

Hydrogen Production via Oxidative Steam Reforming of Biodiesel By-products over Ni/CeO₂-ZrO₂/Al₂O₃ Catalyst

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Abstract. Yellow glycerol and crude glycerol, by-products of biodiesel, are renewable resource that can be used for sustainable production of hydrogen. The oxidative steam reforming of biodiesel by-products over Ni/CeO₂-ZrO₂/Al₂O₃ catalyst were investigated and the effluents from reforming of both by-products were compared with that of pure glycerol. Preliminary analysis of yellow glycerol showed that there were methanol and fatty acid methyl esters in it whereas the presence of potassium (K) and sodium (Na) was observed in crude glycerol. The catalytic activity of Ni/CeO₂-ZrO₂/Al₂O₃ catalyst was studied isothermally under atmospheric pressure at water-to-glycerol and oxygen-to-glycerol molar ratio of 9:1 and 0.5:1, respectively. Under these conditions, the glycerol was reformed to H₂, CO₂, CO and CH₄ with small amount of C₂ gas products that were measured by gas chromatograph. The results showed that the yellow glycerol was completely converted in gas phase and provided hydrogen yield and selectivity at 71% and 72%, respectively, whereas crude glycerol was nearly completed to convert in gas phase and gave the lowest hydrogen yield and selectivity at 37% and 42%, respectively because of the presence of coke formation. Therefore, the potential to produce hydrogen gas with low price feedstock like yellow glycerol was highly recommended with respect to pure glycerol.

Keywords: hydrogen production, glycerol, oxidative steam reforming, Ni/CeO₂-ZrO₂/Al₂O₃

1. Introduction

Biodiesel production has been rapidly increased with the increase of energy demand, and it is forecasted that biodiesel could make up as much as 20% of all transportation fuels in 2020 [1]. It would lead to increase of glycerol production in the amount excess the market demand lowering its price. This by-product glycerol must be treated and purified before using it as an industrial feedstock for applications in food, cosmetics, pharmaceutical and other industries. For the purification process, high cost was spent and energy was consumed. Therefore finding alternative feasible use for by-product glycerol has become imperative. Among possible use for glycerol, hydrogen production from glycerol has recently attracted much attention. The hydrogen can be used to generate electricity directly in fuel cell. Conversion of glycerol to hydrogen has been carried out by several techniques, such as aqueous-phase reforming [2], pyrolysis [3], supercritical water reforming [4], steam reforming [5], partial oxidation reforming [6], and oxidative steam reforming [7]. Many researchers focused on steam reforming process of pure glycerol which were studied on operating parameters [5,8] and performance of catalyst [9-14].

Thermodynamic analysis [7] presented that the most favorable conditions for hydrogen production via autothermal reforming were at temperature, water-to-glycerol molar ratio and oxygen-to-glycerol molar ratio of 900-1000 K, 9-12 and 0.0-0.4, respectively. Douette et al. [15] performed glycerol reforming at various

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ratios of oxygen-to-carbon and steam-to-carbon. 4.4 mol of produced hydrogen per mole of crude glycerol was found but catalyst deactivation was of great concern.

Ni supported on oxide has been widely reported as an active catalyst. Although noble metals are more effective than Ni and less susceptible to carbon formation, such catalysts are not commonly used in industrial applications because of their cost [16]. However, the characteristic of Ni are needed to modify, despite the problems of the catalyst deactivation caused by carbon deposition and sintering of Ni particles under high temperature condition. CeO₂ and ZrO₂ have been used as either support or promoter because of their oxygen storage capacity (OSC) characteristic, which allows them to store and release oxygen. Moreover, they improve the thermal stability and decrease the sintering of Ni particles.

As mentioned above, there have been some works on the steam reforming of glycerol over Ni-based catalysts, but none of the reports has been published on oxidative steam reforming of glycerol over Ni/Al₂O₃ that was promoted with CeO₂-ZrO₂. In this work, the oxidative steam reforming of two types of biodiesel by-products were investigated over Ni/CeO₂-ZrO₂/Al₂O₃ and the results were compared with that of pure glycerol.

