Chapter

Glycerol as a Superior Electron Source in Sacrificial H_2 Production over TiO_2 Photocatalyst

Masahide Yasuda, Tomoko Matsumoto and Toshiaki Yamashita

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 H_2 production over a Pt-loaded TiO_2 catalyst under UV irradiation by high-pressure mercury lamp. H_2 was produced in high yield. The combustion energy (ΔH) of the evolved H_2 reached 100.7% of the total ΔH 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 H_2 production will provide a promising approach in the utilization of by-products derived from BDF synthesis.

Keywords: BDF, photocatalyst, TiO_2, sacrificial agent, glycerol, hydrogen

1. Introduction

The major issue in the current world is an urgent need to stop the increase of CO_2 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

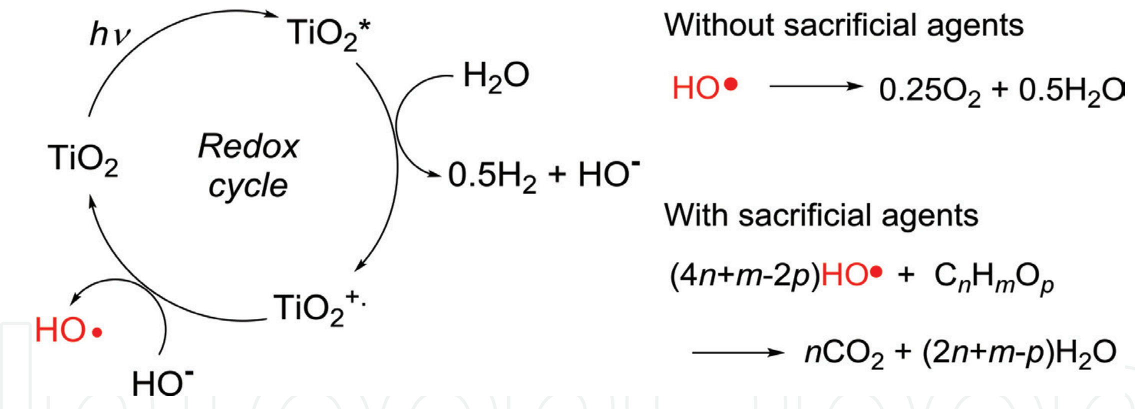
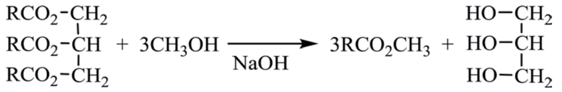


Figure 1.
Photocatalytic water splitting over TiO_2.

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]:



$$\begin{matrix} RCO_2\text{-}CH_2 \\ | \\ RCO_2\text{-}CH \\ | \\ RCO_2\text{-}CH_2 \end{matrix} + 3CH_3OH \xrightarrow[NaOH]{} 3RCO_2CH_3 + \begin{matrix} HO\text{-}CH_2 \\ | \\ HO\text{-}CH \\ | \\ HO\text{-}CH_2 \end{matrix} \qquad (1)$$

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., arabitol, 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 (ΔH = 1995 kJ mol^{-1}) is larger than ΔH of **1a** (1654.3 kJ mol^{-1}) [Eq. (2)]. Also, **1b** can produce three equivalents of hydrogen, whose ΔH (855 kJ mol^{-1}) is larger than ΔH of **1b** (725.7 kJ mol^{-1}) [Eq. (3)] [16]. Thus, photo-energy can promote uphill process:

$$\underset{\mathbf{1a}\ (1654.3\ \mathrm{kJ\ mol^{-1}})}{C_3H_8O_3 + 3H_2O} \xrightarrow[Pt/TiO_2]{h\nu} \underset{(1995\ \mathrm{kJ\ mol^{-1}})}{3CO_2 + 7H_2} \qquad (2)$$

$$\underset{\mathbf{1b}\ (725.7\ \mathrm{kJ\ mol^{-1}})}{CH_3OH + H_2O} \xrightarrow[Pt/TiO_2]{h\nu} \underset{(855\ \mathrm{kJ\ mol^{-1}})}{CO_2 + 3H_2} \quad (3)$$

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_2 production over Pt/TiO_2 using water-soluble materials derived from lignocelluloses [19–21] and chlorella [22] (**Figure 2**).

In this chapter, we will show H_2 production through sacrificial H_2 production over Pt/TiO_2 using **1a** and **1b** from standpoints of construction of renewable energy system and clean synthesis of BDF.

