Study of the hydrogen production by the aqueous phase reforming of glycerol over Ni-based catalysts

Raquel Raso, Eduardo Abad, Lucía García, Joaquín Ruiz, Miriam Oliva, Jesús Arauzo

Thermochemical Processes Group (GPT)
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain.
Tel. +34-976762707, e-mail: rroka@unizar.es

Abstract

The present work studied the effects of loading Fe, Ca, and the impurities of glycerol on the Ni/Al catalytic behavior in the aqueous phase reforming (APR) of glycerol to obtain renewable hydrogen.

Introduction

In the last decades, the consumption of fossil fuels has increased rapidly, resulting in an environmental crisis. The transport sector accounts for around 60 % of global oil consumption and produces one-fifth of global CO_2 emissions. Hence, the development of sustainable and clean sources of combustibles is essential. In this context, biodiesel has become one of the most common worldwide biofuels [1]. Biodiesel is mainly produced by the transesterification of vegetable oils, animal fats, and waste oils using methanol or ethanol in the presence of a catalyst. For every 10 tons of biodiesel produced, around 1 ton of glycerol is generated as a by-product. Therefore, the treatment of glycerol should not be ignored due to could negatively affect the biodiesel economy. In this case, hydrogen production from glycerol is an opportunity to improve the economic viability of biodiesel industries [2,3].

Many methods exist to produce hydrogen from glycerol, such as steam reforming, aqueous phase reforming (APR), and autothermal reforming. Among these processes, the APR method is kinetically and thermodynamically viable in producing inexpensive renewable hydrogen with low CO concentration [1]. In addition, it is a catalytic process and has very high energy efficiency as operating at relatively low temperatures (200-280 ºC) and moderate pressures (15-70 bar) compared to the conventional reforming processes [1,4]. This process was investigated first by the group of Dumesic in 2002 [5].

With this background, the present work studied the APR of glycerol over Ni-based catalysts to obtain hydrogen.

The objectives were to analyze the effects of loading Fe, Ca, and the impurities of glycerol (chemical glycerol and bio-glycerol) on the Ni/Al catalytic behavior in the APR of glycerol to obtain hydrogen.

Experimental

Three different Ni-based catalysts were prepared by the co-precipitation method described by Raso et al. [6], keeping the Ni content constant at 28 molar % and changing the molar ratio of Al/Fe or Al/Ca from 1/0 to 3/1 or 13.3/1, respectively. The catalysts were named Ni/Al, Ni/Al_3Fe_1, and $Ni/Al_{13.3}Ca_1$ and calcined at 500 ºC for 3 h.

Catalytic performance was carried out in a continuous system (Process Integral Development Eng & Tech, Spain), which mainly consisted of a stainless-steel fixed bed reactor heated up using an electric furnace and a micrometric valve that regulates the pressure system. The catalysts were tested at 37 absolute bar and 238 ºC for 3 h, using a solution of 5 wt.% of glycerol from chemical reactive or biodiesel production, obtaining gas and liquid products. Before the reaction, the catalysts were reduced in situ at 500 ºC (Ni/Al_3Fe_1) or 600 ºC (Ni/Al and $Ni/Al_{13.3}Ca_1$) for 1 h using a hydrogen stream of 100 cm^3 (STP)/min, according to the H_2-TPR results. The exit gas mixture (N_2, H_2, CH_4, CO_2, CO, C_2H_6, and C_3H_8) was analyzed online employing an Agilent 490 Micro-GC equipped with Thermal Conductivity Detectors (TCD). The N_2 was used as an internal standard. The total C feed was analyzed offline using Total Organic Carbon (TOC) equipment to determine the carbon yield to gases, and hydrogen yield expressed as mg H_2/mol C fed. In the present work, the liquid product was not examined.

Results and discussion

Almost no differences were found between the ICP-OES analysis and the nominal metal values in the prepared Ni-based catalysts. For all catalysts, the synthesis is appropriate.

Table 1 shows the gas composition (vol. %, N_2, and H_2O free) for the different experiments. According to the catalytic performance results, adding Fe or Ca to the Ni/Al catalyst increased the H_2 (objective product) and CO_2 content. However, the CH_4 content was decreased by adding Fe or Ca to the Ni/Al catalyst. Meanwhile, the C_2H_6 and CH_3H_8 content were almost unchanged, and CO was practically not found. In addition, the use of bio-glycerol (obtained from biodiesel production) as fed also increased the H_2 content for the Ni/Al and Ni/Al_3Fe_1 catalysts. At the same time, it slightly decreased the H_2 content for the $Ni/Al_{13.3}Ca_1$ catalyst.

