Enhancement of Glycerol Conversion to Acetol in High-temperature Liquid Water by High-pressure Carbon Dioxide

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Dehydration of glycerol to acetol proceeded in high-temperature liquid water at 573 K in a batch reactor. The acetol formation rate increased with an addition of high-pressure carbon dioxide.

Production of biodiesel (fatty acid methyl esters) derived from vegetable oils and animal fats has received considerable attention in recent years. 1,2,3-Propanetriol (glycerol) is formed as a by-product in the transesterification process of oils and fats with methanol yielding fatty acid methyl esters. There are a great number of common applications of glycerol in pharmaceuticals, cosmetics, and so on. Also, new applications, such as the production of esters, ethers, and acetals of glycerol and the conversion of glycerol itself to diols and epoxides have been developed.[1] Glycerol can be converted to 1,2-propanediol and 1,3-propanediol, which are not only valuable commercial products but also starting compounds for the production of polymers. There are several reports about glycerol hydrogenolysis to 1,2-propanediol using supported metal catalysts.[2,3] The hydrogenolysis from glycerol to 1,2-propanediol proceeds via two steps; dehydration of glycerol to acetol (hydroxyacetone) and hydrogenation of acetol to 1,2-propanediol.[2,4] It is also reported that the conversion of glycerol to acetol is crucial for better production efficiency in terms of selectivity and yield of the hydrogenolysis processes.

High-temperature liquid water has attracted much attention as a promising solvent as an alternative to harmful organic solvents because of its high values of concentrations of proton and hydroxide ions which can enhance acid-catalyzed or base-catalyzed reactions.[5,6] Here, we report the non catalytic dehydration of glycerol in high-temperature liquid water. We have also investigated the effect of addition of carbon dioxide in high-temperature liquid water on the glycerol dehydration.

The dehydration of glycerol was carried out in a batch reactor using a SUS 316 tube, having an inner volume of 6 cm^3.[7] The aqueous glycerol solution (6 $\mathrm{mol\,dm^{-3}}$, 3 g) was loaded in the reactor. Carbon dioxide was introduced to the reactor containing glycerol solution at 323 K. The reactor was submerged into a molten-salt bath at 573 K for a given reaction time. The partial pressure of carbon dioxide under reaction conditions was estimated by Charles's law. After the reaction, the reactor was submerged into a water bath for cooling to ambient temperature. Gaseous products were analyzed by a gas chromatography equipped with a thermal conductivity detector (GC-TCD) using a Shincarbon ST column. Liquid and solid products in the reactor were recovered with water and separated by filtration. The liquid products were analyzed by gas chromatography using flame ionization detector (GC-FID) on a DB-WAX capillary column. The yields of solid products were determined by their respective weights.

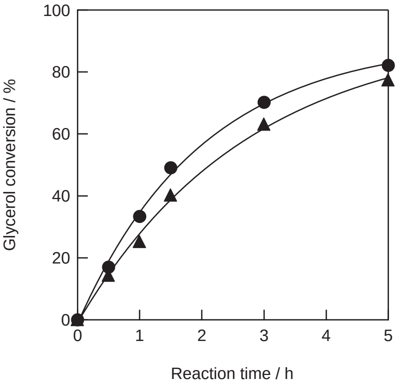

Figure 1. Glycerol conversion in water at 573 K (▲) and with 17.7 MPa of carbon dioxide (●).

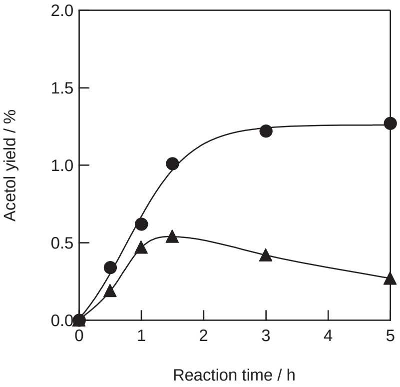

Figure 2. Acetol yields of glycerol dehydration in water at 573 K (▲) and with 17.7 MPa of carbon dioxide (●).