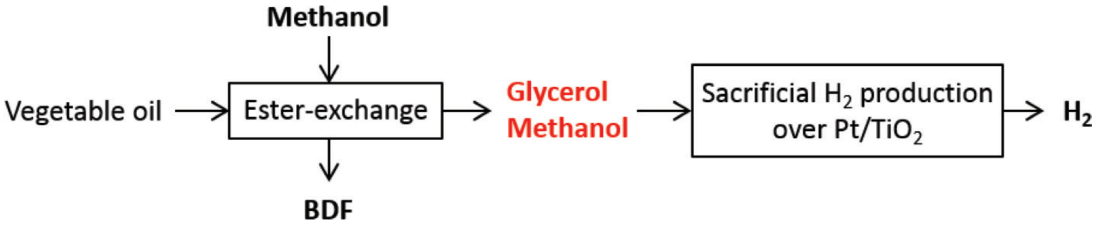


Figure 2.
Outline of conversion of glycerol to hydrogen.

3. Materials and method

3.1 Apparatus

NMR spectra were taken on a Bruker AV 400M spectrometer for $CDCl_3$ 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 × 150 mm) and 1% formic acid in $MeOH\text{-}H_2O$ (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 × 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_2PtCl_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 (Φ) 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 Φ 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 Φ was reported to be 0.057 [24]. Limiting quantum yields (Φ^{∞}) at an infinite concentration of **1** was determined from the intercept of the double reciprocal plots of Φ 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

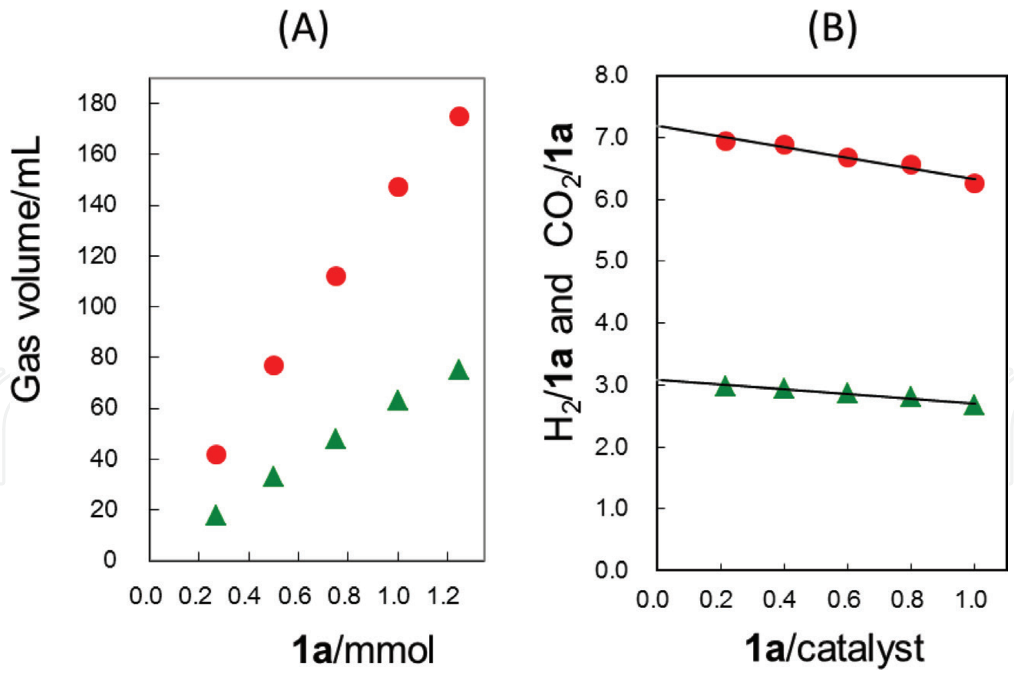


Figure 3.
(A) The gas volume evolved from the sacrificial H_2 production using glycerol (1a) over Pt/TiO_2. (B) Plots of H_2/1a and CO_2/1a against 1a/catalyst: H_2 (●) and CO_2 (▲).

