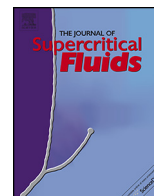




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# Fluorine-doped tin oxide catalyst for glycerol conversion to methanol in sub-critical water

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### ABSTRACT

In this study, a method for the catalytic conversion of glycerol to methanol in sub-critical water (subCW) is proposed. Glycerol conversion to methanol using the subCW method is a new attempt to the best of the authors's knowledge and this process was compared with the conventional hydrogenolysis method. For the first time, fluorine-doped tin oxide (FTO) was applied as a novel heterogeneous catalyst for the conversion of glycerol to methanol. The sub-critical reaction was conducted under optimal and mild conditions at a reaction temperature of 300 °C, reaction time of 30 min, and at a low pressure sufficient to maintain the liquid phase. Initial feedstock (glycerol) concentration and catalyst amount of 20 wt% and 0.01 g respectively, were utilized and glycerol conversion and methanol selectivity were measured using gas chromatography-flame ion detector (GC-FID) analysis. Optimum glycerol conversion of ~80% was achieved, with methanol as the major product with a selectivity of ~100%. The subCW method can also be applied for extraction processes as well as biomass conversion by optimizing some parameters such as reaction time, catalyst amount, reaction temperatures, and catalyst cyclability.

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## 1. Introduction

1,2,3-Propanetriol also known as glycerol has become an important feedstock that can be converted into value-added chemicals. Glycerol has been described as a beneficial biomass resource with a various functions for renewable energy sources [1–3]. Glycerol is produced as an abundant side product during the transesterification of palm oil fruit to produce biodiesel [4,5]. The production of glycerol has been continuously increasing with increase in the production of biodiesel. The production of biodiesel rapidly grew from 1 million tons in 2000 to 10 million tons in 2010. For every 9 kg of biodiesel production, around 1 kg of crude glycerol is produced [6,7]. Owing to the oversupply of glycerol [8], a number of catalytic reactions have received attention from researchers and have

been widely studied. Commonly, glycerol can be converted into chemicals or fuel using various techniques such as oxidation, fermentation, dehydration, carboxylation, esterification, gasification, and reduction (hydrogenolysis) [6,9]. The hydrogenolysis of glycerol has become the most popular and widely used technique for glycerol conversion. This method involves the simultaneous addition of hydrogen gas and it is easy to produce chemical molecular fragments using this method. However, an important demerit of the hydrogenolysis process is the consumption of hydrogen gas.

In the present study, we have attempted to design a new technique involving subcritical water (subCW) to convert glycerol. The subCW method is performed without an external hydrogen gas. In the subCW method, water acts as a solvent as well as a reactant [10–12]. Thus, undermost sub and supercritical condition, water is considered a promising reagent for conducting degradation process. In addition, a shorter reaction time of 30 min is also achieved in the subCW method compare to hydrogenolysis in which the optimum reaction time ranges from 6 to 24 h [13,14].

Secondly, the subCW method can be a new method for the conversion of glycerol to methanol (MeOH), which is a rare glycerol

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conversion product and most difficult to produce. Glycerol conversion commonly leads to the formation of three carbon diol products namely 1,2-propanediol (1,2-PDO) and also 1,3-propanediol (1,3-PDO) with 1,2-PDO as the promising product. Meanwhile, ethylene glycol (EG) is produced as a degradation intermediate product, followed by 1-propanol (PrOH) and 2-propanol (2-PrOH) as excess products during hydrogenolysis [4–6,8–10,13,15–19]. In our study, we attempted to produce MeOH, which is known to be among the most profitable chemicals and a fuel source in the chemical industry. The selective conversion of glycerol to MeOH by the subCW method requires the cleavage of C–O bond by the H<sub>2</sub> sources from water which acts as the solvent. As a result of this step, the conversion process is green and non-toxic. Further, the sub-critical system between the liquid and gas phase involves the dissociation of C–C bonds (covalent bond) in the glycerol molecule. Besides this, the C–C and C–O bonds are also easily dissociated at high temperatures or with hydrothermal water. The subcritical process is mainly involved during thermal cleavage in which various radicals can be obtained, and is observed to stabilize upon the addition of hydrogen which originates from the donor solvent [10,20]. Therefore, subCW is a suitable alternative method and medium for glycerol conversion.

It has been reported that the uses of a heterogeneous catalyst during glycerol conversion can yield better conversion and product selectivity. In the literature, acid, basic, or metal supported catalysts such as Cu/boehmite, Ru/TiO<sub>2</sub>, Cu/SiO<sub>2</sub>, Cu/MgO, Ni/ZnO, Ru/bentonite-TiO<sub>2</sub> etc. [5,21–24] have been used. There are some reports claiming that acid catalysts play an important role in the dehydration of glycerol with EG produced as an intermediate molecule during the generation of 1,2-PDO. The production of EG simultaneously increases conversion and selectivity [25]. The same argument has also been proposed for basic catalysts, but with a different intermediate, which under basic conditions can aid the dehydrogenation of glycerol to glyceraldehyde and finally to 1,2-PDO [7]. Feng et al. [7] also proved that improved conversion and product selectivity can be achieved under basic conditions. Therefore, considering the importance of catalyst properties in enhancing glycerol conversion, we attempted to develop a new heterogeneous catalyst namely fluorine-doped tin oxide (FTO) with amphoteric and conducting properties [26,27] for glycerol conversion to MeOH by the subCW method.

