 (top) and the electronic microscope image of *R. eutropha* cell (bottom, a bar of 500 nm). MBH: membrane-bound hydrogenase; SH: soluble hydrogenase; CYT: cytochrome; ATPase: ATP synthesis enzyme; G-3P: glyceroaldehyde-3-P; PHB: polyhydroxybutyrate.

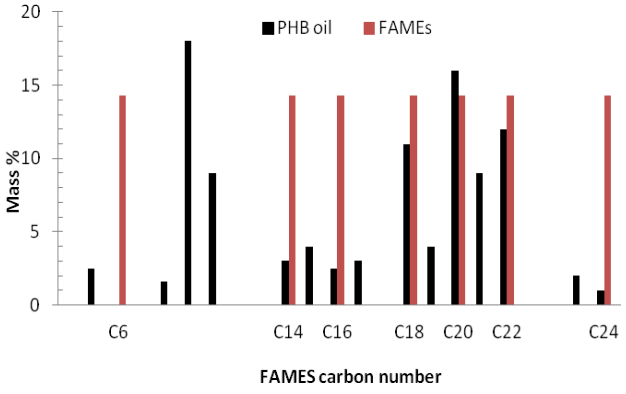

Figure 2. Fraction distribution of PHB bio-oil in a GC biodiesel column against FAME standards (C6:0-C24:0).

2.3 Kientics of biomass synthesis on CO_2

Figure 3 is the time course of cell growth on CO_2, H_2 and O_2, starting at a low optical density (OD_{620} 0.24). After an initial lag time of 10 hours, the optical density increased to 11 in 12 hours. The cell growth continued with increase in cell density from 6 to 14 g/L at a specific growth rate of 0.08 hr^{-1}. In this fast growth stage, cell mass was doubled in 8 hours and the PHB content was kept relatively low around 15 wt%. After the fast growth, the nitrogen nutrient in mineral solution was depleted, and the cells started to accumulate PHB while the residual cell mass concentration was kept at a constant level. The PHB content increased from 15% to 45%. In the PHB formation phase, the specific formation rate of PHB by residual cell mass is 0.023 g PHB (g residual cell mass.hr)$^{-1}$.

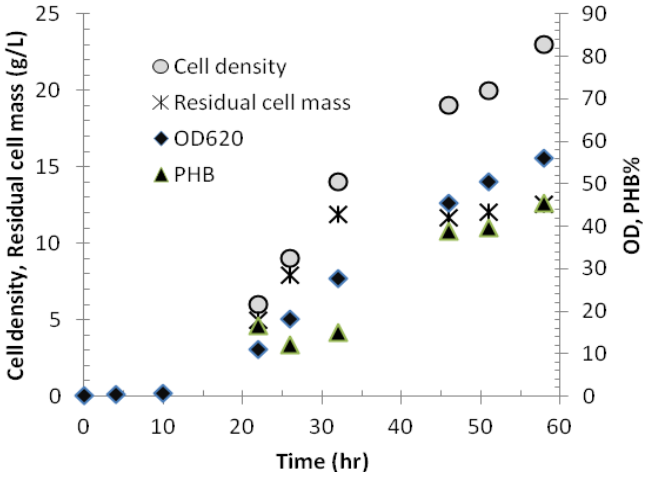

Figure 3. The time course of cell growth and biomass synthesis on CO_2 and H_2 in dark conditions: OD620 is the optical density of mineral solution at 620 nm. Residual cell mass is the amount of real cell mass excluding PHB.

Among the conventional photosynthetic species, photoautotrophic cyanobacteria exhibit the fastest growth rate on CO_2 and light. *Anabaena valialilis*, for instance, has a specific growth rate of 0.03 hr^{-1} in a photobioreactor [6]. The cell mass is doubled in 23 hours under the optimal conditions, which is about three times longer than *R. eutropha* on CO_2 and H_2 as shown above. More importantly, the maximum cell density of cyanobacterium in a photobioreactor is only 0.15 g/L, because of the light scattering by cell themselves. The dark fermentation of *R. eutropha* in this work reached a high concentration of 23 g/L, which is about 150 times higher than the cell density of cyanobacteria. A high productivity of industrial carbon capture can therefore be achieved with the artificial photosynthetic system.

