Original Paper

Hydrogen Production from Residual Glycerol in Biodiesel Synthesis by Photocatalytic Reforming

Masahide YASUDA, Ryo KUROGI, Takayuki TOMO, and Tsutomu SHIRAGAMI

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Biodiesel (BDF) has gained much attention as new sustainable energy alternative to petroleum-based fuels. In particular, BDF market has significantly increased in Europe to adhere energy and climate policies. Therefore, the increased BDF production requires new utilization of glycerol which is by product of BDF synthesis. We have focused on photocatalytic reforming using titanium oxide (TiO_2) photocatalyst using glycerol as sacrificial agent (SaH). Recently we have found that SaH with all of the carbon attached oxygen atoms such as glycerol and methanol continued to serve as an electron source until their sacrificial ability was exhausted in photocatalyzed hydrogen evolution using a Pt-loaded TiO_2 (Pt/ TiO_2) catalyst. Here we investigated the utilization of residual glycerol in BDF synthesis by photocatalytic reforming.

BDF (methyl alkanoate) preparation by transesterification of commercially-available vegetable oil (136.5 g) was performed by heating with MeOH (23.8 g) in the presence of NaOH (0.485 g) at 61 °C for 2 h. After cooling, standard follow-up operation was performed as follows. The products were separated into a lower layer (Solution A) and an upper layer. The upper layer was washed with water and separated into a BDF layer and an aqueous washing solution (Solution B). Glycerol (10.4 g) was obtained from Solution A in 73.3% yield along with methanol (6.85 g). BDF (114.5 g) was isolated in 83.7% yield. Solution B contained methanol in 4.38 g. The residual glycerol and unreacted methanol were turned to hydrogen by TiO_2 -photocatalytic reforming of Solutions A and B using Pt/ TiO_2 (100 mg) in aqueous solution (150 mL) under irradiation by high-pressure mercury lamp. Hydrogen was evolved in 2.82 g and 0.28 g from Solutions A and B, respectively. The combustion energy (ΔH) of the evolved H_2 corresponded to 100.8% based on the total ΔH of glycerol and methanol involved in Solutions A and B. Similar experiment was performed using pre-used vegetable oil. Hydrogen was recovered from Solutions A and B as 69.6% of ΔH . Presence of sodium alkanoate disturbed the hydrogen evolution.

バイオ燃料は化石燃料に替わる再生可能エネルギーの観点から重要である。その中でバイオディーゼル燃料 (BDF) は油脂とメタノールとのエステル交換反応で合成される。その際、グリセロールが BDF の約 10% 副生成し、未反応のメタノールと共に多くの場合は廃棄されている。我々はグリセロールを犠牲剤とする光触媒リフォーミングに関心を持っている。既に、我々は酸化チタン光触媒による水素発生反応において、すべての炭素に酸素原子が置換したグリセロールやメタノールは犠牲剤として優れており、完全分解することを見出している。そこで、本論文では、これらの副生成を犠牲剤とする白金担持酸化チタン光触媒 (Pt/ TiO_2) による光触媒リフォーミングによって有効活用を図った。

BDF (脂肪酸メチルエステル) の合成は、市販の植物油 (136.5 g) をメタノール (23.8 g) と NaOH (0.485 g) の存在下で 61°C、2 時間エステル交換反応させることで行なった。冷却後、反応液は上層と下層 (溶液 A) に分離された。上層は水洗浄されて、BDF 層と水洗溶液 (溶液 B) に分離された。グリセロール (10.4 g) が溶液 A から未反応のメタノール (6.85 g) とともに収率 73.3% で得られた。BDF (114.5 g) の収率は 83.7% であった。溶液 B にはメタノール 4.38 g が含まれていた。次に、残渣のグリセロールおよび未反応のメタノールの光触媒リフォーミングについて検討した。Pt/ TiO_2 (100 mg) を溶液 A または B の入った水溶液 (150 mL) に分散させ、窒素流通による脱気後、高圧水銀灯で照射した結果、水素が溶液 A および B からそれぞれ 2.82 g および 0.28 g 得られた。発生した水素の燃焼熱 (ΔH) は、溶液 A および B に含まれるグリセロールおよびメタノールの ΔH の 100.8% に相当するエネルギー回収率であった。同様の実験を使用済みの植物油を用いた BDF 副産物でも行ない、エネルギー回収率 69.6% で水素を回収した。収率の低下は溶液 A および B 中に含まれる脂肪酸塩が水素発生を阻害しているためと思われる。