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^{max}) obtained from 1 mol of **1a** when the amount of the catalyst was extrapolated to infinite. The H_2^{max} became 7.2. The limiting amount of CO_2 (CO_2^{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^{max} and CO_2^{max} are summarized in **Table 1**. If the sacrificial agent ($C_nH_mO_p$) is entirely decomposed into CO_2 and H_2O 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^{max}/P. In the case of **1a**, the yield of H_2 production was found to be 103%. Also, the CO_2^{max} value was close to the theoretical value. Similarly, the H_2^{max} and CO_2^{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:

$$C_nH_mO_p + (2n\text{-}p)H_2O \xrightarrow[Pt/TiO_2]{h\nu} nCO_2 + (2n\text{+}0.5m\text{-}p)H_2 \qquad P = 2n\text{+}0.5m\text{-}p \tag{4}$$

4.2 Degradation mechanism of 1a and 1b

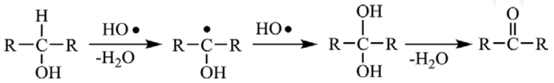
Generally, hydroxyl radical can abstract hydrogen atom more efficiently from the hydroxylated carbon rather than the non-hydroxylated carbon. Therefore, degradation of alcoholic sacrificial agents proceeds through hydrogen-atom abstraction by hydroxyl radical from the hydroxylated alkyl group [Eq. (5)] [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

Sacrificial agents	**Formula**	***P***[a]	**Products/mol mol^{-1}**			**Yield/%**[b]	**Φ^{∞}**[c]
			H_2^{max}	CO_2^{max}	CH_4^{max}		
Alcohols							
Glycerol (**1a**)	$C_3H_8O_3$	7	7.2	3.1		103	0.078
Methanol (**1b**)	CH_4O	3	3.0	1.0		100	0.057
1-Hydroxy-2-propanone (**1c**)	$C_3H_6O_2$	7	4.9	2.5	0.30	87	0.045
1,2-Propanediol (**1d**)	$C_3H_8O_2$	8	4.8	1.0	Trace	60	
1,3-Propanediol (**1e**)	$C_3H_8O_2$	8	4.2	0.5		53	
1-Propanol (**1f**)	C_3H_8O	9	4.1	1.0		46	0.069
2-Propanol (**1g**)	C_3H_8O	9	1.3	0.0		14	
Carboxylic acids							
Glycolic acid (**2a**)	$C_2H_4O_3$	3	2.8	1.8		93	
Oxalic acid (**2b**)	$C_2H_2O_4$	1	1.0	2.0		100	
Formic acid (**2c**)	CH_2O_2	1	1.0	1.0		100	
Acetic acid (**2d**)	$C_2H_4O_2$	4	2.9	1.7	0.27	100	
Pyruvic acid (**2e**)	$C_3H_4O_3$	5	3.9	2.7	0.30	102	
Lactic acid (**2f**)	$C_3H_6O_3$	6	4.1	2.3	0.30	88	
Malonic acid (**2g**)	$C_3H_4O_4$	4	2.6	2.7	0.31	96	
Propanoic acid (**2h**)	$C_3H_6O_2$	7	2.3	1.0		33	

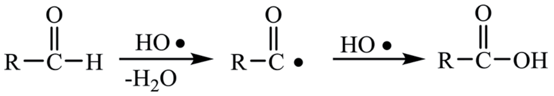
[a] *Theoretical amount of hydrogen was calculated using Eq. (4).*
[b] *Total chemical yield of H_2 and CH_4 = 100 (H_2^{max} + $4CH_4^{max}$)/P.*
[c] *Limiting quantum yield (Φ^{∞}) for H_2 evolution with infinite amounts of 1.*

Table 1.
Sacrificial H_2 production over Pt/TiO_2 using alcohols (1) and carboxylic acids (2).

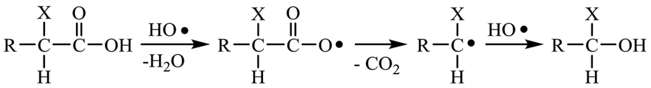
[Eq. (6)]. Furthermore, H abstraction from carboxylic acid by hydroxyl radical induces decarboxylation from carboxylic acids through the formation of carboxyl radical ($RCO_2\cdot$) [Eq. (7)]. When hydroxyl group was substituted on α-position of carboxylic acid [X = OH in Eq. (7)], the decarboxylation 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:



$$R-\overset{H}{\underset{OH}{C}}-R \xrightarrow[-H_2O]{HO\bullet} R-\overset{\bullet}{\underset{OH}{C}}-R \xrightarrow{HO\bullet} R-\overset{OH}{\underset{OH}{C}}-R \xrightarrow[-H_2O]{} R-\overset{O}{\overset{\|}{C}}-R \tag{5}$$



