A Green Plastic and Drop-in Transportation Fuels from Carbon Dioxide and Renewable Energy

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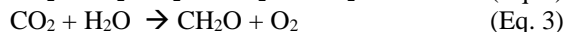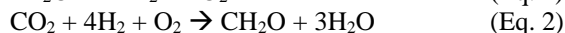
ABSTRACT

A hydrogen-oxidizing bacterium fixed carbon dioxide (CO_2) by using clean hydrogen obtained from water electrolysis with solar power. Under nitrogen nutrient limitation, CO_2 was assimilated at 0.21 g L^{-1} h^{-1}, about 7 times faster than an oil-producing green microalga. More importantly, a large portion of the reduced carbon is stored in polyhydroxybutyrate (PHB), accounting for 65% of dry cell mass. PHB is a biodegradable thermoplastic that can find a variety of environmentally friendly applications. With a solid acid catalyst, the biopolyester can be reformed into hydrocarbon oil (C6-C18) from which a gasoline-grade fuel (77 wt%) and a biodiesel-grade fuel (23 wt%) are obtained. Aromatic compounds can also be formed from PHB under acid catalysis. This paper presents an alternative route through which drop-in transportation fuels and aromatic chemicals can be directly produced from CO_2, water and renewable power.

Keywords: CO_2 fixation, microbial factory, bioplastic, green gasoline, green aromatics

1 INTRODUCTION

Carbon dioxide (CO_2) from fossil fuel combustion has caused concerns on climate change and ocean acidification. Chemolithoautotrophs including hydrogen-oxidizing bacteria play a role in the natural carbon cycle [1]. Clean hydrogen (H_2), generated from water electrolysis with solar and wind power, is a renewable energy carrier. With the rapid progress in photovoltaic (PV) technologies, solar power is now competitive with conventional powers, but has to be converted into other energy forms such as hydrogen for storage [2]. Clean hydrogen could become an inexpensive feedstock in the near future [3]. Hydrogen-oxidizing bacteria are microbial factories that can produce valuable products from CO_2 and clean H_2, including polyhydroxybutyrate (PHB), bio-oils, gasoline-grade liquid fuel, and aromatic chemicals. Since hydrogen is generated from water electrolysis with solar electricity (Eq. 1) and used for CO_2 fixation by hydrogen-oxidizing bacteria (Eq. 2), the overall CO_2 fixation reaction (Eq. 3) is the same as the natural photosynthesis. The microbial factory is particularly suitable for large scale industrial production because it can be continuously operated regardless of the intermittency of renewable powers.

$$4H_2O \rightarrow 4H_2 + 2O_2 \qquad \text{(Eq. 1)}$$
$$CO_2 + 4H_2 + O_2 \rightarrow CH_2O + 3H_2O \qquad \text{(Eq. 2)}$$
$$CO_2 + H_2O \rightarrow CH_2O + O_2 \qquad \text{(Eq. 3)}$$

2 MATERIALS AND METHODS

Strain and medium: *Cupriavidus necator* is a type strain of hydrogen-oxidizing bacteria. The autotrophic bacterium was cultivated on gas substrates (H_2:O_2:CO_2 = 70:20:10 mol%) in a mineral solution containing (1 L): 2.3 g KH_2PO_4, 2.9 g $Na_2HPO_4.2H_2O$, 1 g NH_4Cl, 0.5 g $MgSO_4.7H_2O$, 0.5 g $NaHCO_3$, 0.01 g $CaCl_2.2H_2O$, 0.05 g ferric ammonium citrate, and 1 mL trace element solution [4].

