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Chapter

Glycerol as a Superior Electron Source in Sacrificial H₂ Production over TiO₂ Photocatalyst

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Abstract

Biodiesel fuel (BDF) has gained much attention as a new sustainable energy alternative to petroleum-based fuels. BDF is produced by transesterification of vegetable oil or animal fats with methanol along with the co-production of glycerol. Indeed, transesterification of vegetable oil (136.5 g) with methanol (23.8 g) was performed under heating at 61°C for 2 h in the presence of NaOH (0.485 g) to produce methyl alkanoate (BDF) and glycerol in 83.7 and 73.3% yields, respectively. Although BDF was easily isolated by phase separation from the reaction mixture, glycerol and unreacted methanol remained as waste. In order to construct a clean BDF synthesis, the aqueous solution of glycerol and methanol was subjected to sacrificial H₂ production over a Pt-loaded TiO₂ catalyst under UV irradiation by high-pressure mercury lamp. H₂ was produced in high yield. The combustion energy (∆H) of the evolved H₂ reached 100.7% of the total ∆H of glycerol and methanol. Thus, sacrificial agents such as glycerol and methanol with all of the carbon attached to oxygen atoms can continue to serve as an electron source until their sacrificial ability was exhausted. Sacrificial H₂ production will provide a promising approach in the utilization of by-products derived from BDF synthesis.

Keywords: BDF, photocatalyst, TiO₂, sacrificial agent, glycerol, hydrogen

1. Introduction

The major issue in the current world is an urgent need to stop the increase of CO₂ levels. A large amount of consumption of fossil resources causes serious environmental problems such as global warming and air pollution. Therefore, biofuels such as bioethanol, bio-hydrogen, and biodiesel (BDF) have gained much attention as renewable and sustainable energy alternative to petroleum-based fuels [1]. However, the problems to be solved for practical uses still remain in each biofuel. In bioethanol, the ethanol concentrations are still too low to isolate pure ethanol by distillation at a low energy cost [2, 3]. Bio-hydrogen is isolated spontaneously from reaction mixtures without operations to separate. However, it is needed to construct newly a supply system to vehicles.

BDF is produced by transesterification of vegetable oil or animal fats with methanol along with the co-production of glycerol [Eq. (1)] [4]. Although methyl alkanoate (BDF) is easily isolated by phase separation, a mixture of glycerol and unreacted methanol remains in aqueous solution as waste. New utilization of these
wastes is required. Reforming of glycerol has been extensively investigated through pyrolysis [5, 6], steam gasification [7, 8], and biological reforming [9, 10]. We have focused on photocatalytic reforming over titanium dioxide (TiO$_2$) [11]:

\[
\begin{align*}
&\text{RCO}_2-\text{CH} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{RCO}_2-\text{CH} + 3\text{CH}_2\text{OH} \\
&\xrightarrow{\text{N}_2\text{O}} \quad 3\text{RCO}_2\text{CH}_2 + \frac{\text{H}_2}{2} + \frac{\text{HO}}{2}
\end{align*}
\]

Figure 1. Photocatalytic water splitting over TiO$_2$.

TiO$_2$ has a semiconductor structure with 3.2 eV of bandgap, which corresponds to 385 nm of light wavelength [12]. Therefore, the TiO$_2$ can be excited by 366 nm emitted from a high-pressure mercury lamp. Irradiation of the TiO$_2$ induces charge separation into electrons and holes (Figure 1). Electron excited to the conduction band serves to reduce water to H$_2$. Evolution of H$_2$ is usually accelerated by deposition of noble metals (Pt, Pd, and Au) onto the TiO$_2$. The positive charge (hole) oxidizes hydroxide absorbed on the surface of TiO$_2$ to generate hydroxyl radicals, which is eventually transformed to O$_2$ [13]. However, spontaneous conversion of hydroxyl radical into O$_2$ is inefficient. Moreover, water splitting into O$_2$ and H$_2$ is a large uphill reaction, resulting in rapid reverse reaction.

On the other hand, the hydroxyl radicals can be effectively consumed by the use of electron-donating sacrificial agents (hole scavengers), thus accelerating the H$_2$ production (Figure 1) [14]. This method is named “sacrificial H$_2$ production.” The sacrificial H$_2$ production is an uphill process, but the energy change is small. Therefore, the sacrificial H$_2$ production proceeds more smoothly compared with water splitting without sacrificial agents, thus providing a convenient method to generate H$_2$ [15]. When one equivalent of hydroxyl radical is consumed, one equivalent of electron is generated to produce 0.5H$_2$.