$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[-H_2O]{HO\bullet} R-\overset{O}{\overset{\|}{C}}\bullet \xrightarrow{HO\bullet} R-\overset{O}{\overset{\|}{C}}-OH \tag{6}$$



$$R-\overset{X}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-H_2O]{HO\bullet} R-\overset{X}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O\bullet \xrightarrow[-CO_2]{} R-\overset{X}{\underset{H}{C}}\bullet \xrightarrow{HO\bullet} R-\overset{X}{\underset{H}{C}}-OH \tag{7}$$

In 2009, Kondarides et al. reported sacrificial H_2 production from **1a** over Pt/TiO_2 (0.1–0.5 wt% Pt) [30]. They proposed that the decomposition of **1a** 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

Pt/TiO_2 in the absence and in the presence of glycerol, they detected H_2O_2 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 H_2 but also dehydration of **1a**. Bowker et al. examined the photocatalytic reforming of **1a** over M/TiO_2 (M = 0.5 wt% Pd, 2.0 wt% Au) [34]. However, chemical yield of H_2 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 H_2 production over Pt/TiO_2 using **2a** and **2b**. The H_2^{max} and CO_2^{max} values of **2a** and **2b** were shown in **Table 1**. The **2a** and **2b** were completely decomposed to CO_2 and water, since the CO_2^{max} 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 CO_2 and water, since the CO_2^{max} value of **2c** was 1.0. However, **2a**, **2b**, and **2c** were not detected in the reaction mixture of sacrificial H_2 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/TiO_2 to give one equivalent H_2 under irradiation [35, 36].

According to Eqs. (5)–(7), a possible degradation mechanism of **1a** and **1b** by hydroxyl 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 $3CO_2$. At the same time, seven equivalents of H_2 were evolved. Actually, 7.2 of H_2^{max} and 3.1 of CO_2^{max} values of **1a** were provided from sacrificial H_2 production using **1a**. In the case of **1b**, six equivalents of hydroxyl radicals were consumed along with the formation of one equivalent of CO_2 and $3H_2$, providing actually 3.0 of H_2^{max} and 1.0 of CO_2^{max}.

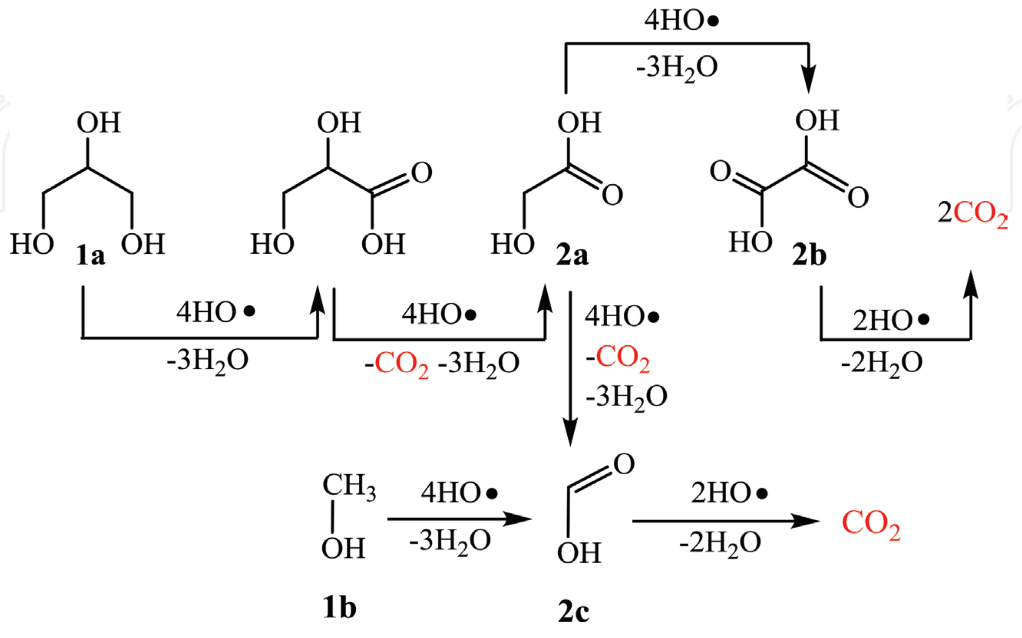
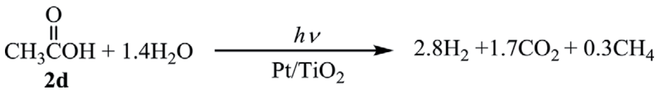


Figure 4.
Degradation pathways of glycerol (1a) and methanol (1b) by hydroxyl radical in the sacrificial H_2 production over Pt/TiO_2.