Facility: Figure 1 illustrates the laboratory facilities used in the work, consisting of a solar panel (60 W, 23V_{open}), a membrane water electrolizer (50W, 14 V DC), a gas fermenter and a thermal reactor. CO_2, H_2 and O_2 were introduced into the gas fermenter through mass flow meters according to the gas composition. The overall gassing rate was maintained at 0.2 vvm (gas volume per liquid volume per minute) throughout a fed-batch operation. The gas fermenter was designed and operated to provide a volumetric gas mass transfer rate (k_La, $_{O2}$ = 180 h^{-1}) at the low gassing rate. The culture was initiated by adding a *C. necator* inoculum (10% v/v) and maintained at 30 °C and pH 6.5-7.0.
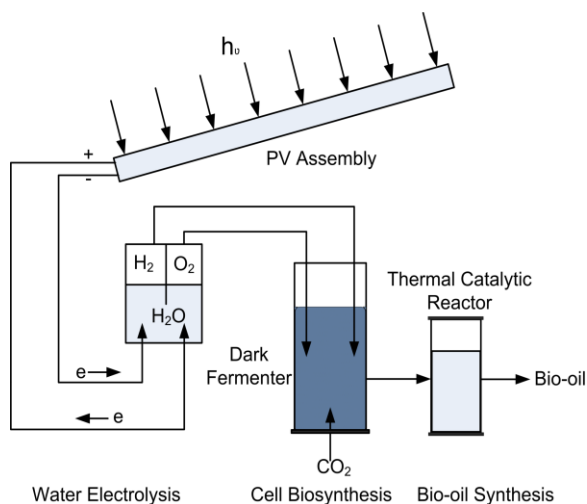

Figure 1: Schematic facility for microbial CO_2 fixation with clean hydrogen

3 RESULTS AND DISCUSSION

3.1 Microbial CO_2 fixation

Figure 2 is the time courses of gas uptake rates and microbial growth without nutrients' control. The maximum cell density reached 12.5 g L^{-1} in 39 hours, giving an average biomass productivity of 0.32 g L^{-1} h^{-1}. When the cell density reached 3.5 g L^{-1} in 16 hours, however, the dissolved oxygen (DO) concentration in the mineral solution dropped to zero and became undetectable with a DO probe. The CO_2 fixation was limited by oxygen mass transfer since then. Under the oxygen limited conditions, however, the concentrations of dissolved H_2 and CO_2 were maintained at sufficiently high levels [5]. Before the oxygen limitation, the specific growth rate was 0.13 h^{-1} and the dry cell mass (DCM) concentration was doubled in 5.3 hours. CO_2 assimilation reached the maximum rate of 1.5 g L^{-1} h^{-1}. At the maximum H_2 uptake rate of 201 mmole L^{-1} h^{-1}, the uptake rates of O_2 and CO_2 were 65 and 28 mmole L^{-1} h^{-1}, respectively. The molar ratios of H_2/CO_2 and O_2/CO_2 were 7.1 and 2.3, respectively. Since H_2 is the only source of energy and reducing agent for CO_2 fixation, 4.6 moles of hydrogen was oxidized (H_2/O_2=2) for energy supply and 2.5 moles of hydrogen used as the reducing equivalents for fixation of 1 mole CO_2.
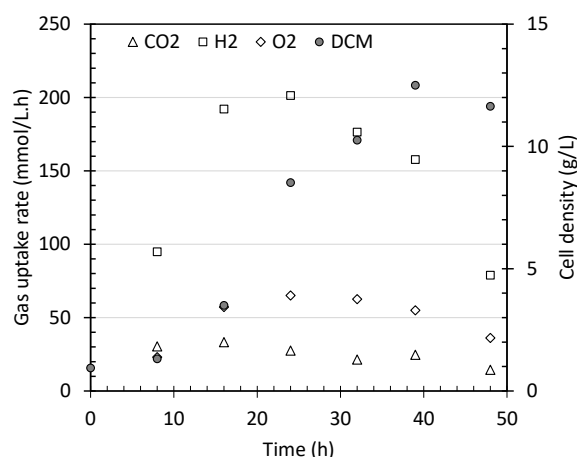

Figure 2. Time courses of cell density (DCM) and gas uptake rates in a fed-batch gas fermentation.