2. Experimental Section

2.1. Biodiesel By-product Samples and Characterization

The by-products of biodiesel used in this research consist of crude glycerol and a so-called “yellow glycerol”. They were obtained from PTT Chemical Co., Ltd., Rayong, TH. The yellow glycerol and crude glycerol consist of glycerol 90% and 40%, respectively. The ultimate analysis and physical property of glycerol were analyzed by using CHN Analyzer (LECO model CHN-2000). The proximate analysis of the samples was also performed. Glycerol of 99.5% purity supplied by Ajax Finechem (conforms to ACS) was also examined to compare the results with both samples.

Table 1. The composition and density of each glycerol.

Parameter	Pure Glycerol ^b	Yellow Glycerol	Crude Glycerol
Moisture (%)	0.50	5.25	3.39
Ash (%)	n.d.	0.04	2.42
C (%)	39.13	36.67	36.45
H (%)	8.76	9.69	8.28
N (%)	n.d.	2.18	n.d.
O (%)	52.12	46.17	49.46
Density ^a (kg m ⁻³)	1257	1192	1297

n.d. means not detected., aMeasured at 298 K., and bCalculated based on its formula.

2.2. Catalyst Preparation and Characterization

The 15%Ni/Al₂O₃ catalyst promoted with 8%CeO₂-ZrO₂ was prepared by deposition method that was reported the details elsewhere [16,21]. Ce(NO₃)₃·6H₂O (supplied by Acros Organics), ZrO(NO₃)₂·xH₂O (supplied by Sigma Aldrich) and Ni(NO₃)₂·6H₂O (supplied by Carlo Erba) were used as promoter and active metal precursors, respectively. A commercial Al₂O₃ powder (JRC-ALO6, product of Japan Chemical Co. Ltd.), which has surface area of 189 m²/g, was used as the support. The ceria and zirconia precursors were first deposited onto Al₂O₃ powder. After that, CeO₂-ZrO₂/Al₂O₃ promoter-support was dried in air at 393 K for 3 h and calcined at 773 K for 3 h. Ni was then deposited on this CeO₂-ZrO₂/Al₂O₃ by using an aqueous solution Ni(NO₃)₂·6H₂O under stirring followed by drying and calcining in air at 393 K for 3 h and 773 K for 3 h, respectively. After that, the 15%Ni/8% CeO₂-ZrO₂/Al₂O₃ was pelletized to the size of 1.18-1.70 mm.

The catalyst was analyzed for its physical properties as described in our previous work [16]. The catalyst surface area was measured in Belsorp Mini II (BEL Japan, Inc.) by applying the Brunauer-Emmett-Teller method (BET). Prior to physisorption measurements, the catalyst was reduced by flowing H₂ at 773 K for 3 h. Following the reduction of the catalyst, subsequent flushing under He until the temperature decreased to

room temperature was applied. The X-ray diffraction (XRD) was used to identify the catalyst structure before oxidative steam reforming reaction that was obtained by using a Phillips PW 1830 equipped with CuK α radiation. Additionally, the amount of carbon formation on the catalyst was estimated by using Thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851 $^{\circ}$).

