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Energy analysis for an artificial tree generating polymer fuels from water and CO_2

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ABSTRACT

Solar energy is one of the most abundant sources of renewable energy. The utilization of solar energy and CO_2 in the atmosphere to generate fuels is regarded as a great way to resolve both the problems of fossil fuel depletion and global warming. An artificial tree was constructed to generate polymer fuels from water and CO_2 in the atmosphere. Solar panels acted as leaves to absorb solar energy and generate electric energy, and the CO_2 in the air was absorbed by alkalized water and then converted to polymer fuels in an electrolytic cell. This tree yielded an energy efficiency of 53.3% for the generation of polymer fuels, and the ratio between the combustion heat of the polymers and the electric energy consumption was 701.6%. Additionally, the energy conversions in the process of polymer generation were investigated, and the evidences of radicals generated from water by electric field induction were provided. The results provide an alternative method to utilize solar energy.

1. Introduction

The current shortages of fossil fuels and global warming have attracted worldwide attention. The consumption of fossil fuels has rapidly increased due to the increasing energy demands of anthropogenic activities [1,2]. This increase is expected to lead to a shortage in fossil fuels and a severe increase in the carbon dioxide levels in the atmosphere, which causes global warming [3,4].

The utilization of solar energy [5,6] and other renewable energies [7–9] is necessary to address this shortage in fossil fuels. Solar energy is the most abundant renewable energy in modern society and is generally utilized to generate electric power via photovoltaic cells (PVC). The most familiar PVC is the multi-crystalline silicon PVC, which reaches efficiencies of approximately 14.0 to 19.0% [10,11]. Solar energy can be converted into hydrogen fuel energy via photovoltaic electrolysis [12] and photocatalysis [7]. Eker and Kargi [13,14] reported a hydrogen energy and electric energy consumption ratio via photovoltaic electrolysis of 92.0% for wastewater. Abdi, et al. reported an energy efficiency of (hydrogen/solar) 4.90% for photocatalytic hydrolysis [15].

Reducing the CO_2 concentration in the atmosphere is usually considered the key method to address global warming. In addition to limiting fossil fuel combustion, the large-scale planting of trees is effective to reduce the CO_2 concentration in the atmosphere [16]. However, forest areas are limited by the conditions of the land area, soil quality and the climate. Thus, the CO_2 in the atmosphere needs to be reduced by artificial means in addition to planting trees [17].

Solar energy can be utilized to convert CO_2 to fuels by artificial means. This process is commonly referred to as artificial photosynthesis and regarded as a great way to resolve both the problems of fossil fuel depletion and global warming [18]. To date, a variety of artificial photosynthesis approaches have been carried out. Although these approaches have successfully produced H_2, CO, HCOOH, and CH_3OH, their efficiencies remain too low to act as green plants, which auto absorb the CO_2 from the atmosphere and generate complex organic molecules, such as sugar, cellulose, and lignin [19]. Anyway, our group has developed an artificial photosynthesis apparatus with a photovoltaic reactor and recorded current efficiencies of 5.18% for polymers [20,21]. This technology was further developed to mimic plant reactor that auto-absorbs CO_2 from the atmosphere and produces complex organic polymer at a very high apparent current efficiency.

2. Methods and materials

2.1. Construction of the artificial tree

The artificial tree mainly consists of a solar panel, an accumulator, and an electrolytic cell, as shown in Fig. 1. The main features of the artificial plant are listed below:

(1) Instead of chloroplasts in leaves [22,23], a solar panel was used to absorb solar energy, which was then converted into electric energy. (2) Instead of the lines of complex organic compounds in the reaction

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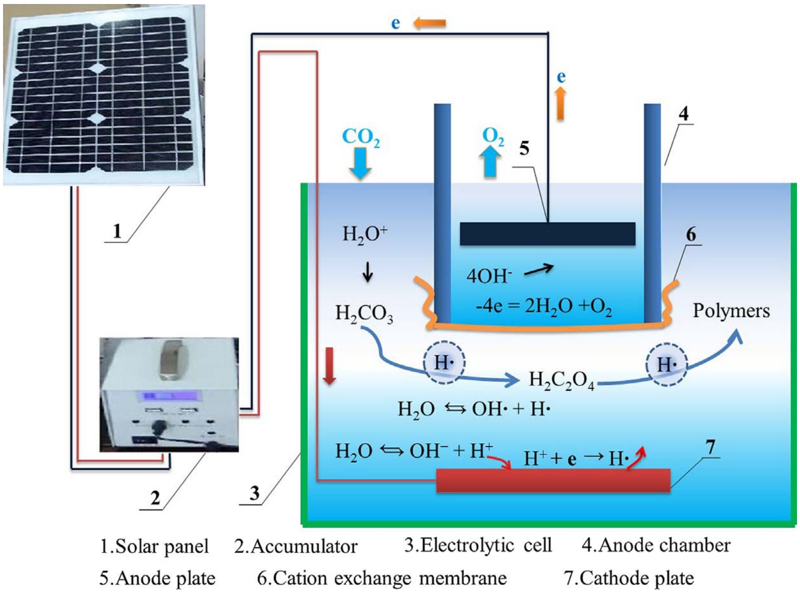

Fig. 1. Structure of the artificial tree.

centers of chloroplasts [22,24], wires were used to lead the electronic transformation. (3) The CO_2 in the air was absorbed by water and converted to H_2CO_3. (4) Instead of the chloroplast in leaves, a special electrolytic cell served as the sites of carbon reactions. Oxalates and some complex organic compounds are generated in the special electrolytic cell.