Key Words

Photocatalyst, Reforming, TiO_2 , Bio-diesel, BDF, Hydrogen

1. Introduction

Biofuels such as bioethanol, biodiesel (BDF), and biogas have gained much attention as new sustainable energy alternative to petroleum-based fuels¹⁾. In particular, BDF market has significantly increased in Europe to adhere energy and climate policies²⁾. BDF (methyl alkanoate) is produced by transesterification of vegetable oil or animal fats with methanol along with the co-production of glycerol (eq 1)³⁾. Therefore, the increased BDF production requires new utilization of glycerol. Glycerol has a potential to produce hydrogen in maximum theoretical yield of seven equivalents (eq 2). Therefore, the transformation from glycerol to hydrogen, synthetic gas, and hydrocarbon have been extensively investigated through pyrolysis^{4) 5)}, steam gasification^{6) 7)}, and biological reforming^{8) 9)}. We have focused on photocatalytic reforming using titanium oxide (TiO₂) photocatalyst¹⁰⁾.

The TiO₂-photocatalytic reaction is initiated by charge-separation into electrons and holes under irradiation¹¹⁾. The electron reduces water to generate H₂ while hole oxidizes the HO[•] to give a hydroxyl radical¹²⁾. It is well known that the use of electron-donating sacrificial agents (SaH) remarkably accelerates the TiO₂-photocatalyzed hydrogen evolution since the hydroxyl radical is consumed by the SaH¹³⁾. During our investigations, we have found that SaH with all of the carbon attached oxygen atoms such as saccharides (eg. glucose and xylose) and polyalcohols (eg. 1,2-ethandiol, glycerol, arabitol) continued to serve as an electron source until their sacrificial ability was exhausted in photocatalyzed hydrogen evolution using a Pt-loaded TiO₂ (Pt/TiO₂) catalyst^{10) 14) 15)}. However, there are no reports on practical photocatalytic reforming of glycerol.

Here, we applied the photocatalyzed hydrogen evolution (photocatalytic reforming) using Pt/TiO₂ to the reforming of residual glycerol in BDF synthesis and examined the effectiveness of hydrogen evolution and usefulness of the photocatalytic reforming.

2. Experimental

2.1 Synthesis of BDF

Two kinds of lipid, commercially-available virgin vegetable oil and the oil pre-used in Japanese restaurant, were used for BDF synthesis. Virgin vegetable oil was mainly composed of the oleic acid (C₁₇H₃₃CO₂H) triglyceride whose average molecular weight was thought to be 884 g/mol. In the case of the pre-used oil, oil was heated to

remove water before BDF synthesis. At first, lipid (1 mL, 0.884 g) was solved in 2-propanol (10 mL) and neutralized by aqueous NaOH solution. The amounts of NaOH (a g/kg-lipid) which was required to achieve pH of 8 - 9 were determined. The amounts of NaOH necessary to the trans- esterification was calculated by sum of a g/kg and the amount of 3.5 g/kg which was usual optimal amount for transesterification of neutral lipid.

Typical procedure using virgin oil was shown as follows. A lipid (150 mL, 136.5 g, 0.155 mol) was set in a reaction vessel. Methanol (30 mL, 23.8 g, 0.743 mol) was mixed with NaOH (0.485g, 0.012 mol). About half of mixture of methanol and NaOH was poured in a reaction vessel and then kept at 61 °C for 1 h. Moreover, the remaining mixture of methanol and NaOH was added into the reaction vessel and the reaction mixture was kept at 61 °C for another 1 h. After cooling, the products were separated into a lower layer and an upper layer. The lower layer (Solution A) contained glycerol and methanol. The upper layer was washed with water (300 mL) and separated to the BDF layer and the aqueous washing solution (Solution B). 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, which were taken on a Bruker AV 400M spectrometer using CDCl₃ solution. The contents of glycerol and methanol in Solutions A and B were analyzed on a Shimadzu 14A gas liquid chromatograph (GLC) with FID detector at a temperature raised from 50 °C to 250 °C using a capillary column (J & W CP-Sil 5CB, 0.32 mmφ × 50 m).