During our investigations on sacrificial H$_2$ production over a Pt-loaded TiO$_2$ (Pt/TiO$_2$) [15], it was found that sacrificial agents with all of the carbon attached oxygen atoms such as saccharides, polyalcohols (e.g., arabinol, glycerol, 1,2-ethandiol), and methanol continued to serve as an electron source until their sacrificial ability was exhausted. Glycerol (1a) and methanol (1b) are by-products from BDF synthesis. The 1a has the potential to produce hydrogen in theoretical yield of seven equivalents, whose combustion energy ($\Delta H = 1995$ kJ mol$^{-1}$) is larger than $\Delta H$ of 1a (1654.3 kJ mol$^{-1}$) [Eq. (2)]. Also, 1b can produce three equivalents of hydrogen, whose $\Delta H$ (855 kJ mol$^{-1}$) is larger than $\Delta H$ of 1b (725.7 kJ mol$^{-1}$) [Eq. (3)] [16]. Thus, photo-energy can promote uphill process:

\[
\begin{array}{c}
\text{C}_3\text{H}_4\text{O}_3 + 3\text{H}_2\text{O} \\
1\text{a} (1654.3 \text{ kJ mol}^{-1})
\end{array}
\xrightarrow{\text{h} \nu \text{ Pt/TiO}_2}
\begin{array}{c}
3\text{CO}_2 + 7\text{H}_2 \\
(1995 \text{ kJ mol}^{-1})
\end{array}
\]

[2]
Glycerol as a Superior Electron Source in Sacrificial H\textsubscript{2} Production over TiO\textsubscript{2} Photocatalyst
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2. Outline of conversion of glycerol to hydrogen

Generally, biomass reforming is started by the production of water-soluble materials from biomass through biological treatment as well as chemical reaction [17, 18]. The resulting water-soluble materials (saccharides, amino acids) are converted to biofuels such as ethanol, methane, and hydrogen through various catalytic reactions in aqueous solution. Our biomass reforming is performed in aqueous solution through sacrificial H\textsubscript{2} production over Pt/TiO\textsubscript{2} using water-soluble materials derived from lignocelluloses [19–21] and chlorella [22] (Figure 2).

In this chapter, we will show H\textsubscript{2} production through sacrificial H\textsubscript{2} production over Pt/TiO\textsubscript{2} using 1\textsubscript{a} and 1\textsubscript{b} from standpoints of construction of renewable energy system and clean synthesis of BDF.

![Figure 2. Outline of conversion of glycerol to hydrogen.](image)

3. Materials and method

3.1 Apparatus

NMR spectra were taken on a Bruker AV 400M spectrometer for CDCl\textsubscript{3} solution. LC-MS analysis were performed on a Waters Alliance 2695 under conditions (ESI ionization, capillary voltage 3.5 kV, source temperature 120°C and desolvation temperature 350°C) using column (Waters, SunFire C18, 2.1 mmΦ \times 150 mm) and 1% formic acid in MeOH-H\textsubscript{2}O (6:4) as an eluent solution. GLC analysis of solution was performed on a Shimadzu 14A gas liquid chromatograph with FID detector at a temperature raised from 50 to 250°C using a capillary column (J & W CP-Sil 5CB, 0.32 mmΦ \times 50 m).

3.2 Photoreaction apparatus

Reaction vessel was a cylindrical flask with 30 cm of height and 7.5 cm of diameter, which had three necks on the top. A high-pressure mercury lamp (100 W, UVL-100HA, Riko, Japan), which emitted mainly a light at 313 and 366 nm, was inserted into the large central neck of the reaction vessel. The reaction vessel was connected to a measuring cylinder with a gas-impermeable rubber tube to collect the evolved gas. The reaction vessel was set in a water bath to keep it at 20°C. The stirring of the solution was performed by magnetic stirrer.
3.3 Preparation of photocatalyst