Figure 1 shows the conversion of glycerol in water at 573 K and 17.7 MPa of carbon dioxide. The glycerol conversion slightly increased with the addition of carbon dioxide. Table 1 shows product yields and composition of glycerol dehydration in water at 573 K. The major product is a solid, which would be formed by polymerization of glycerol and/or by-products.[8] Liquid products, such as acetol, 1-propanol, and 1,2-propanediol, are also obtained. The effect of carbon dioxide was clearly observed on acetol yields for 5 h which increased form 0.3 to 1.3%. Figure 2 shows yield of acetol as a function of time in water at 573 K and with addition of 17.7 MPa of carbon dioxide. In the case of high-temperature liquid water, acetol yield increased from 0 to 0.5% up to 1 h, after which it started decreasing. With

Table 1. Product yield and composition of glycerol dehydration in water at 573 K

Reaction time/h	CO_2 pressure /MPa	Glycerol conversion /%	Liquid products yield/%[a]				Solid product yield/%[a]
			Acetol	1-PO[b]	1,2-PDO[c]	Others	
1	0	25	0.5	0.0	0.2	0.1	24
	17.7	33	0.6	0.0	0.4	0.4	32
5	0	77	0.3	0.5	0.1	1.0	76
	17.7	82	1.3	0.8	0.2	1.9	78

[a] Yields were calculated based on the number of initial glycerol moles. [b] 1-Propanol. [c] 1,2-Propanediol.

addition of carbon dioxide, acetol yield increased dramatically to 1.3% which also remained constant up to 5 h. Thus, the addition of carbon dioxide accelerated the dehydration of glycerol to acetol and suppressed decreasing of acetol yield.

The increase in acetol yield by the addition of carbon dioxide could be explained by the increased acidity of carbonic acid formed by dissolution of carbon dioxide in high-temperature liquid water, as shown below.

$$H_2O + CO_2 \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows 2H^+ + CO_3^{2-} \quad (1)$$

Hunter and Savage estimated proton concentration of high-temperature liquid water with an addition of carbon dioxide (eq 2).[6]

$$[H^+] = \frac{K_W}{[H^+]} + \left(\frac{K_{a1}}{[H^+]}\right)[CO_2(aq)] \quad (2)$$

where $[H^+]$, $[CO_2(aq)]$, K_W, and K_{a1} represent the concentrations of proton and dissolved carbon dioxide, ionization constant of water, and the first ionization constant of carbonic acid, respectively. They claimed that proton concentration depends on first dissociation of carbonic acid essentially because its second dissociation is negligible. Equation 2 can be written as

$$[H^+] = (K_W + K_{a1}[CO_2(aq)])^{1/2} = \left(K_W + \frac{K_{a1}}{K_H}P_{CO2}\right)^{1/2} \quad (3)$$

where K_H and P_{CO2} represent the Henry's law constant of carbon dioxide dissolved in water and the pressure of carbon dioxide, respectively. Equation 3 indicates that the concentration of proton in high-temperature liquid water increases linearly with increasing square root of carbon dioxide pressure in the region of high-pressure carbon dioxide (eq 4).

$$P_{CO2} \gg \frac{K_W K_H}{K_{a1}} \quad (4)$$

Figure 3 shows acetol formation rates of glycerol dehydration in water at 573 K, which were estimated from the initial slope of acetol yield at $t = 0$ from each reaction profile, as a function of square root of carbon dioxide pressure. The acetol formation rates increased linearly with increasing square root of carbon dioxide pressure when the pressure of carbon dioxide was more than 1 MPa. This linear dependence would show that the proton derived from carbonic acid dominantly catalyses glycerol dehydration to acetol for over 1 MPa of carbon dioxide. In summary, we have successfully demonstrated that the addition of high-pressure carbon dioxide to high-temperature liquid water is highly beneficial in providing protons for the dehydration of glycerol and this technique can also be extended to other acid-catalyzed reactions, which leads to a new technology for conversion of biomass derivatives to useful materials.

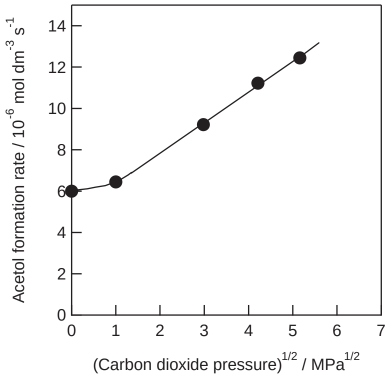

Figure 3. Acetol formation rates of glycerol dehydration in water at 573 K as a function of square root of carbon dioxide pressure (initial glycerol concentration: 6 mol dm^{-3}).

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