2.2 Photocatalytic reforming

Anatase-type TiO₂ (ST-01) was purchased from Ishihara Sangyo (Japan). According to literature¹⁶⁾, an aqueous solution (50 mL) containing TiO₂ (1.0 g), K₂PtCl₆ (50 mg), and 2-propanol (0.38 mL) was irradiated by high-pressure mercury lamp for 24 h with stirring to give the Pt/TiO₂ where optimal amount of Pt (2.0 wt%) was loaded on TiO₂.

Typical procedure of photocatalytic reforming is shown as follows. The Pt/TiO₂ powder (100 mg, 1.25 mmol) was set in a reaction vessel. Furthermore, sampling was performed from Solution A that included glycerol and methanol in molar ratio (b) of methanol to glycerol so that the amounts of glycerol became 0.25, 0.50, 0.75, 1.00, and 1.25 mmol. The solution containing glycerol (0.25-1.25 mmol) and MeOH ($b \times 0.25 - b \times 1.25$ mmol) was introduced into a reaction vessel. The volume of the solution was adjusted to 150 mL by adding water. A high-pressure mercury lamp (100 W, UVL-100HA, Riko, Japan) was inserted into the

reaction vessel, which was attached to a measuring cylinder with a gas-impermeable tube to collect the evolved gas. After the O_2 was purged from the reaction vessel by N_2 gas, irradiation was performed at room temperature under vigorous stirring by a magnetic stirrer for 6–135 h until the gas evolution ceased. The evolved gas was collected by the measuring cylinder to measure the volume of the evolved gas and analyzed on a Shimadzu GC-8A equipped with a TCD detector at temperature increasing from 40 °C to 180 °C using a stainless column (3 mm Φ $\times$ 6 m) packed with a SHINCARBON ST (Shimadzu). H_2 and CO_2 were detected in addition to N_2 which was used as the purging gas.

3. Results and Discussion

3.1 Separation of residual glycerol in BDF synthesis

When BDF was prepared using virgin oil, the BDF layer contained $C_{17}H_{33}CO_2Me$ (114.5 g, 0.387 mol) and unreacted LP (2.2 g). GLC analysis of Solution A showed that Solution A contained glycerol (10.4 g, 0.113 mol) and MeOH (6.85 g, 0.214 mol) where molar ratio (b) of glycerol to MeOH was 1.89. Solution B contained MeOH (4.38 g, 0.137 mol) and a small amount of $C_{17}H_{33}CO_2Na$ (Fig. 1). If the quantitative trans-esterification of lipid with MeOH occurred, 137 g (0.463 mol) of BDF and 14.2 g (0.154 mol) of glycerol could be obtained. The yields of BDF and glycerol were calculated to be 83.7% and 73.3%, respectively. Thus, MeOH were found in both Solutions A and B.

Moreover, a similar operation was applied to the BDF

synthesis from pre-used lipids containing water to some extent. Therefore, considerable amounts of $C_{17}H_{33}CO_2Na$ was formed and incorporated into Solutions A and B. Solution A contained glycerol (0.087 mol) and methanol (0.072 mol) and $C_{17}H_{33}CO_2Na$ (MW 304, 0.029 mol). The b value was 0.83. Solution B contained methanol (0.17 mol). The yields of BDF and glycerol were 81.3% and 56.0%, respectively.

3.2 Photocatalytic reforming

The photocatalytic reforming of glycerol and MeOH was examined using Solutions A and B according to the procedure described in section 2.2. Irradiation was performed by a high pressure mercury lamp under vigorous stirring with a magnetic stirrer. Table 1 lists the evolved H_2 and CO_2 amounts in every amount of SaH obtained from Solutions A and B. The evolved H_2 increased with an increase in the amount of glycerol. However, the molar ratio of the evolved H_2 to glycerol (H_2 /glycerol) was dependent on the amount of glycerol used. Therefore, the H_2 /glycerol was plotted against the molar ratio of glycerol to the catalyst (glycerol/catalyst) which was adjusted to 0.2, 0.4, 0.6, 0.8, and 1.0, as shown in Fig. 2. As the GL/catalyst decreased, the H_2 /glycerol values increased. The intercept of the plots represented a limiting amount of H_2 (H_2^{max}) obtained from one mole of glycerol at an infinite amount of the catalyst.