2.3. Catalytic Activity Test

Oxidative Steam Reforming was operated isothermally at 923 K under atmospheric pressure in a packed-bed reactor made of stainless steel (SS316) tube with outer diameter of 12.7 mm which was placed inside a temperature-controlled furnace. The reaction temperature was measured and controlled using a K-type thermocouple located at the middle of the catalyst bed that was kept in the middle of the reactor by using quartz wool. Prior to the reaction, the catalyst was reduced *in situ* at 773 K with H₂ flowing at 30 ml min⁻¹ for 3 h. After the catalyst activation, a solution of glycerol was introduced into the reactor by means of HPLC pump (2SMP, Eldex) carried by He flow co-fed with oxygen gas. It was passed through a vaporizer where it was heated at 673 K before being fed into the reactor. The operating condition at water-to-glycerol molar ratio of 9:1 and molar ratio of oxygen-to-glycerol of 0.5:1 was kept constant for all experiments. It was the suitable conditions for autothermal reforming of glycerol presented by Wang et al.[7]. The outlet gas stream was cooled with a condenser to condense liquid products. The gas product was passed through a moisture trap before periodically sampled and analyzed with a gas chromatograph (GC-14B, Shimadzu) equipped with thermal conductivity detector (TCD), using a molecular sieve 13X and a Porapak N columns, to analyze for H₂ level, CO, CO₂ and CH₄ levels. Additionally, hydrocarbon gas product (C₂H₂, C₂H₄ and C₂H₆) were examined using flame ionized detector (FID) and a Porapak Q column.

The catalytic activity was evaluated in terms of glycerol conversion, gas product's yield, gas product's selectivity and coke formation that were calculated according to the following definitions:

$$\text{Glycerol conversion (\%)} = \frac{\text{mole C in gas product}}{\text{Total mole C in feed}} \times 100 \quad (1)$$

$$\text{H}_2 \text{ yield (\%)} = \frac{\text{mole H}_2 \text{ in gas product}}{\text{mole H}_2 \text{ in feed}} \times 100 \quad (2)$$

$$\text{H}_2 \text{ selectivity (\%)} = \frac{\text{mole H}_2 \text{ in gas product}}{\text{Total mole C in gas product}} \times \frac{1}{\text{RR}} \times 100 \quad (3)$$

where RR is the fraction ratio of H₂ to CO₂ based on the stoichiometry. In this case, it was 6/3 according to the following reaction,



$$\text{Yield of } i \text{ (\%)} = \frac{\text{mole } i \text{ in gas product}}{\text{Total mole C in feed}} \times 100 \quad (5)$$

$$\text{Selectivity of } i \text{ (\%)} = \frac{\text{mole } i \text{ in gas product}}{\text{Total mole C in gas product}} \times 100 \quad (6)$$

where species *i* = CO, CO₂, and CH₄.

The coke formation was determined based on the weight loss of the spent catalysts obtained from TGA per weight of catalyst per reaction time.

3. Results and Discussion

3.1. Properties of Biodiesel By-products

The ultimate analysis results of the samples used in this study are shown in Table 1. The calculated molar formula of yellow glycerol and crude glycerol were $C_{3.06}H_{9.89}O_{2.89}N_{0.16}$ and $C_{3.04}H_{8.28}O_{3.09}$, respectively. The H/C molar ratio of yellow glycerol and crude glycerol were higher than pure glycerol. The O/C molar ratio of yellow glycerol was lower whereas O/C molar ratio of crude glycerol was higher when compared with pure glycerol. This indicated that the yellow glycerol property would have been partly influenced by the presence of methanol and fatty acid methyl esters (FAMES) that were reactant and product in biodiesel production, respectively. The proximate analysis showed that the amount of ash in crude glycerol was higher than that in yellow glycerol because there was potassium (K) and sodium (Na) that was used as the catalyst in the transesterification process.