Almost all research has used TiO$_2$ in anatase form such as P25 (Degussa Co. Ltd., Germany) and ST01 (Ishihara Sangyo Co. Ltd., Japan) for photocatalytic H$_2$ production. A Pt-loaded TiO$_2$ catalyst (Pt/TiO$_2$) was prepared by photo-deposition method according to the previous literature [23]. An aqueous solution (400 mL) containing TiO$_2$ (4.0 g, ST01), K$_2$PtCl$_6$ (40–400 mg), and 2-propanol (3.06 mL) was introduced reaction vessel, which was large scale of cylindrical flask with 35 cm of height and 9.0 cm of diameter. After the oxygen was purged by N$_2$ gas bubbling for 20 min, the solution was irradiated by stirring. After irradiation for 24 h, the water was entirely removed from the reaction mixture by an evaporator. The resulting black precipitate was washed with water on a filter and then dried under reduced pressure to produce Pt/TiO$_2$ [14]. The Pt content on TiO$_2$ was optimized to be 2.0 wt% by the comparison of the H$_2$ amounts evolved from photocatalytic reaction using 1a (115 mg, 1.25 mmol) over various Pt contents of the Pt-doped TiO$_2$ (100 mg, 1.25 mmol) [15]. The structure of Pt/TiO$_2$ was analyzed by a Shimadzu XRD 7000 diffractometer.

3.4 Photocatalytic H$_2$ production

Pt/TiO$_2$ (100 mg) and the given amounts of aqueous solution of sacrificial agent were introduced to reaction vessel. The volume of the reaction solution was adjusted to 150 mL with water. Oxygen was purged from reaction vessel by N$_2$ gas for 20 min. TiO$_2$ was suspended in aqueous solution by vigorous stirring during the irradiation. Total volume of the evolved gas was measured by a measuring cylinder. Irradiation was performed until the gas evolution ceased. The evolved gas (0.5 mL) was taken through rubber tube using syringe and was subjected to the quantitative analysis of H$_2$, N$_2$, CH$_4$, and CO$_2$. Gas analysis was performed on a Shimadzu GC-8A equipped with TCD detector at temperature raised from 40 to 180°C using a stainless column (3 mmΦ, 6 m) packed with a SHINCARBON ST (Shimadzu).

In order to determine the quantum yield ($\Phi$) for H$_2$ evolution, the H$_2$ amount per hour was measured for various concentrations of 1 (8–40 mM). The H$_2$ amount per hour was converted to $\Phi$ using an actinometer which was H$_2$ amount per hour evolved from the sacrificial H$_2$ production using ethanol (0.434 M) at pH 10.0 over Pt/TiO$_2$ (Pt content 1.0 wt%), whose $\Phi$ was reported to be 0.057 [24]. Limiting quantum yields ($\Phi^\infty$) at an infinite concentration of 1 was determined from the intercept of the double reciprocal plots of $\Phi$ vs. the concentration of 1 [25].

4. Results

4.1 Sacrificial H$_2$ production using glycerol (1a) and methanol (1b)

Sacrificial H$_2$ production was applied to 1a and 1b. The Pt/TiO$_2$ (100 mg, 1.25 mmol, 2.0 wt% of Pt) was suspended in an aqueous solution (150 ml) of 1a and 1b, whose concentration was varied in a range of 0.25–1.25 mmol. After O$_2$ was purged from the reaction vessel using N$_2$ gas, UV irradiation was continued under vigorous stirring for 10–17 h until gas evolution had ceased [15]. The evolved gas volumes were plotted against the amounts of sacrificial agent used. In the absence of sacrificial agents, the evolved H$_2$ from water was small (<2 mL). Figure 3A is a typical example of the plots of volume of H$_2$ and CO$_2$ against the amounts of 1a used. Gas volume increased as an increase of the
Glycerol as a Superior Electron Source in Sacrificial H$_2$ Production over TiO$_2$ Photocatalyst

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amounts of 1a used. However, the molar ratio of the evolved H$_2$ to 1a (H$_2$/1a) was dependent on the amount of 1a used. Therefore, the H$_2$/1a values were plotted against the molar ratios of 1a to catalyst (1a/catalyst). This plot gave a good linear relationship, as shown in Figure 3B. The intercept of the plot equaled the limiting amount of H$_2$ (H$_2^{\text{max}}$) obtained from 1 mol of 1a when the amount of the catalyst was extrapolated to infinite. The H$_2^{\text{max}}$ became 7.2. The limiting amount of CO$_2$ (CO$_2^{\text{max}}$) obtained from 1 mol of 1a at an infinite amount of the catalyst was also determined to be 3.1 from the plots of CO$_2$/1a against 1a/catalyst (Figure 3B). The H$_2^{\text{max}}$ and CO$_2^{\text{max}}$ are summarized in Table 1. If the sacrificial agent (C$_n$H$_m$O$_p$) is entirely decomposed into CO$_2$ and H$_2$O by hydroxyl radicals, theoretically (2n + 0.5m − p) equivalents (P) of H$_2$ will be evolved in the TiO$_2$ photocatalytic reaction [Eq. (4)]. The P values are listed in Table 1. Therefore, the chemical yield of H$_2$ production was defined to be 100 H$_2^{\text{max}}$/P. In the case of 1a, the yield of H$_2$ production was found to be 103%. Also, the CO$_2^{\text{max}}$ value was close to the theoretical value. Similarly, the H$_2^{\text{max}}$ and CO$_2^{\text{max}}$ values of 1b were determined to be 3.0 and 1.0, respectively. This shows that 1a and 1b are superior sacrificial agents, which are completely decomposed into CO$_2$ and water by sacrificial H$_2$ production:

