

Microwave-Intensified CO₂-H₂O-Carbocatalysis for Valorization of Glycerol

Armando T. Quitain,^{*1,3} Yuri Ogasawara,² Shinnosuke Uchikado,² Nao Takata,² Jonas Karl N. Agutaya,³ Mitsuru Sasaki,⁴ Yusuke Inomata,⁵ Suttichai Assabumrungrat⁶, Tetsuya Kida⁵

¹Center for International Education, Kumamoto University, Kumamoto, 860-8555, Japan

²Graduate School of Science and Technology, Kumamoto University, Kumamoto, 860-8555, Japan

³International Research Organization for Advanced Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

⁴Institute of Industrial Nanomaterials, Kumamoto University, Kumamoto 860-8555 Japan

⁵Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto, 860-8555, Japan

⁶Department of Chemical Engineering, Chulalongkorn University, Bangkok, Thailand

*Corresponding author: quitain@kumamoto-u.ac.jp

Highlights

- The proposed green approach can enhance reaction rate, products yield and selectivity.
- A high glycerol to glycerol *tert*-butyl ether conversion of 51.1 % could be obtained.
- The high catalytic performance of GO is attributed to the presence of hydrophilic functional groups on the hydrophobic carbon surface.
- CO₂ pressurization also aids catalysis due to reaction with H₂O on the catalyst surface.

1. Introduction

The use of renewable energy is increasing worldwide attention as a solution to mitigate global warming. As a substitute to fossil-derived fuels, one of the most frequently employed biomass-derived energy sources is biodiesel. Biodiesel is a mixture of fatty acid methyl esters (FAMES) obtained by the transesterification or esterification of vegetable oils and fatty acids, respectively, using various catalysts and methods. In the process of producing 100 kg of biodiesel, about 10 kg of glycerin arises as a by-product. As a result, this reduces world market price of glycerin, and it also contributes to environmental concerns associated with the disposal of waste glycerin. Thus, with expected high consumption and demand for biodiesel, treatment of glycerin becomes an issue. Many applications of glycerin have been developed over the past few decades, one of the many possible derivatives is glycerol *tert*-butyl ether (GTBE), which is an excellent additive and has a large potential for diesel, biodiesel and sustainable aviation fuel (SAF) reformulation.

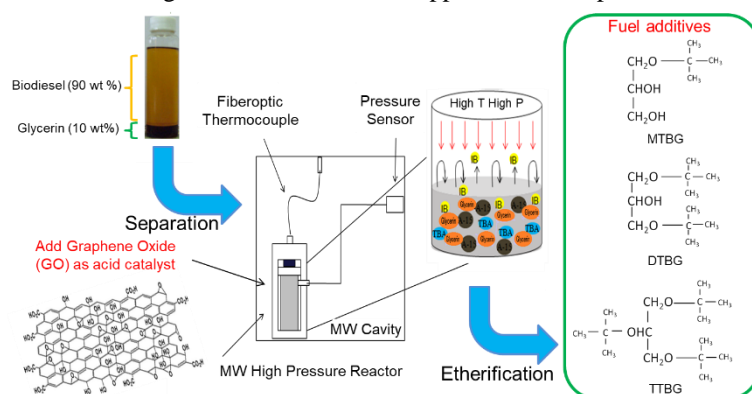
GTBE can be obtained by reacting glycerin with isobutene (IB) in the presence of acid catalysts. However, IB's boiling point is -6.9°C , which means high pressure conditions are necessary to keep it in the liquid phase. Considering the price and handling costs, *tert*-butyl alcohol (TBA) is cheaper, and this can also be produced from biomass. In addition, TBA not only serves as a reactant but a solvent for glycerin, thus it encompasses the technological problems arising from the need to use appropriate solvents to dissolve glycerin. Glycerin etherification reaction with TBA is a complex acid-catalyzed consecutive equilibrium reactions forming mono-, di- and tri- *tert*-butyl glycerol (MTBG, DTBG and TTBG, respectively). In addition, TBA dehydration can also take place producing IB and H₂O as shown in Fig. 1.