3.2. Physical Properties of catalyst before reaction

The properties of Ni/CeO₂-ZrO₂/Al₂O₃ were determined by BET and XRD. The catalyst has a BET surface area of 174 m² g⁻¹. The XRD pattern of the reduced catalyst is displayed in Figure 1. The diffraction peaks at 45.7° and 66.8° was attributed to γ -Al₂O₃. The intensity peaks at 44.5°, 51.8° and 76.3° are identified as Ni metal while that at 37.0° corresponded to NiAl₂O₄. The cubic phase of ceria-zirconia solid solution, Ce_{0.75}Zr_{0.25}O₂, was observed from the shift of the (111) reflection from 28.5° to higher 2-theta values, at 28.7°. That could be attributed to shrinkage of the corresponding lattice because of the replacement of Ce⁴⁺ by Zr⁴⁺ with smaller cation radius, thereby incorporating ZrO₂ into CeO₂ lattice to form solid solution of ceria-zirconia. That indicated that Ce and Zr are highly homogeneously distributed on the catalyst [16,17]. The average crystallite size of the Ni particles was calculated from the X-ray line broadening peak at 51.8° and corresponding to the (200) reflection using the Debye-Scherrer equation, thereby the mean crystallite size of Ni particles was 9.7 nm.

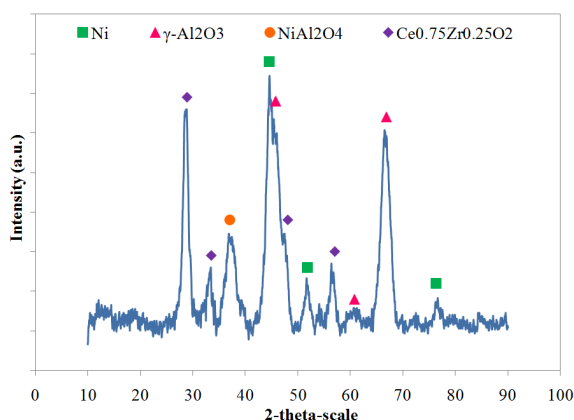
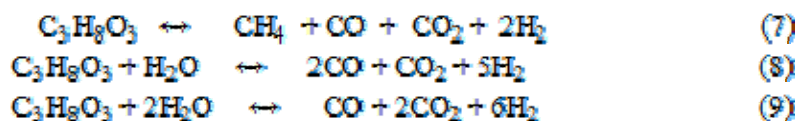


Fig. 1: XRD diffraction patterns of fresh Ni/CeO₂-ZrO₂/Al₂O₃ catalyst.

3.3. Catalytic reforming of glycerol

The oxidative steam reforming of three types of glycerol over Ni/CeO₂-ZrO₂/Al₂O₃ catalyst at H₂O:Glycerol and O₂:Glycerol molar ratio of 9 and 0.5 and 923 K was investigated over 6 h. The conversion of glycerol in gas phase is presented in Figure 2(a). The pure glycerol and yellow glycerol were totally converted to gaseous product whereas the conversion of crude glycerol was 91%.

A gaseous mixture consisting of H₂, CO₂, CO, CH₄ and small amount of C₂ species was observed as the product. Figure 2(b) and 2(c) depicted yield and selectivity of gas product, respectively. The high yield and selectivity for H₂, CO₂ and CO came from glycerol decomposition and steam reforming [7] that were the main reactions,



In addition, the oxidation of glycerol could take place when oxygen is presented in the system.