\[
C_nH_mO_p + (2n-p)H_2O \xrightarrow{hv/\text{Pt/TiO}_2} nCO_2 + (2n+0.5m-p)H_2 \quad (4)
\]

4.2 Degradation mechanism of 1a and 1b

Generally, hydroxyl radical can abstract hydrogen atom more efficiently from the hydroxylated carbon rather than the non-hydroxylated carbon. Therefore, degradation of alcoholic sacrificial agents proceeds through hydrogen-atom abstraction by hydroxyl radical from the hydroxylated alkyl group [Eq. (5)] [15]. Hydroxyl radical reacts with the secondary alcohols to produce ketones, which does not undergo further degradation. The primary alcohols reacted with hydroxyl radical to produce aldehyde, which undergoes further oxidation to carboxylic acid.
Furthermore, H abstraction from carboxylic acid by hydroxyl radical induces decarboxylation from carboxylic acids through the formation of carboxyl radical (RCO·) \[\text{Eq. (7)}\]. When hydroxyl group was substituted on α-position of carboxylic acid \[X = \text{OH in Eq. (7)}\], the decarboxylation took place more smoothly.

Many researchers proposed that the decomposition of carboxylic acids is initiated by hole transfer to the carboxylic group rather than H abstraction by hydroxyl radicals \[26–29\]. Thus, the degradation of alcohols proceeds through the formation of carboxylic acids:

\[
\begin{align*}
\text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{C} = \text{O} \\
\text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{O} = \text{OH} \\
\text{O} = \text{OH} & \rightarrow \text{H}_2 + \text{O} = \text{OH} \\
\text{O} = \text{OH} & \rightarrow \text{H}_2 + \text{O} = \text{OH}
\end{align*}
\]

In 2009, Kondarides et al. reported sacrificial H\(_2\) production from \(1\text{a}\) over Pt/TiO\(_2\) (0.1–0.5 wt% Pt) \[30\]. They proposed that the decomposition of \(1\text{a}\) proceeded through the formation of methanol and acetic acid which were eventually decomposed into CO\(_2\) and H\(_2\) in a ratio of 3:7 \[31\]. Also, in irradiation of
Glycerol as a Superior Electron Source in Sacrificial H₂ Production over TiO₂ Photocatalyst
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Pt/TiO₂ in the absence and in the presence of glycerol, they detected H₂O₂ which was produced by dimerization of hydroxyl radicals [32]. Also, Ratnawati et al. detected a small amount of 1,2-ethanediol and acetic acid in reaction mixture [33]. They elucidated that Pt catalyzed not only reduction of water to H₂ but also dehydration of 1a. Bowker et al. examined the photocatalytic reforming of 1a over M/TiO₂ (M = 0.5 wt% Pd, 2.0 wt% Au) [34]. However, chemical yield of H₂ was still unclear.

We thought that degradation of 1a was initiated by the oxidation of terminal alcohol by hydroxyl radical. It was thought that glycolic acid (2a) and oxalic acid (2b) were the intermediates intervening in degradation process of 1a. Therefore, we performed sacrificial H₂ production over Pt/TiO₂ using 2a and 2b. The H₂max and CO₂max values of 2a and 2b were shown in Table 1. The 2a and 2b were completely decomposed to CO₂ and water, since the CO₂max values of 2a and 2b were determined to be 1.8 and 2.0, respectively. Although the degradation of 2a could proceed through 2b and/or formic acid (2c), we could not determine which degradation pathway occurred. In the case of 1b, it was thought that 2c was undoubtedly the intermediates intervening in degradation process of 1b.

The 2c was completely decomposed to CO₂ and water, since the CO₂max value of 2c was 1.0. However, 2a, 2b, and 2c were not detected in the reaction mixture of sacrificial H₂ production using 1a and 1b due to easy decomposition of these carboxylic acids by hydroxyl radical. Also, Lu et al. have reported the degradation of 2b and 2c, which can adsorb on Pt/TiO₂ to give one equivalent H₂ under irradiation [35, 36].