4.3 Structural dependence on H_2 yields in sacrificial H_2 production using several alcohols (1c–1g)

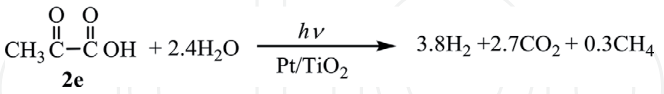
In order to elucidate the relationship between molecular structure of sacrificial agents and degradation yield, sacrificial H_2 production was performed using propane-based alcohols such as 1-hydroxy-2-propanone (**1c**); 1,2-propanediol (**1d**); 1,3-propanediol (**1e**); 1-popanol (**1f**); and 2-propanol (**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^{max}) obtained from 1 mol of **1c** was 0.30 along with 4.9 of H_2^{max} and 2.5 of CO_2^{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: Yield = 100 $(H_2^{max} + 4CH_4^{max})/P$. 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_3CO^+). 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^{max} of **2d** was determined to be 0.27 along with 2.9 of H_2^{max} and 1.7 of CO_2^{max} values. The total yield was calculated to be 100% (=100 (2.9 + 4 × 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):



$$\underset{\mathbf{2d}}{CH_3\overset{\overset{O}{\|}}{C}OH} + 1.4H_2O \xrightarrow[Pt/TiO_2]{h\nu} 2.8H_2 + 1.7CO_2 + 0.3CH_4 \qquad (8)$$

It was thought that pyruvic acid (**2e**) was an intermediate of degradation process from **1c** to **2c**. The H_2^{max}, CO_2^{max}, and CH_4^{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 **2e** followed by **2d**:



$$\underset{\mathbf{2e}}{CH_3\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}OH} + 2.4H_2O \xrightarrow[Pt/TiO_2]{h\nu} 3.8H_2 + 2.7CO_2 + 0.3CH_4 \qquad (9)$$

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^{max}, CO_2^{max}, and CH_4^{max} values of **2f** were 4.1, 2.3, and 0.30, respectively. On the other hand, the H_2^{max} and CO_2^{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**

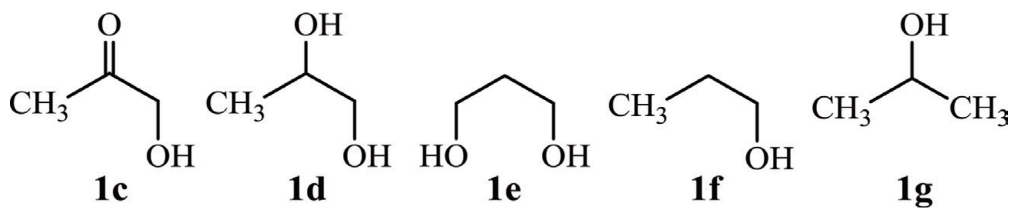
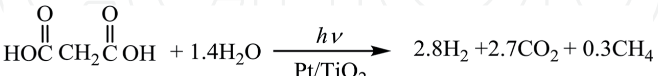


Figure 5.
Propane-based alcohols (1c–1g) as sacrificial agents for the photocatalytic H_2 production.

into H_2 and CO_2 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 H_2 production using **1e**, H_2^{max} and CO_2^{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 H_2 production using **2g** showed that the H_2^{max}, CO_2^{max}, and CH_4^{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 CO_2^{max} and no CH_4 emission. This suggests that the degradation process of **2g** is slow:



$$\underset{\mathbf{2g}}{HO\overset{O}{\overset{\|}{C}}\,CH_2\overset{O}{\overset{\|}{C}}\,OH} + 1.4H_2O \xrightarrow[Pt/TiO_2]{h\nu} 2.8H_2 + 2.7CO_2 + 0.3CH_4 \qquad (10)$$

Moreover, sacrificial H_2 production was applied to **1f**. The H_2^{max} and CO_2^{max} values of **1f** were determined to be 4.1 and 1.0, respectively. CH_4 was not formed. It is suggested that the degradation of **1f** proceeded via the formation of propanoic acid (**2h**). The H_2^{max} and CO_2^{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 H_2 production using **1g**, acetone was detected by GLC analysis of the reaction mixture. The H_2^{max} value was determined to be 1.3 and CO_2 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 CO_2