3 ENERGY EFFICIENCY ANALYSIS

Figure 4 is a schematic artificial photosynthetic system consisting of a photovoltaic assembly to capture solar energy, a water electrolyzer to convert solar electricity to chemical energy (H_2 and O_2), and a dark bioreactor in which *R. eutropha* cells fix CO_2 by using H_2 and O_2. Carbohydrate (CH_2O) is the primary product from the conversion of CO_2, water and solar energy (Eq. 1).

$$CO_2 + H_2O + hv \rightarrow CH_2O \quad (1)$$

The amount of solar energy stored in biomass (CH_2O) can be estimated from its oxidation reaction (Eq. 2).

$$CH_2O + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(L)$$

$$\Delta H_{c,\,25C} = -466.7\ \text{kJ/mol} \quad (2)$$

In view of thermodynamcis, more solar energy (*hv*) is consumed in CO_2 fixation (Eq. 1) than the energy stored in biomass. The amount of solar energy required to fix CO_2, however, depends on the efficiency of whole system, which is determined by the indivudal efficiecy of PV assembly, water electrolyzer, and biosyntheiss in dark conditions.

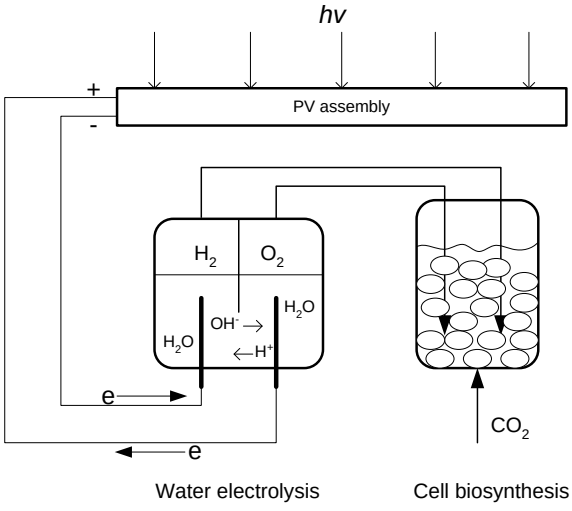

Figure 4. A schematic artificial photosynthetic system consisting of a phtvoltaic assembly, a water electrolyzer, and a dark bioreactor in which CO_2 fixation is conducted continoulsy on stored H_2 and O_2.

3.1 Efficiency of Photovoltaic Assembly and Water Electrolysis

For years, photovoltaic systems have been expansive to generate electricity from solar energy [7]. As the technology matures, the cost has been reduced significantly. Commercial PV panels with about 17% efficiency are now available at an affordable price. New technologies such as multi-junction concentrator systems have been demonstrated to achieve 39% efficiency or higher [8].

Solar electricity cannot be directly used to fix CO_2, and neither a stable source for continuous carbon capture. Water electrolysis is a cost effective mature technology by which electrical energy can be immediately converted to chemical energy stored in H_2. Hydrogen gas can be stored and used as a stable energy source. A commercial alkaline electrolyzer, for instance, can achieve 70-80% of energy efficiency [9]. The amount of energy stored in hydrogen can be estimated from its oxidation (Eq. 3).