According to Eqs. (5)–(7), a possible degradation mechanism of 1a and 1b by hydroxy radical is shown in Figure 4. In the case of 1a, 14 equivalents of hydroxyl radicals were consumed by 1a along with the formation of 3CO₂. At the same time, seven equivalents of H₂ were evolved. Actually, 7.2 of H₂max and 3.1 of CO₂max values of 1a were provided from sacrificial H₂ production using 1a. In the case of 1b, six equivalents of hydroxyl radicals were consumed along with the formation of one equivalent of CO₂ and 3H₂, providing actually 3.0 of H₂max and 1.0 of CO₂max.

![Figure 4. Degradation pathways of glycerol (1a) and methanol (1b) by hydroxyl radical in the sacrificial H₂ production over Pt/TiO₂.](image-url)
4.3 Structural dependence on H\(_2\) yields in sacrificial H\(_2\) production using several alcohols (1c–1g)

In order to elucidate the relationship between molecular structure of sacrificial agents and degradation yield, sacrificial H\(_2\) production was performed using propane-based alcohols such as 1-hydroxy-2-propanone (1c); 1,2-propanediol (1d); 1,3-propanediol (1e); 1-popolanol (1f); and 2-propanol (1g) (Figure 5) as well as the related carboxylic acids (2d–2h) [15].

Sacrificial H\(_2\) evolution using 1c produced CH\(_4\) along with the formation of H\(_2\) and CO\(_2\). Limiting amount of CH\(_4\) (CH\(_4\)\(_{\text{max}}\)) obtained from 1 mol of 1c was 0.30 along with 4.9 of H\(_2\)\(_{\text{max}}\) and 2.5 of CO\(_2\)\(_{\text{max}}\) values. In the case of sacrificial H\(_2\) production along with the formation of CH\(_4\), the chemical yield was defined by the following equation: 

\[
\text{Yield} = 100 \left( \frac{H_2_{\text{max}} + 4CH_4_{\text{max}}}{P} \right)
\]

The yield for the sacrificial H\(_2\) production using 1c was calculated to be 87%. Moreover, acetic acid (2d) was detected by LC-MS of the reaction solution at low conversion. A peak appeared at 2.24 min of retention time which showed mass peaks at \(m/z\) 60 (M\(^+\)) and 43 (CH\(_3\)CO\(^+\)). Therefore, 2d was subjected to sacrificial H\(_2\) production. Mozia et al. reported that 2d was decomposed into H\(_2\), CO\(_2\), and CH\(_4\) over TiO\(_2\) without Pt [37], although Zheng et al. reported that a trace amount of CH\(_4\) was detected from 2d over Pt/TiO\(_2\) (Pt = 1.0 wt%) [38]. We determined the chemical yields [39]. The CH\(_4\)\(_{\text{max}}\) of 2d was determined to be 0.27 along with 2.9 of H\(_2\)\(_{\text{max}}\) and 1.7 of CO\(_2\)\(_{\text{max}}\) values. The total yield was calculated to be 100% (=100 \((2.9 + 4 \times 0.27)/4\)) in the sacrificial H\(_2\) production using 2d. Considering the experimental error, stoichiometric equation for conversion of 2d into H\(_2\), CH\(_4\), and CO\(_2\) was shown in Eq. (8):

\[
\overset{O}{\underset{2d}{\text{CH}_3\text{COH} + 1.4\text{H}_2\text{O}}} \xrightarrow{h\nu} \overset{Pr/TiO_2}{2.8\text{H}_2 + 1.7\text{CO}_2 + 0.3\text{CH}_4} \tag{8}
\]

It was thought that pyruvic acid (2e) was an intermediate of degradation process from 1c to 2e. The H\(_2\)\(_{\text{max}}\), CO\(_2\)\(_{\text{max}}\), and CH\(_4\)\(_{\text{max}}\) values of 2e were found to be 3.9, 2.7, and 0.3, respectively [39]. Degradation scheme of 2e can be expressed by Eq. (9).