3.2 Bioplastic

Under nitrogen nutrient limitation, CO_2 was not used for cell mass formation, but for biosynthesis of polyhydroxybutyrate (PHB) as an intracellular energy storage (Figure 3). The PHB content accounted for 65 wt% of dry cell mass [5]. By using a proprietary technology, the PHB granules were recovered and purified (>98 wt%)

while the residual cell mass (RCM) was left for further treatment. As shown in Figure 3, the purified PHB is a thermoplastic material (melting point 175 °C) and can be processed with conventional extruders [6]. The material properties of PHB are similar to those of polypropylene.
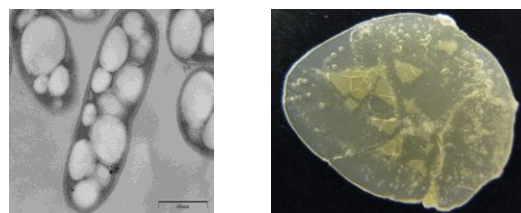

Figure 3: PHB granules formed in bacterial cells (left) and purified PHB plastic in melting condition (right).

3.3 Drop-in liquid fuels

PHB is a homopolyester of 3-hydroxybutyrate (3HB) with a chemical formula of $C_4H_6O_2$ (MW 86). It could be oligomerized into a liquid, but with a low heating value (HHV=22.5 MJ/kg) because of the high oxygen content (37.2 wt%). Under catalysis of a solid phosphoric acid (SPA), the biopolyester is degraded and deoxygenated via decarboxylation into hydrocarbons as shown in Scheme 1. The theoretical carbon recovery of hydrocarbons is 75 wt% (3 out of 4 carbons recovered). Table 1 gives the products distribution and carbon recovery in gas, liquid and solid phases after the reforming. The combined carbon recovery of oil and propylene is 61.7 wt%, which is 82% of the theoretical carbon recovery. A small amount of water (H_2O) and char was formed as the byproducts of deoxygenation with hydrogen. The water soluble products account for 11% of orignial carbon.

Table 1: Products distribution and carbon recovery of catalytic PHB refining

Phase	Products	C recovery (wt%)
Gas	CO_2	18.0
	C_3H_6	4.9
Liquid	Oil (C4-C16)	57.0
	Water soluble	11.0
Solid	Char	<2
Total		>91
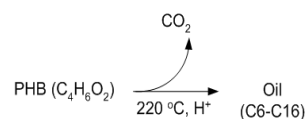
Scheme 1: PHB decarboxylation into hydrocarbons

The hydrocarbon oil is a mixture of C4-C16 and can be separated into two fractions: a light oil (77 wt%, bp 40 °C-250 °C) and a heavy oil (23 wt%, bp 250 °C-310 °C) via distillation. Table 2 compares their elemental compositions and high heating values with a commercial gasoline.

Obviously, the light oil is a bio-based gasoline-grade liquid fuel and the heavy oil is very close to a commercial biodiesel [7].

Table 2: Comparison of PHB oils with a commercial gasoline

Fuels	Gasoline	Light oil	Heavy oil
BP (°C)	40-200	40-250	250-310
Water (wt%)	0.14	0.02	0.02
Ash (wt%)	<0.001	<0.001	<0.001
S (wt%)	0.664	0.061	0.061
C (wt%)	80.4	83.2	65.5
H (wt%)	12.3	10.3	8.6
N (wt%)	0.15	0.16	0.17
O (wt%)	6.35	6.3	25.6
HHV (MJ/kg)	41.8	42.1	34.4