Next photocatalytic reforming was performed with Solution B which contained MeOH. After Solution B was neutralized with dilute H_2SO_4 , an aqueous solution (150

Fig. 1 BDF synthesis using virgin vegetable oil (left) and pre-used vegetable oil (right) and the TiO_2 -photocatalytic reforming of the residues

Table 1 Photocatalytic H₂ and CO₂ evolution using Solutions A and B^{a)}

Lipid	SaH	glycerol /mmol	methanol /mmol	T/h ^{b)}	Volume/mL			Molar ratio ^{c)}		$H_2^{\max}$ [CO ₂ ^{max}]
					Gas	H ₂	CO ₂	H ₂ /SaH	CO ₂ /SaH	
Virgin lipid	Solution A $b=1.89$	0.25	0.47	28	97	70	27	12.5	4.8	12.52
		0.50	0.95	57	174	126	48	11.2	4.3	[4.81]
		0.75	1.42	73	287	207	80	12.3	4.8	
		1.00	1.89	101	335	242	93	10.8	4.2	
		1.25	2.37	105	435	314	121	11.2	4.3	
	Solution B		0.25	6	10	8	3	1.3	0.4	1.08
			0.50	23	16	11	5	1.1	0.4	[0.54]
			0.75	28	25	19	6	1.1	0.4	
			1.00	48	32	24	8	1.1	0.4	
			1.25	51	37	28	9	1.0	0.3	
Pre-used lipid	Solution A $b=0.83$	0.25	0.21	57	51	36	15	6.5	2.6	6.65
		0.50	0.42	70	88	63	25	5.6	2.3	[2.67]
		0.75	0.62	88	110	79	31	4.7	1.9	
		1.00	0.83	120	140	100	40	4.5	1.8	
		1.25	1.04	135	180	129	51	4.6	1.8	
	Solution B		0.25	6	10	8	3	1.4	0.5	1.26
			0.50	23	20	15	5	1.3	0.5	[0.51]
			0.75	28	28	21	7	1.3	0.4	
			1.00	48	35	26	9	1.2	0.4	
			1.25	51	40	30	10	1.1	0.4	

a) Irradiation was performed for an aqueous solution (150 mL) containing SaH and Pt/TiO₂ (the Pt content was 2 wt%, 100 mg, 1.25 mmol).

b) Irradiation time in h.

c) SaH indicated GL and MeOH in the cases of the Solutions A and B respectively.

mL) containing MeOH (0.25–1.25 mmol) was irradiated in the presence of Pt/TiO₂ (100 mg) in a similar manner as Solution A. The plots of H₂/MeOH was plotted against the molar ratio of MeOH to catalyst (MeOH/catalyst), as shown in Fig. 2. The $H_2^{\max}$ values were determined from the intercept of the plots.

In the case of virgin oil, photocatalytic reforming using Solution A would give the theoretical $H_2^{\max}$ which was calculated to be 12.67 (=7+3*b*) using $b=1.89$ according to eq (3). The actual $H_2^{\max}$ was determined to be 12.52. The yield was calculated to be 98.8%. The $H_2^{\max}$ value for solution B was determined to be 1.38. The H₂ yields were calculated to be 36.0% based on the theoretical $H_2^{\max}$ (3.00) (eq 4). The presence of C₁₇H₃₃CO₂Na in Solution B retarded the H₂ production remarkably. It is well known that the carboxylic acid can strongly adsorbed on TiO₂. Therefore, it is suggested that the adsorption of C₁₇H₃₃CO₂Na on TiO₂ lowered the photocatalytic activity of TiO₂. Thus, the total amount of H₂ from Solutions A and B was calculated to be 1.57 mol by the equation of $0.113 \times 12.52 + 0.137 \times 1.08$ using 0.113 mol of glycerol in Solution A and 0.137 mol of

Fig. 2 Determination of $H_2^{\max}$ values by the plots of H₂/SaH against SaH/catalyst using Solutions A ($b=1.89$, ○) and B (◇) obtained from the BDF synthesis using virgin oil and Solutions A ($b=0.83$, ●) and B (◆) obtained from the BDF synthesis using the pre-used oil. SaH= glycerol and methanol