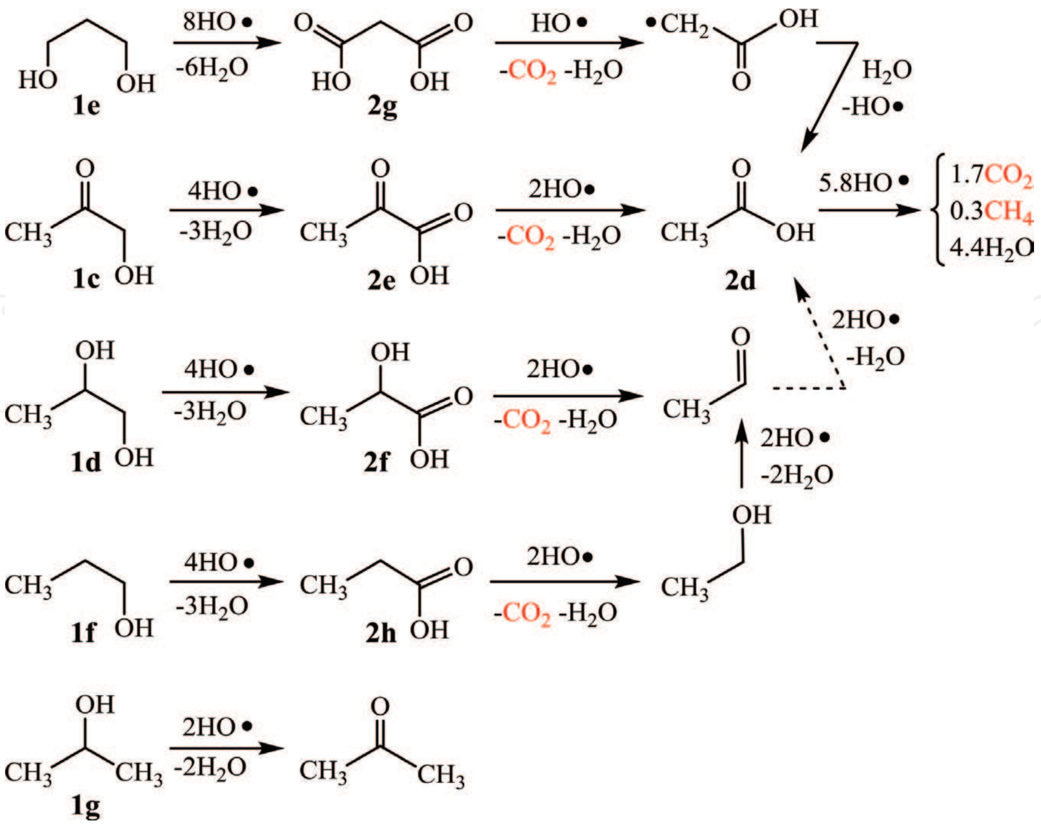


Figure 6.
Degradation pathway of sacrificial agents by hydroxyl radical in the sacrificial H_2 production over Pt/TiO_2 using propane-based alcohols: 1-hydroxyl-2-propanone (1c); 1,2-propanediol (1d); 1,3-propanediol (1e); 1-propanol (1f); and 2-propanol (1g).

were evolved from **1c** to **1f**, the CO_2^{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^{max} and CO_2^{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 ($C_{17}H_{33}CO_2H$) 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