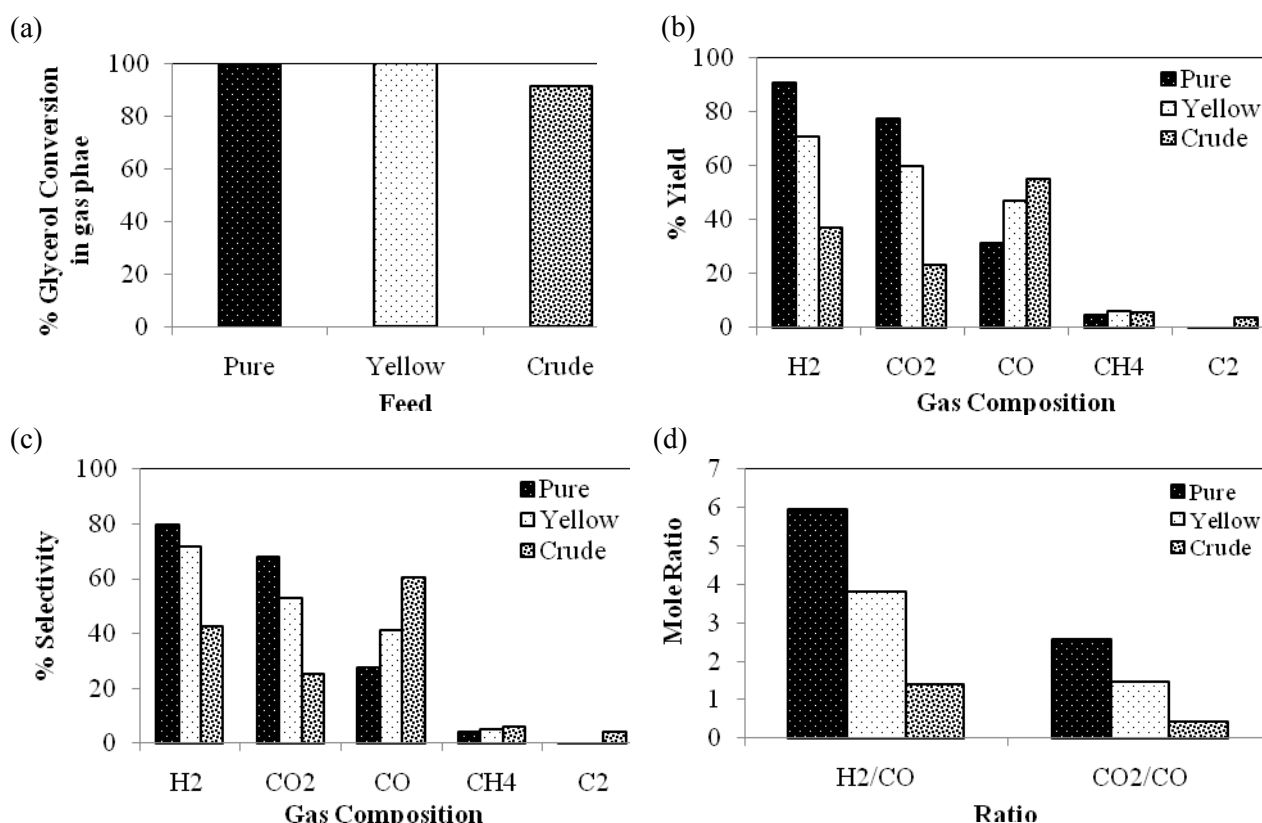
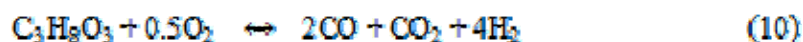


Fig. 2: (a) Glycerol conversion in gas phase (b) Yield (c) Selectivity of gas product and (d) H₂/CO and CO₂/CO molar ratio obtained from oxidative steam reforming. Comparison between pure glycerol, yellow glycerol and crude glycerol.

The average hydrogen yield of yellow glycerol was 78% of the hydrogen yield of pure glycerol whereas 41% of hydrogen yield from crude glycerol was obtained. This was because the long chain of fatty acid methyl ester mainly contained in the crude glycerol was harder to reform [18]. Even though the hydrogen yield of yellow glycerol was lower than that of pure glycerol, the hydrogen selectivity of yellow glycerol was similar to that of pure glycerol as shown in Figure 2(b) whereas hydrogen selectivity of crude glycerol was the lowest, 53% of the selectivity of hydrogen of pure glycerol. Considering the CO₂ and CO yields and selectivities, a much higher CO₂ yield and selectivity than CO yield and selectivity were observed with yellow glycerol, with the difference being greater than that was observed with pure glycerol. This could be explained by the water-gas shift reaction presented in equation (11) leading to higher selectivity of CO₂ and lower selectivity of CO.