In this work, we focus on the etherification of glycerin to GTBE with TBA by carbocatalysis using graphene oxide (GO) under MW heating aided with CO₂. Specifically, the effect of operation temperature, TBA/Glycerin molar ratio, reaction time, catalyst loading, GO's acidic site concentration to glycerin conversion to GTBE was investigated using an GO as catalyst and compared to commercial Amberlyst 15 catalyst.

2. Methodology

GO was prepared from purified natural graphite (98.0%, Wako Chemical, Japan) by Hummers method. Glycerin and TBA were purchased from Wako Chemical (Japan). Methanol (99.8 %, Wako Chemical, Japan) was used as the solvent for analysis and 2,6-dimethylnaphthalene (DMN, Tokyo Chemical, Japan) was used as an internal standard. Amberlyst-15 hydrogen form was purchased from Sigma-Aldrich Co. (Japan). In a typical microwave-assisted experiments, 25 mL of mixture of glycerin and TBA was placed into a 100-ml high-pressure microwave reactor (XP-1500, CEM Corporation), and mixed with various amounts of catalysts. The reactor was then placed inside the microwave apparatus (MARS6, CEM Corporation) (Fig.1), attached to the pressure sensor then the fiberoptic thermocouple was inserted to measure the pressure and temperature of the system, respectively. The prepared samples were subjected to a maximum microwave power of 600 W, and heated to the desired temperature at various reaction times ranging from 0-240 min. TBA/glycerin molar ratios from 4 to 12, catalyst amount from 0 to 20 wt% (based on the amount of glycerin), reaction temperature ranging from 90 to 140 °C, After the reaction, the sample was taken for component analyses using GC-MS.

Figure 1. Schematic diagram of the microwave apparatus and experimental methodology



3. Results and discussion

Results indicated the highest conversion of glycerin to GTBE of 51.1 % (selectivity to MTBG : 32 %, selectivity to DTBG + TTBG : 19.1 %) was obtained at reaction time of 240 min, at 130 °C, at TBA / glycerin molar ratio of 6, at 13.5 wt% catalyst amount, 3.49 mmol/g acidic site concentration using microwave power of 600 W. GTBE products were also quantified into MTBG, DTBG and TTBG. This high catalytic performance of GO at high temperature is attributed the presence of hydrophilic functional groups on the hydrophobic carbon surface. Increasing TBA/glycerin molar ratio up to 6 leads to an increase glycerin conversion to GTBE. At TBA / glycerin molar ratio of 9 and 12, excess TBA enhanced the side reaction. A significant increase in the glycerin conversion to GTBE can be observed as the amount of catalyst increased. At the lower acidic site concentration, glycerin conversion to GTBE was low because the protonation of TBA on the acid site was not enhanced. In addition, it should also be considered that GO's particle size has an effect on glycerin conversion to GTBE. CO₂ pressurization also aids catalysis due to reaction with H₂O on the catalyst surface.

4. Conclusions

The proposed microwave-intensified CO₂-H₂O-carbocatalysis approach is a promising method for valorization of glycerol into GTBE obtaining conversion up to 51%. CO₂ pressurization also aids catalysis by providing additional acidic sites due to reaction with H₂O on the catalyst surface.

Acknowledgement

The authors gratefully acknowledge the financial support from JSPS Grant-in-Aid for Scientific Research (Grant Numbers 17KK0118 and 18K05202), the Japan Science and Technology Agency via the e-ASIA joint research program in the field of Bioenergy (SICORP Grant Number JPMJSC18E2) and JSPS-NRCT Bilateral Joint Research Program with Chulalongkorn University (Thailand) .

Keywords

Microwave; Glycerol etherification; GTBE; graphene oxide; carbocatalysis