Table 2 Residues of BDF synthesis and photocatalytic reforming

Lipid	Residues of BDF synthesis ^{a)}			Photocatalytic reforming ^{b)}	
	Solution	Products/mol		$H_2^{\max c)}$	$H_2/\text{mol (yield/\%)}^d)$
Virgin lipid	A ^{e)}	0.113	0.214	12.52 (12.67)	1.41
	B		0.137	1.08 (3.00)	0.14
	Total	0.113	0.351		1.57
	$[\Delta H/\text{kJ}]^f)$	[187]	[255]		[444] (100.8)
Pre-used lipid	A ^{g)}	0.087	0.072	6.61 (9.49)	0.57
	B		0.170	1.26 (3.00)	0.21
	Total	0.087	0.242		0.78
	$[\Delta H/\text{kJ}]^f)$	[144]	[176]		[222] (69.6)

a) Transesterification was performed by the reaction of lipid (136.5 g, 0.154 mol) with methanol (23.8 g, 0.743 mol) in the presence of NaOH (0.485 g, 0.012 mol or 0.825 g, 0.021 mol) at 61 °C for 2 h.

b) Photocatalytic reforming was performed by irradiation of Pt/TiO₂ in aqueous solution of glycerol and/or methanol obtained from Solutions A and B

c) The limiting amount of H₂ ($H_2^{\max}$) was obtained from Fig. 1. The values in parenthesis were the theoretical $H_2^{\max}$ obtained from eq (3) and (4).

d) The values in parenthesis was energy-recovery yield which was calculated by $100 \times (\Delta H \text{ of the evolved } H_2)/(\Delta H \text{ of glycerol} + \Delta H \text{ of methanol})$.

e) Molar ratio (b) of methanol to glycerol was 1.89

f) Combustion energy (ΔH) of glycerol, methanol, and hydrogen were 1654.3, 725.7, and 285.0 kJ mol⁻¹, respectively.

g) Molar ratio (b) of methanol to glycerol was 0.83.

methanol in Solution B (Table 2).

In the case of the pre-used oil, the $H_2^{\max}$ values were determined to be 6.61 and 1.26 in the photocatalytic reforming of Solutions A ($b = 0.83$) and B, respectively (Fig. 2). The total amount of H₂ was calculated to be 0.78 mol. According to eq (3) and (4), the theoretical $H_2^{\max}$ values of Solutions A and B were calculated to be 9.49 and 3.00, respectively (Table 2). It was thought that the presence of C₁₇H₃₃CO₂Na retarded the H₂ production yield to 69.7% and 42.0% in the cases of Solutions A and B, respectively.

3.3 Combustion energy

Table 2 also shows the combustion energy (ΔH) of glycerol and methanol isolated from BDF synthesis and hydrogen evolved by photocatalytic reforming. In both cases of virgin and pre-used oils, the ΔH of unreacted methanol was larger than that of glycerol. The energy recovery from residual glycerol and methanol was evaluated by comparing the ΔH of H₂ with those of sum of glycerol and methanol.

In the case of virgin oil, the H₂ (1.55 mol) evolved from Solutions A and B had 444 kJ of ΔH . The energy recovery yield was 100.8% based on sum of ΔH (442 kJ) of glycerol (0.113 mol, $\Delta H = 187$ kJ) and methanol (0.351 mol, $\Delta H = 255$ kJ). Since energy recovery was over 100%, it is thought that photocatalytic reforming is promising process as reforming method. In the case of pre-used oil, total ΔH of

H₂ (0.78 mol) was 222 kJ and the energy recovery yield was 69.6% based on sum of ΔH of glycerol (144 kJ) and methanol (176 kJ).

Conclusion

The residual materials in biomass reforming were usually produced in an aqueous solution. Moreover, the residue in BDF synthesis involved unreacted methanol other than glycerol. Photocatalytic reforming can transform aqueous solutions of both glycerol and methanol to H₂. Gaseous H₂ can be spontaneously isolated from reaction mixture without being separated. Therefore, photocatalytic reforming will provide a promising approach in the utilization of glycerol and methanol derived from BDF synthesis.

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