The yield for the sacrificial H\(_2\) production using 2e was 100%. Since the degradation yield of 1c was found to be 87%, the degradation of 1c to H\(_2\), CO\(_2\), and CH\(_4\) proceeded effectively through the formation of 2e followed by 2d:

\[
\overset{O}{\underset{2e}{\text{CH}_3C\text{\-C\-OH} + 2.4\text{H}_2\text{O}}} \xrightarrow{h\nu} \overset{Pr/TiO_2}{3.8\text{H}_2 + 2.7\text{CO}_2 + 0.3\text{CH}_4} \tag{9}
\]

The next sacrificial H\(_2\) production was examined using 1d. Oxidation of 1d with hydroxyl radical was initiated by oxidation of primary alcohol part to afford lactic acid (2f). Sacrificial H\(_2\) production using 2f produced H\(_2\), CH\(_4\), and CO\(_2\). The H\(_2\)\(_{\text{max}}\), CO\(_2\)\(_{\text{max}}\), and CH\(_4\)\(_{\text{max}}\) values of 2f were 4.1, 2.3, and 0.30, respectively. On the other hand, the H\(_2\)\(_{\text{max}}\), CO\(_2\)\(_{\text{max}}\), and CH\(_4\)\(_{\text{max}}\) values of 1d were determined to be 4.8 and 1.0, respectively. Trace amount of CH\(_4\) was formed. Thus, complete decomposition of 1d

\[
\text{Figure 5. Propane-based alcohols (1c–1g) as sacrificial agents for the photocatalytic H}_2\text{ production.}
\]
into H₂ and CO₂ did not take place. Therefore, it is speculated that degradation of 1d proceeds via 2f which was decomposed to acetaldehyde. It is suggested that oxidation of acetaldehyde by hydroxyl radical was slow.

In sacrificial H₂ production using 1e, $H₂^{\text{max}}$ and $CO₂^{\text{max}}$ values of 1e were 4.2 and 0.50, respectively. Moreover, malonic acid (2g, $m/z$ 104 (M+)) was detected in LC-MS of the photolysate. The sacrificial H₂ production using 2g showed that the $H₂^{\text{max}}$, $CO₂^{\text{max}}$, and $CH₄^{\text{max}}$ values were determined to be 2.6, 2.7, and 0.31, respectively. Degradation scheme of 2g can be expressed by Eq. (10). Although the degradation yield of 2g was relatively high yield (96%), 1e was not completely decomposed, resulting in 0.5 of the $CO₂^{\text{max}}$ and no CH₄ emission. This suggests that the degradation process of 2g is slow:

$$\text{HOOC-CH₂-CH₂-OH} + 1.4\text{H₂O \rightarrow hν \rightarrow 2.8\text{H₂} + 2.7\text{CO₂} + 0.3\text{CH₄}}$$  \hspace{1cm} (10)$$

Moreover, sacrificial H₂ production was applied to 1f. The $H₂^{\text{max}}$ and $CO₂^{\text{max}}$ values of 1f were determined to be 4.1 and 1.0, respectively. CH₄ was not formed. It is suggested that the degradation of 1f proceeded via the formation of propanoic acid (2h). The $H₂^{\text{max}}$ and $CO₂^{\text{max}}$ values of 2h were determined to be 2.3 and 1.0, respectively. The decarboxylation of 2h and the subsequent oxidation gave acetaldehyde, which was subjected to the further degradation, but it was slow process [39]. In the case of sacrificial H₂ production using 1g, acetone was detected by GLC analysis of the reaction mixture. The $H₂^{\text{max}}$ value was determined to be 1.3 and CO₂ was not evolved. Further degradation of acetone did not proceed.

Based on these results, the degradation pathways of 1c, 1d, 1e, 1f, and 1g by hydroxyl radical are summarized in Figure 6. Though considerable amounts of CO₂...
were evolved from 1c to 1f, the $\text{CO}_2^{\text{max}}$ (0.5–2.5) did not reach the theoretical values. In the case of 1g, CO$_2$ was not formed at all. Thus, in the case of these polyols which have one or two non-hydroxy-substituted carbons, the $H_2^{\text{max}}$ and $\text{CO}_2^{\text{max}}$ values did not reach the theoretical values. Therefore, we conclude that sacrificial agents with all of the carbon attached to oxygen atoms such as 1a and 1b continued to serve as an electron source until their sacrificial abilities were exhausted.

4.4 Separation of residual glycerol and methanol in BDF synthesis

Vegetable oil was mainly composed of the oleic acid (C$_{17}$H$_{33}$CO$_2$H) triglyceride whose average molecular weight was thought to be 884 g/mol. At first, since carboxylic acid was included in used oil as impurity, the amounts of NaOH ($a$ g/kg-lipid) which was required to achieve pH of 8–9 were determined. Lipid (ca. 1 mL, 0.884 g) was solved in 2-propanol (10 mL) and neutralized by an aqueous NaOH solution. In this case, $a$ was determined to be 0 g since fresh vegetable oil was used.