In the present study, we mainly focused on the conversion of glycerol to MeOH in subCW with FTO as the catalyst. To the best of our knowledge, this is the first study on glycerol conversion to produce MeOH as a major product by the subCW method with FTO as a heterogeneous catalyst. The effects of various parameters such as temperature, reaction time, and catalyst cyclability on glycerol conversion and product selectivity were investigated.

## 2. Materials and experimental methods

### 2.1. Chemicals

Powder of FTO, which was used as the catalyst, was purchased from Walkers & Keeling Company. Glycerol with 99.8% purity was purchased as the feedstock material from Sigma Aldrich. Distilled water was used as the solvent for feedstock dilution. Solvents such as MeOH, ethanol, 1,2-PDO, and EG were purchased from Wako Pure Chemicals Industries, Ltd. (Osaka, Japan), and were used as standard solutions for gas chromatography-flame ion detector (GC-FID) analysis. The purities of these chemicals were ~99.5%. 1,4-Butanediol (purity ~99%) was used as the internal standard for the GC instrument and was obtained from Sigma Aldrich. All the chemicals were used as received without further purification processes.

### 2.2. Catalyst preparation

The FTO catalyst powder was activated by sintering at a temperature of 450 °C for 3 h. This process activated the surface and pores of the catalyst providing active surface sites for the reaction to occur. After the sintering process, the FTO catalyst powder was stored in a sample bottle, and purged with argon gas to prevent exposure to moisture.

### 2.3. SubCW reactor experimental procedure

The experiments were carried out using a stainless steel tube reactor with a capacity of 5.0 cm<sup>3</sup>, (16.0 mm o.d, 6.0 mm and 180.0 mm in length) fabricated at AKICO Co., Ltd., Tokyo, Japan. The glycerol feedstock was prepared at a concentration at 20 wt% (2 mL), to which 0.01 g of FTO catalyst was mixed in the reactor. The reactor was then sealed and tightened to prevent leakage during the reaction. Subsequently, the reactor was placed in an electric furnace (Isuzu Co. Ltd., model NMF-13AD), heated to 573 K, and shaken using a mechanical device. The reaction was conducted for 30–180 min. After the reaction, the reactor was removed from the electric furnace and quenched in a water bath at ambient temperature. After the cooling process, the liquid and catalyst were collected and separated using centrifugation and filtration processes. After each reaction, the FTO catalyst was collected and washed 3 times with distilled water in order to remove any reactant, product or impurities that may have been stuck to the catalyst. This cleaning process allowed the catalyst to be tested for recyclability. Lastly, the reaction products were analyzed using GC-FID, and glycerol conversion and product selectivity were calculated using the following equation:

$$\text{Glycerol conversion (\%)} = \frac{\text{Moles of glycerol consumed}}{\text{Moles of glycerol initially charged}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{Moles of carbon in a specific product}}{\text{Moles of carbon in all detected product}} \times 100$$

### 2.4. Characterization

The catalyst properties and catalyst performance were characterized next. The surface morphology and particle size of the catalyst were analyzed by using a field-emission scanning electron microscope (FE-SEM: with Supra55vp model) and transmission electron microscope (TEM: Super Twin Philips Technai 20). Meanwhile, the catalyst composition was analyzed by energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS), Kratos (XSAM HS). X-ray diffraction (XRD: Bruker DB advance) was used to analyze the structure and crystallinity of the catalyst. XRD pattern were acquired in the 2θ range of 20–80°. The acidity and basicity properties of the catalyst, were determined using chemisorption measurements by the temperature programmed desorption method (TPD). Two types of gases, namely 5% NH<sub>3</sub> in 95% He, and 5% CO in 95% He were used for the acidity and basicity tests respectively. In addition, using the temperature programmed reduction (TPR) method, the catalyst reduction phase and oxidation state were determined. These experiments were conducted in the temperature range of 30–850 °C in the presence of a mixture gases composed of 10% N<sub>2</sub> and 90% H<sub>2</sub>. Both the TPD and TPR analysis instruments were procured from Micromeritics Autochem II model.

The catalyst performance was analyzed using gas GC-FID (model series of Shimadzu, GC-2014). The yield was quantified by the HP-Innowax column (Agilent Technologies, length 30 m, i.d. 0.250 mm, film 0.25 μm). The temperature program was run from 45 (3) to 240 (5) with a gas flow rate of 5 mL/min. 1,4-Butanediol was used

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