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(L)$$

$$\Delta H_{c,\,25C} = -285.8\ \text{kJ/mol} \quad (3)$$

3.2 Efficiency of Biosynthesis

By a membrane-bound hydrogenase (MBH) located near the electron transport chain, hydrogen is split into protons and electrons (Figure 1). The electrons are transferred through the electron transport chain to O_2 to form water. The oxidation-reduction has a negative change in free energy (Eq. 4),

$$H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O \qquad \Delta G^{0'} = -56.12\ \text{kcal/mole} \quad (4)$$

The protons are transferred to form a proton motive force across the membrane, which drives ATPase to generate ATP from ADP (Eq. 5),

$$ADP + Pi \rightarrow ATP \qquad \Delta G^{0'} = +7.3\ \text{kcal/mole} \quad (5)$$

In bacterial cells, the number of ATP formed with transfer of two protons or electrons (P/2e) ranges from 1 to 4 [10]. It is not clear why there is a huge gap between the potential and real ATP formation. Environmental factors such as pH and ionic strength may play a role in the formation of ATPs. The negative change of free energy (Eq. 6) in standard conditions seems high enough for formation of 4 ATPs.

$$H_2 + \tfrac{1}{2}\,O_2 + 4(ADP + Pi) \rightarrow H_2O + 4\ ATP$$

$$G^{0'} = -26.9\ \text{kcal/mole} \quad (6)$$

With a soluble hydrogenase in cytoplasm, the cells oxidize hydrogen to drive the reduction of $NAD(P)^+$ (Eq. 7).

$$H_2 + NAD(P)^+ \rightarrow NAD(P)H + H^+$$

$$\Delta G^{0'} = -4.17\ \text{kcal/mole} \quad (7)$$

The thermodynamic analysis above indicates that one molecule H_2 may generate one molecule NADPH or one to four molecules of ATPs.

Similar to plants and algae, *R. eutropha* fixes CO_2 by using the Calvin cycle in which Rubisco is the key enzyme and glyceraldehyde-3-P ($C_3H_5O_3$-P) the product that is further converted to carbohydrates (CH_2O) [4]. It is widely accepted that fixation of 1 mole of CO_2 via the Calvin cycle needs 2 moles of NAD(P)H and 3 moles of ATP (Eq. 8).

$$CO_2 + 2NAD(P)H + 3ATP \rightarrow CH_2O \quad (8)$$

Obviously, how efficiently ATP can be formed under a protonmotive force determines to a great extent the energy efficiency of CO_2 fixation. Since the energy stored in H_2 and CH_2O is 286 kJ/mol and 467 kJ/mol, respetively (Eqs 2 & 3), the energy efficiency from hydrogen to biomass depends on how many H_2 is consumed to fix one CO_2 as shown in Table 1. It ranges from 32.6% to 59.4%, depending on how many moles of ATP are formed per mole of H_2.

ATP/H_2 (mole/mole)	4	3	2	1
NADPH/H_2 (mole/mole)	1	1	1	1
H_2/CO_2 for NADPH	2	2	2	2
H_2/CO_2 for ATP	0.75	1	1.5	3
H_2/CO_2 total (mole/mole)	2.75	3	3.5	5
Hydrogen energy (kJ)	786	857	1000	1429
Energy in biomass (%)	59.4	54.4	46.6	32.6

Table 1 Energy efficiency of biosynthesis on CO_2 and H_2.

3.3 The Overall Efficiency of Artificial Photosynthetic System

The overall efficiency from solar energy to biomass of an artificial photosynthetic system depends on:

- the energy efficiency of solar electricity of a photovoltaic assembly. A typical high efficiency of commercial PV assemblies is around 17% [11];
- The energy efficiency of solar electricity to H_2 via water electrolysis. A typical high efficiency of up to 80% can be achieved with a commercial alkaline eletrolyzer [9];
- The energy efficiency from H_2 to biomass (CH_2O) via autotrophic CO_2 fixation in dark conditions. It ranges from 32.6% to 59.4% as shown in Table 1.

The overall energy efficiency of the artificial photosyntheitc system therefore ranges from 4 % to 8%, which is higher than the theoretical efficiency (3-4%) and real efficiency (0.5-1%) of photosynthesis in plants [2]. It is also higher than the highest efficiency (2-3%) of microalgae [12]. Equally important, the artificial system can be operated 24 hours per day using the solar energy stored in H_2 to give a high productivity of the facility.

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