The carbon yield to gas and the H_2 yield were higher for all catalysts when chemical glycerol was fed than when bio-glycerol was provided. The $Ni/Al_{13.3}Ca_1$ catalyst showed the lowest carbon yield to gas, while the Ni/Al catalyst indicated the lowest H_2 yield.

Conclusions

The chemical composition of the catalyst and glycerol impurities influenced the H_2 production by APR of glycerol. The H_2 yield decreased in the following order: $Ni/Al_3Fe_1 > Ni/Al_{13.3}Ca_1 > Ni/Al$.

Acknowledgments

The authors wish to express their gratitude to project PID2020-114985RB-I00, funded by MCIN/AEI/10.13039/501100011033. The authors acknowledge the funding from the Aragon Government (ref. T22_20R), co-funded by FEDER 2014-2020 “Construyendo Europa Desde Aragón”. In addition, Eduardo Abad acknowledges the research grant from I3A funded by “Cátedra de Transformación Industrial”. The authors would also like to acknowledge the use of the Servicio General de Apoyo a la Investigación-SAI of the Universidad de Zaragoza.

REFERENCES

[1]. GUO, Y., AZMAT, M., LIU, X., WANG, Y., LU, G, Effect of support's basic properties on hydrogen production in aqueous-phase reforming of glycerol and correlation between WGS and APR. *Applied Energy*, 2012, 92, 218-223. Available from: doi:10.1016/j.apenergy.2011.10.020.

[2]. MAHLIA, T., SYAZMI, Z., MOFIJUR, M., ABAS, A., BILAD, M., ONG, H., SILITONGA, Patent landscape review on biodiesel production: Technology updates. *Renewable & Sustainable Energy Reviews*, 2020, 118. Available from: doi:10.1016/j.rser.2019.109526.

[3]. WU, K.; DOU, B.; ZHANG, H.; LIU, D.; CHEN, H.; XU, Y, Aqueous phase reforming of biodiesel byproduct glycerol over mesoporous $Ni-Cu/CeO_2$ for renewable hydrogen production. *Fuel*, 2022, 308. Available from: doi:10.1016/j.fuel.2021.122014.

[4]. MORALES-MARIN, A.; AYASTUY, J.; IRIARTE-VELASCO, U.; GUTIERREZ-ORTIZ, M, Nickel aluminate spinel-derived catalysts for the aqueous phase reforming of glycerol: Effect of reduction temperature. *Applied Catalysis B-Environmental*, 2019, 244, 931-945. Available from: doi:10.1016/j.apcatb.2018.12.020.

[5]. CORTRIGHT, R.; DAVDA, R.; DUMESIC, J, Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature*, 2002, 418, 964-967. Available from: doi:10.1038/nature01009.

[6]. RASO, R.; GARCIA, L.; RUIZ, J.; OLIVA, M.; ARAUZO, J. Aqueous phase hydrogenolysis of glycerol over Ni/Al-Fe catalysts without external hydrogen addition. *Applied Catalysis B-Environmental*, 2021, 283. Available from: doi:10.1016/j.apcatb.2020.119598.

Table 1. Gas composition (vol.%, N_2, and H_2O free) for the different experiments.

Experiments		H_2	CO_2	CO	CH_4	C_2H_6	C_3H_8
Ni/Al	(1)*	16.80	49.95	0.00	31.18	1.58	0.50
	(2)**	21.82	56.04	0.00	20.20	1.51	0.43
Ni/Al_3Fe_1	(1)*	32.61	54.62	0.02	10.54	1.72	0.49
	(2)**	34.45	57.69	0.00	6.05	1.41	0.40
$Ni/Al_{13.3}Ca_1$	(1)*	39.71	58.31	0.02	0.16	1.36	0.44
	(2)**	37.82	58.85	0.00	1.56	1.41	0.36

*: Chemical glycerol (Sigma-Aldrich, purity: 99.5 %). **: Bio-glycerol (obtained from biodiesel production, purity: 86.1 %).