3.4 Green aromatics

It has been confirmed that the first key intermediate of PHB thermal catalytic reforming is crotonic acid (CA, $CH_3CH=CHCOOH$) [8]. CA is then deoxygenated into propylene (C_3H_6) from which alkanes and alkenes are formed. In a high acid solution (100% H_3PO_4), however, ketonization of CA became a major route generating aromatic compounds as shown in Scheme 2 [8]. The aromatic compounds were identified with GCMS and the major one is 1,2,3,4-tetramethyl-5-(1-methylethyl)-benzene (1) with a retention time of 32.5 min in the chromatogram (Figure 4). It has a high degree matching (>80%) with NIST 11 mass spectral library. The hydrocarbons derived from PHB under special conditions could be a rich source of green aromatic compounds.
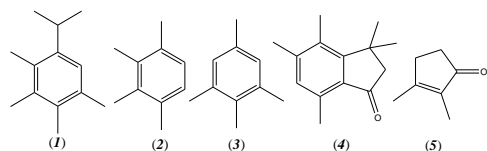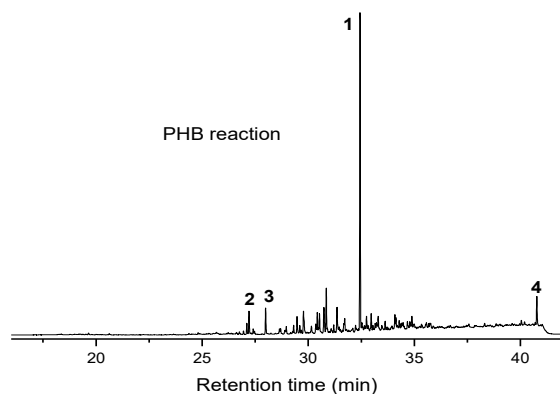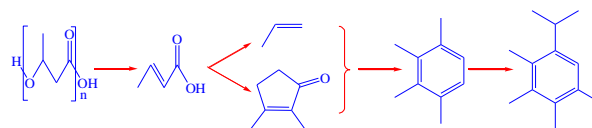

Figure 4. GCMS chromatogram and major aromatic compounds derived from PHB

A main reaction route for H_3PO_4 catalytic conversion of PHB to aromatic hydrocarbons

Scheme 2: Aromatics formation from PHB

3.5 Bio-oil and nutrients derived from residual cell mass (RCM)

In addition to PHB ($C_4H_6O_2$), the reduced carbon was also stored in residual cell mass (RCM) and its chemical formula ($CH_{1.69}O_{0.46}N_{0.25}$) is determined from elemental analysis [9]. After PHB are recovered, RCM was left and could be liquefied at a moderate temperature (150-300 °C). According to their solubility in methylene chloride, the thermal hydrolysates can be separated into two fractions: the hydrophobic compounds in the solvent and the hydrophilic compounds in an aqueous solution. The hydrophobic liquid is similar to the bio-oils obtained from hydrothermal liquefaction of high plants and microalgae biomass. Table 3 compares the elemental composition and high heating value of bio-oils derived from *C. necator* RCM, microalgae and cellulosic biomass. The bio-oil derived from *C. necator* RCM is similar to those derived from microalgae, but has a higher heating value than the bio-oils derived from plant biomass, because of lower oxygen content. The hydrophilic compounds are rich with nitrogen and up to 67% of nitrogen (primarily proteins) in the original RCM was left in water. The N-rich solution can be reused in microbial CO_2 fixation to save nutrients. It was found out that the nutrient value of 0.2 g N of RCM hydrolysates was equivalent to 1.2 g $(NH_4)_2SO_4$ for autotrophic growth of *C. necator* on CO_2 and H_2.

Table 3. The elemental composition and high heating value of bio-oils derived from *C. necator* RCM, microalgal and cellulosic biomass [9]

Biomass	C%	H%	O%	N%	HHV (MJ/kg)
C. necator	70.9	9.4	11.8	7.9	34.6
Spirulina	68.3	8.3	16.4	6.2	31.5
Nannochloropsis	77.9	9.0	8.6	3.4	38.0
Corncob	63.0	6.8	28.8	0.4	25.4
Cheery stones	63.2	6.9	29.6	0.5	25.4