Vegetable oil (150 mL, 136.5 g, 0.154 mol) was set in a reaction vessel. Since usual optimal amount for transesterification of neutral lipid is known to be 3.55 g/kg [11], the amount of NaOH necessary to the transesterification was determined to be 0.485 g ($=0 + 0.485$ g) by the sum of $a$ g/kg and 3.55 g/kg. Usually, 20% of weight of 1b to vegetable oil is used for BDF synthesis. 1b (30 mL, 23.8 g, 0.743 mol) was mixed with NaOH (0.485 g, 0.012 mol). About half of the mixture of 1b and NaOH was poured in a reaction vessel and then kept at 61°C for 1 h under stirring. Moreover, the remaining

![Figure 7](image_url)

**Figure 7.** Mass balance for BDF preparation and the sacrificial H$_2$ production using residual 1a and 1b.
mixture of 1b and NaOH was added into the reaction vessel, and the reaction mixture was kept at 6°C for another 1 h.

Follow-up operation is shown in Figure 7. After cooling, the reaction mixture was separated into a lower layer and an upper layer. The lower layer (solution A) contained 1a and 1b. The upper layer was washed with water (300 mL) and separated to the BDF upper layer. Aqueous solution (solution B) was obtained from the lower layer. In order to check the contamination of lipid to BDF layer, the purity of BDF was determined by the peak-area ratio of methyl and methoxy groups in NMR spectra. The BDF layer contained C_{17}H_{33}CO_{2}Me (114.5 g, 0.387 mol) and unreacted vegetable oil (2.2 g). The yield of C_{17}H_{33}CO_{2}Me (BDF) was 83.7% based on the theoretical amounts of 137 g (0.463 mol).

GLC analysis showed that solution A contained 1a (10.4 g, 0.113 mol) and 1b (6.85 g, 0.214 mol) where molar ratio (b) of 1a to 1b was 1.89. The yield of 1a was 73.3% based on the theoretical amounts of 14.2 g (0.154 mol). NMR analysis of solution A showed that RCO_{2}Na (2.2 g) was contained in solution A. Solution B contained 1b (4.38 g, 0.137 mol) and a small amount of C_{17}H_{33}CO_{2}Na. Thus, 1b was found in both solutions A and B.

4.5 Hydrogen production from residual methanol and glycerol in BDF synthesis

The photocatalytic reforming of 1a and 1b was examined using solution A. Irradiation was performed by a high-pressure mercury lamp under vigorous stirring with a magnetic stirrer. Figure 8 shows the plots of the H_{2}/1a against the molar ratio of 1a to the catalyst (1a/catalyst), which was adjusted to 0.2, 0.4, 0.6, 0.8, and 1.0. From the intercept of the plots, H_{2}^{\text{max}} obtained from 1 mol of 1a at an infinite amount of the catalyst was determined to be 12.52. The yields of H_{2} production of solution A were determined as follows. According to Eq. (11), the H_{2} amount (P) was theoretically calculated to be 12.67 using \( P = 7 + 3b \) and \( b = 1.89 \). Since actual \( H_{2}^{\text{max}} \) was determined to be 12.52, the yield was calculated to be 98.8% (\( \approx 100H_{2}^{\text{max}}/P \)). The results are summarized in Table 2:

\[
C_{2}H_{4}O_{3} + bC_{2}H_{5}OH + (3+b)H_{2}O \xrightarrow{k'_{\text{Pt/TiO}_2}} (3+b)CO_{2} + (7+3b)H_{2} \quad P = 7 + 3b \tag{11}
\]

\[
CH_{3}OH + H_{2}O \xrightarrow{k'_{\text{Pt/TiO}_2}} CO_{2} + 3H_{2} \quad P = 3 \tag{12}
\]

Next, photocatalytic reforming was performed with solution B containing 1b. Solution B was neutralized with dilute H_{2}SO_{4} in order to reduce the effect of excess NaOH on TiO_{2}. After that, an aqueous solution (150 mL) containing 1b (0.25–1.25 mmol) was irradiated in the presence of Pt/TiO_{2} (100 mg) in a similar manner as solution A. The plots of H_{2}/1b against the molar ratio of 1b to catalyst (1b/catalyst) are overlaid on Figure 8. The H_{2}^{\text{max}} values were determined to be 1.08. The H_{2} yields were calculated to be 36.0% based on the theoretical P (3.00) [Eq. (12)]. In solution B, C_{17}H_{33}CO_{2}Na was converted to C_{17}H_{33}CO_{2}H by neutralization. It is well known that the carboxylic acid can strongly be adsorbed on TiO_{2}. Therefore, it is suggested that the adsorption of C_{17}H_{33}CO_{2}H on TiO_{2} lowered the photocatalytic activity of TiO_{2}. The presence of C_{17}H_{33}CO_{2}H retarded the H_{2} production of solution B remarkably.