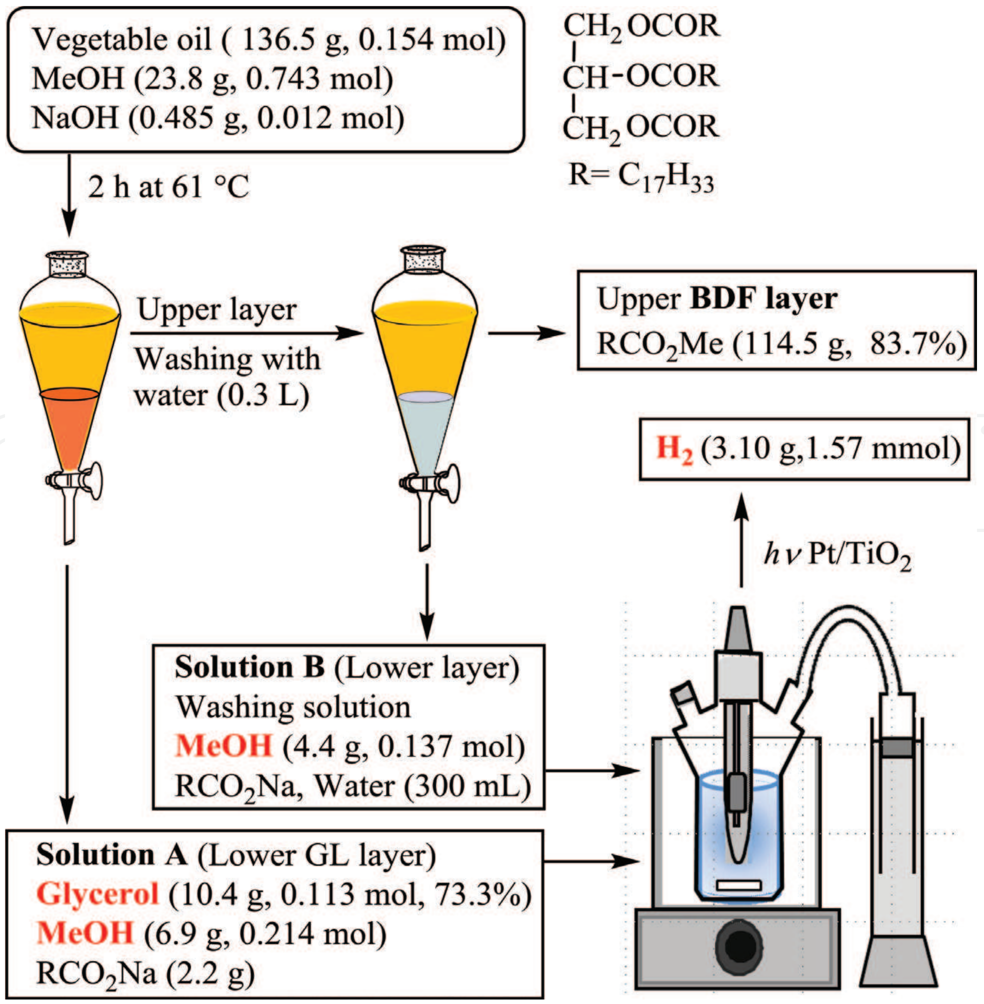


Figure 7.
Mass balance for BDF preparation and the sacrificial H_2 production using residual 1a and 1b.

mixture of **1b** and NaOH was added into the reaction vessel, and the reaction mixture was kept at 61°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 $C_{17}H_{33}CO_2Me$ (114.5 g, 0.387 mol) and unreacted vegetable oil (2.2 g). The yield of $C_{17}H_{33}CO_2Me$ (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_2Na (2.2 g) was contained in solution A. Solution B contained **1b** (4.38 g, 0.137 mol) and a small amount of $C_{17}H_{33}CO_2Na$. 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, $H_2^{\max}$ 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 $H_2^{\max}$ was determined to be 12.52, the yield was calculated to be 98.8% (=100$H_2^{\max}$/P). The results are summarized in **Table 2**:

$$C_3H_8O_3 + bCH_3OH + (3+b)H_2O \xrightarrow[\text{Pt/TiO}_2]{h\nu} (3+b)CO_2 + (7+3b)H_2 \quad P = 7 + 3b \tag{11}$$

$$CH_3OH + H_2O \xrightarrow[\text{Pt/TiO}_2]{h\nu} CO_2 + 3H_2 \qquad P = 3 \tag{12}$$

Next, photocatalytic reforming was performed with solution B containing **1b**. Solution B was neutralized with dilute H_2SO_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 $H_2^{\max}$ 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, $C_{17}H_{33}CO_2Na$ was converted to $C_{17}H_{33}CO_2H$ 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 $C_{17}H_{33}CO_2H$ on TiO_2 lowered the photocatalytic activity of TiO_2. The presence of $C_{17}H_{33}CO_2H$ 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 (ΔH) was 445 kJ was evolved from solutions A and B. The ΔH of H_2 was compared with ΔH