3.6 Energy efficiency

Biological CO_2 fixation needs reducing equivalents (NADH, NADPH) and energy that is usually obtained through hydrolysis of adenosine triphosphate (ATP). In plants and microalgae, they are generated from water splitting under sunlight. The solar energy conversion

efficiency of higher plants, however, is quite low. The theoretical maximum energy efficiency of photosynthesis is less than 5% and a real efficiency less than 1% [10]. A high energy efficiency (about 2%) of microalgae is observed in a small two dimensional photobioreactor [11]. With the artificial photosynthesis system (Figure 1), solar energy was converted to chemical energy of biomass in three steps: sunlight to electricity with solar panel, electricity to hydrogen with water electrolyzer, and hydrogen energy to cell mass via gas fermentation. The efficiencies of commercial solar module and water electrolyzer have now reached 20% and 75%, respectively, giving a combined solar hydrogen efficiency of 15%. As shown in Figure 2, *C. necator* fixes one mole CO_2 by using 7.1 moles of H_2. The following overall stoichiometry is obtained from elemental balance, not considering the cell maintenance energy:

$$CO_2 + 7.1H_2 + 2.5O_2 + 0.25NH_3 \rightarrow CH_{1.74}O_{0.46}N_{0.19} + 6.6H_2O$$
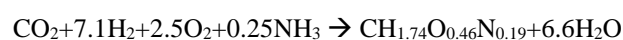
The energy efficiency of CO_2 fixation is 24.4% based on the heats of combustion of hydrogen (142 MJ/kg) and cell biomass (20.1 MJ/kg) [5]. The overall energy efficiency from sunlight to biomass is therefore 3.6%, which is about two folds of microalgae [11]. The stoichiometry also indicates that the biomass yield on hydrogen could reach 1.7g DCM/g H_2. With increase of cell density in a fed-batch fermentation, however, more energy is used for cell maintenance, which may be upto 7 mmole H_2 g DCM^{-1} h^{-1} or 2 MJ kg^{-1} DCM h^{-1}.

3.7 Comparison with microalgae

Microalgae can produce lipid as an intracellular energy storage under nutrient limitation conditions. A green microalga *Neochloris oleoabundans* cultivated in a photobioreactor under stable indoor conditions was used for comparison [12]. The strain was cultivated in a mineral solution at 30 ºC with continuous gassing of an enriched air (5% CO_2). Sixteen fluorescent lamps provided continuous illumination of 360 µmol m^2 s^{-1} from which the total electrical power is estimated [5]. Table 4 compares the CO_2 fixation by *C. necator* and *N. oleoabundans* under the conditions of high PHB or lipid productivity. Both strains exhibited high productivity of intracellular energy storage (PHB or lipid) under nitrogen nutrient limitation, but usually at the expense of biomass productivities. The CO_2 uptake rates are estimated by using an average carbon content of biomass (48 wt%). Electrical power is the energy input either for lighting or for water electrolysis, and only a small portion of the energy is stored in cell mass and the intracellular products (PHB or lipids) [5]. Obviously, chemolithotrophic CO_2 fixation gives much higher cell density, CO_2 fixation rate, bioproduct productivity and energy efficiency than conventional photosynthesis.

Table 4: Comparison of chemoautotrophic and photosynthetic CO_2 fixation

CO_2 fixation	Chemoautotroph	Photosynthesis
Species	*Cupriavidus necator*	*Neochloris oleoabundans*
Cell density (g/L)	8.8	2.4
Biomass (g/L/h)	0.12	0.017
CO_2 uptake (g/L/h)	0.21	0.03
PHB or Lipid (wt%)	65	33.2
Productivity (g/L/d)	1.87	0.13
Electrical energy efficiency (%)	6.4	0.98
Reference	[5]	[12]

4 CONCLUSION

This paper presents an alternative route through which renewable powers can be used to convert CO_2 into valuable products. The green factory of hydrogen-oxidizing bacterium exhibits much higher CO_2 fixation rate, product productivity and energy efficiency than conventional photosynthesis. The new technology is suitable for large scale industrial production because it can be continuously operated regardless of the intermittency of renewable powers.

ACKNOWLEDGEMENT

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