Total amount of H_{2} from solutions A and B was calculated to be 1.56 mol by Eq. (13) using 0.113 mol of 1a in solution A and 0.137 mol of 1b in solution B: 0.113 × 12.52 + 0.137 × 1.08 (Table 2). H_{2} (1.56 mol) whose combustion energy (\( \Delta H \)) was 445 kJ was evolved from solutions A and B. The \( \Delta H \) of H_{2} was compared with \( \Delta H \).
As shown in Table 2, 0.113 mol of 1a and 0.351 mol of 1b were isolated from BDF synthesis which had 442 kJ of ΔH. The energy recovery yield was calculated to be 100.7% by using Eq. (14):

\[
\text{Energy recovery} = 100 \times \frac{\Delta H \text{ of } \text{H}_2}{\Delta H \text{ of } 1a + \Delta H \text{ of } 1b} \quad (14)
\]

Table 2. Photocatalytic reforming of residues of BDF synthesis.

<table>
<thead>
<tr>
<th>Residues of BDF synthesis</th>
<th>Photocatalytic reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1a/mol</td>
</tr>
<tr>
<td>Solution A</td>
<td>0.113</td>
</tr>
<tr>
<td>Solution B</td>
<td>0.137</td>
</tr>
<tr>
<td>Total</td>
<td>0.113</td>
</tr>
</tbody>
</table>

\[\Delta H /kJ\] for Solution A: [187], for Solution B: [255], for Total: [445] (100.7)

*[Transesterification was performed by the reaction of lipid (136.5 g, 0.154 mol) with 1b (23.8 g, 0.743 mol) in the presence of NaOH (0.485 g, 0.012 mol) at 61°C for 2 h. BDF (114.5 g) was isolated.]

*bPhotocatalytic reforming was performed by irradiation of Pt/TiO₂ in aqueous solution of 1a and 1b obtained from solutions A and B.

cThe values were the theoretical amounts (P) obtained from Eqs. (11) and (12).

dThe limiting amount of H₂ (H₂ max) was obtained from Figure 8.

eThe values in parenthesis were the yield of H₂ = 100H₂ max/P.

fThe molar ratio (b) of 1b to 1a was 1.89.

gThe combustion energy (ΔH) of 1a, 1b, and H₂ were 1654.3, 725.7, and 285.0 kJ mol⁻¹, respectively [16].

hThe energy recovery yield was calculated to be 100.7% by Eq. (14).
5. Conclusion and perspective

Sacrificial H₂ production can produce H₂ in aqueous solutions. Gaseous H₂ can be spontaneously isolated from reaction mixture without being separated. Therefore, sacrificial H₂ production will provide a promising approach in the utilization of 1a and 1b derived from BDF synthesis.

Recent trends are shifting to the development of solar light-responsive photocatalysts. For example, nanotube-type Pt-N/TiO₂ (1 wt% Pt) was applied to sacrificial H₂ production with 1a where quantum yield for H₂ evolution reached 0.37–0.36 [27]. CuO/TiO₂ (1.3 wt% of CuO) was used for sacrificial H₂ production using 1a [40]. Heteroatom (B, N)-doped Pt/TiO₂ catalyst produced H₂ in 88.7–90.9% yields from 1a under xenon lamp irradiation [41]. The B, N-doped Pt/TiO₂ had absorption in visible light region (400–500 nm). Photo-reforming of 1a over CuOₓ/TiO₂ (Cu = 0.01–2.8 wt%) gave H₂ under visible light irradiation [42]. H₂ production was performed over a CuO-TiO₂ composite using 1a and 1b under sunlight irradiation [43]. Sacrificial H₂ production over Ag₂/TiO₂ from 1a was performed by irradiation with a xenon lamp [44].

BDF market has significantly increased to adhere to energy and climate policies [45]. If H₂ is produced by a photocatalytic process using solar energy and biomass-derived sacrificial agents, it will be the most promising process to construct clean BDF synthesis.

Conflict of interest

The authors declare that they have no competing interests.

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