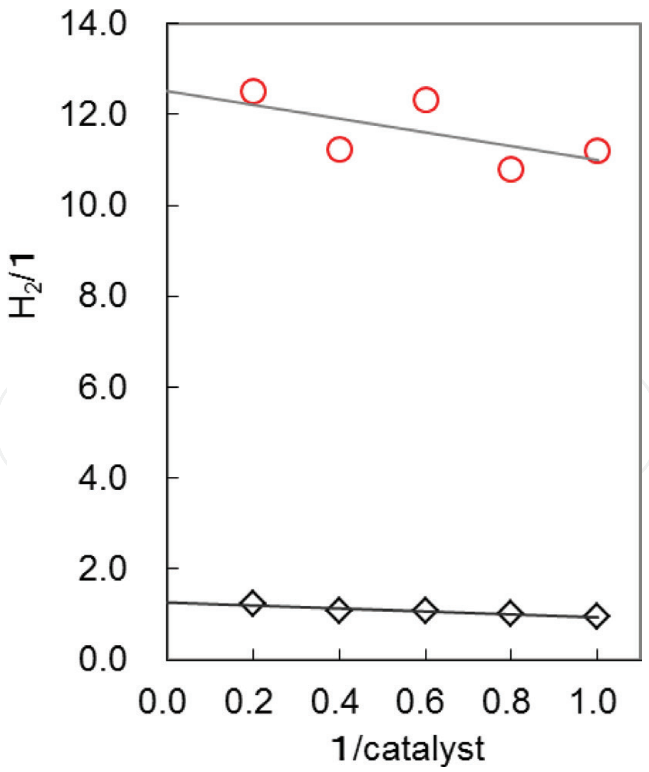


Figure 8.
Determination of H_2^{max} values by the plots of $H_2/\mathbf{1}$ against ***1****/catalyst using solution A (○, b = 1.89) and solution B (◇) obtained from the BDF synthesis.*

	Residues of BDF synthesis[a]			**Photocatalytic reforming**[b]	
	1a/mol	**1b/mol**	***P*** [c]	**$H_2^{max\ d}$**	**H_2/mol (yield/%)**[e]
Solution A[f]	0.113	0.214	12.67	12.52	1.41 (98.8)
Solution B		0.137	3.00	1.08	0.15 (36.0)
Total	0.113	0.351			1.56
[ΔH/kJ][g]	[187]	[255]			[445] (100.7)[h]

[a] *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.*
[b] *Photocatalytic reforming was performed by irradiation of Pt/TiO_2 in aqueous solution of* ***1a*** *and* ***1b*** *obtained from solutions A and B.*
[c] *The values were the theoretical amounts (P) obtained from Eqs. (11) and (12).*
[d] *The limiting amount of H_2 (H_2^{max}) was obtained from* **Figure 8***.*
[e] *The values in parenthesis were the yield of $H_2 = 100H_2^{max}/P$.*
[f] *The molar ratio (b) of* ***1b*** *to* ***1a*** *was 1.89.*
[g] *The combustion energy (ΔH) of* ***1a****,* ***1b****, and H_2 were 1654.3, 725.7, and 285.0 kJ mol^{-1}, respectively [16].*
[h] *The energy recovery yield was calculated to be 100.7% by Eq. (14).*

Table 2.
Photocatalytic reforming of residues of BDF synthesis.

of **1a** and **1b**. 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):

$$\text{Amount of } H_2 = (\text{mole of } \mathbf{1}) \text{ x } (H_2^{\text{max}}) \tag{13}$$

$$\text{Energy recovery} = 100\ \frac{\Delta H \text{ of } H_2}{\Delta H \text{ of } \mathbf{1a} + \Delta H \text{ of } \mathbf{1b}} \tag{14}$$

5. Conclusion and perspective

Sacrificial H_2 production can produce H_2 in aqueous solutions. Gaseous H_2 can be spontaneously isolated from reaction mixture without being separated. Therefore, sacrificial H_2 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/TiO_2 (1 wt% Pt) was applied to sacrificial H_2 production with **1a** where quantum yield for H_2 evolution reached 0.37–0.36 [27]. CuO/TiO_2 (1.3 wt% of CuO) was used for sacrificial H_2 production using **1a** [40]. Heteroatom (B, N)-doped Pt/TiO_2 catalyst produced H_2 in 88.7–90.9% yields from **1a** under xenon lamp irradiation [41]. The B, N-doped Pt/TiO_2 had absorption in visible light region (400–500 nm). Photo-reforming of **1a** over CuO_x/TiO_2 (Cu = 0.01–2.8 wt%) gave H_2 under visible light irradiation [42]. H_2 production was performed over a CuO-TiO_2 composite using **1a** and **1b** under sunlight irradiation [43]. Sacrificial H_2 production over Ag_2/TiO_2 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 H_2 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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