Besides, the H₂/CO and CO₂/CO molar ratio confirmed that in reforming of yellow glycerol and pure glycerol, result in water-gas shift reaction could take place easily than in crude glycerol. In addition the carbon contained in pure glycerol was the highest, thereby it could be oxidized to CO and CO₂ in presence of oxygen. With yellow glycerol, trace of methanol-containing could be further decomposed to CO and CO₂, and then the amount of CO and CO₂ were higher than when using pure glycerol. With crude glycerol, the lowest yield and selectivity of hydrogen and CO₂ were observed whereas the highest yield and selectivity of CO were obtained. This was attributed to the complicated water-gas shift reaction as it could be verified by CO₂/CO molar ratio of approximately 0.4.

The highest yield of methane level from yellow glycerol suggested that thermal cracking of fatty acid methyl ester and methanation possibly occurred [19]. Furthermore, the presence of alkali metal catalyst, such as Na, K in crude glycerol caused coke formation and higher methane yield [15]. Minor amounts of C₂ species (0.3%), such as C₂H₄ and C₂H₆, were also observed in pure glycerol and yellow glycerol whereas

they revealed a significant value at 3.7% in crude glycerol. The C₂ species could be occurred from glycerol dehydration forming C₂H₄ which was immediately converted to C₂H₆ [20,21]. The C₂H₄ and C₂H₆ yields indicated that crude glycerol favored the dehydration of glycerol. Then, yellow glycerol was more suitable as a fuel for hydrogen production than crude glycerol.

3.4. Coke formation on the catalyst

To evaluate the coke formation over the spent catalysts, the results showed that the coke formation rate from oxidative steam reforming of glycerol under similar conditions in steam reforming of glycerol over Ni/CeO₂ catalyst was reported to be 19 mg carbon 100 mg catalyst⁻¹ h⁻¹ by Adhikari et al [5]. This value is higher than 3.6, 3.3 and 4.5 mg carbon 100 mg catalyst⁻¹ h⁻¹ when using pure glycerol, yellow glycerol and crude glycerol, respectively, obtained in this work. This could possibly be the combination result of the oxidative steam reforming operation and CeO₂-ZrO₂ promoter of the Ni catalyst that reduces the coke formation better than steam reforming and un-promoted Ni catalyst.

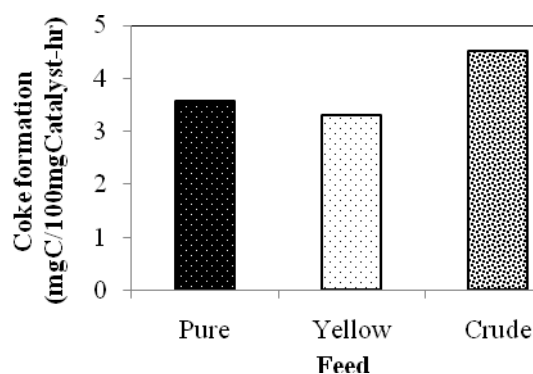


Fig. 3: Coke formation of spent catalyst after performing oxidative steam reforming reaction at H₂O:Glycerol = 9, O₂:Glycerol = 0.5 and 923 K for 6 h.

4. Conclusion

Oxidative steam reforming of biodiesel by-products, yellow glycerol and crude glycerol, for hydrogen production were investigated in a fixed-bed reactor over Ni/CeO₂-ZrO₂/Al₂O₃ catalyst at 923 K, water-to-glycerol molar ratio of 9:1 and oxygen-to-glycerol molar ratio of 0.5:1. The results were compared with that of pure glycerol under the same condition. At the condition studied, yellow glycerol showed to be a promising feed for hydrogen production by oxidative steam reforming reaction giving complete conversion yield of 71% with low carbon formation. While crude glycerol was not a suitable alternative feedstock for hydrogen production, it should be pretreated or a proper operating condition should be applied. Oxidative steam reforming of the biodiesel by-products yielded low coke deposit on the Ni/CeO₂-ZrO₂/Al₂O₃ catalyst.

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