The anode plates were constructed using a titanium metal electrode, and the cathode plates were constructed using a Nickel-chromium-iron alloy electrode (Ni: 14.2%; Cr: 16.7%; Fe: 69.1%). To improve the efficiency of the artificial tree, a cation exchange membrane was used as the separation membrane instead of a micro membrane used in previous research [20]. Instead of 5.0 V, a voltage of 3.0 V was obtained from the accumulator, which was charged from a solar panel with an effective area of 0.25 m^2. The area of the cathode plate was 0.00625 m^2.

2.2. *Operation of the artificial tree*

One liter of water was fed into the special electrolytic cell, and approximately 10 ml of 0.50% NaOH solution was then added to adjust the pH to 7.5. The reactor was then operated at atmospheric condition, room temperature (12–28 °C) and voltages of 3.0 V for 144 h to produce a solution.

2.3. *Separation and analysis of the polymers*

The produced solution was first treated with an acidic cation-exchange resin followed by treatment with a strong basic anion-exchange resin to remove the generated oxalate and other electrolytic compounds, and produce a neutral solution. Finally, the neutral solution was evaporated and dried to generate a neutral solid product, i.e., a polymer. The polymer consisted of the basic units of oxalate, glycol and 2-α-hydroxyl acetic acid; called polyoxalate-glycol-2-α-hydroxyl acetic acid-glycol, or $H(C_8H_{10}O_8)_nOH$ [20]. (See Section 1 of supplemental materials)

2.4. *Determination of glycol and oxalate*

The mass of the oxalate was determined using high performance liquid chromatography (HPLC), and the mass of glycol was determined using high performance gas chromatography (HPGC). (See Section 2 and 3 of supplemental materials)

2.5. *Thermal calculations*

The formation heat of hydrogen free radical ($H_{f,H^{\cdot}}$) is estimated to be 218.0 kJ/mol, calculated based on following scheme. Where, ΔH_1 is the reaction heat, which is equivalent to the H—H bonding energy; H_{f,H_2} is the formation heats of hydrogen gas.

$$H\text{–}\ H \xrightarrow{\Delta H_1} H^{\cdot} + H^{\cdot} \tag{1}$$

$\Delta H_1 = 436.0$ kJ/mol,

$$2H_{f,H^{\cdot}} - H_{f,H_2} = 436.0\ \text{kJ/mol} \tag{2}$$

The formation heat of hydroxyl free radical ($H_{f,^{\cdot}OH}$) is estimated to be −40.83 kJ/mol, calculated based on following scheme. Where, ΔH_2 is the reaction heat, which is equivalent to the one broken H—O bonding energy. H_{f,H_2O} is the formation heat of water.

$$H\text{—}O\text{–}\ H \xrightarrow{\Delta H_2} H^{\cdot} + {}^{\cdot}OH \tag{3}$$

$\Delta H_2 = 463.0$ kJ/mol,

$$H_{f,H^{\cdot}} + H_{f,\dot{O}H} - H_{f,H_2O} = 463.0\ \text{KJ/mol} \tag{4}$$

The formation heat of the polymer ($H_{f,pol.}$) is estimated to be −1844.52 kJ/mol (n = 1), calculated based on following scheme. Where ΔH_3 is the reaction heat, which was determined using a calorimeter; H_{f,H_2O} and H_{f,CO_2} are the formation heats of water and CO_2 gas, respectively.

$$H(C_8H_{10}O_8)nOH + 13/2O_2 \xrightarrow{\Delta H_3} 8nCO_2 + (5n+1)H_2O \tag{5}$$

Order, n = 1;
$\Delta H_3 = -12.9$ kJ/g $= -3018.6$ kJ/mol,

$$(8H_{f,CO_2} + 6H_{f,H_2O})-(H_{f,pol.} + 13/2H_{f,O_2}) = -3018.6\ \text{kJ/mol} \tag{6}$$

The change of enthalpy of the total polymer generation reaction (ΔH_4) was estimated to be +3018.6 kJ/mol (n = 1); for it was the reverse of reaction (5). Calculated by Gauss software, the formation Gibbs free energy of the generated polymer (n = 1) is −908.59 kJ/mol. Thus, calculated by Eq. (8), the change of Gibbs free energy of the total polymer generation reaction (ΔG_1) is estimated to be +3669.59 kJ/mol.

$$8nCO_2 + (5n+1)H_2\ O \xrightarrow[\Delta G_1]{\Delta H_4} H(C_8H_{10}O_8)nOH + 13/2O_2 \uparrow \tag{7}$$

$$\Delta G_1^0 = (\Delta G_{Pol.}^0 + 6.5\Delta G_{O_2}^0)-(8\Delta G_{CO_2}^0 + 6\Delta G_{H_2O}^0) \tag{8}$$