



## Research article

# Reforming of glycerol to hydrogen over Ni-based catalysts in a microchannel reactor



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## ABSTRACT

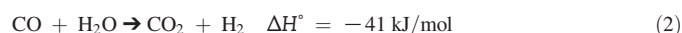
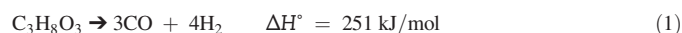
The aim of this work is to investigate non-oxidative and oxidative glycerol steam reforming (GSR and OGSr, respectively) over Ni-based catalysts in a microchannel reactor. The effects of reaction temperature (500–600 °C), molar inlet steam-to-carbon ( $S/C = 3-6$ ) and carbon-to-oxygen ( $C/O = 0.75-2.25$ ) ratios, total feed flow rate (64–128 Nml/min) and Ni-loading (5 and 10% by weight) on glycerol conversion and product distribution are studied. Experiments are conducted in a Ni/Al<sub>2</sub>O<sub>3</sub> coated microchannel reactor integrated with precise metering of gas and liquid flows and temperature control. The results show that increasing the amount of inlet steam in GSR reduces the deposition of coke through its gasification and favors water-gas shift (WGS), but also causes sintering of Ni. GSR responses of catalysts with 5 and 10% Ni loadings are found to be similar. Increasing feed flow rate of reactants affects the relative extents of glycerol decomposition and WGS to deliver higher H<sub>2</sub>/CO and CO<sub>2</sub>/CO ratios. Coke formation, that is found to occur under all conditions of GSR, decreases significantly upon addition of O<sub>2</sub> into the feed in the context of OGSr. Conversions and product yields obtained in OGSr are notably higher than those obtained in GSR. Decreasing C/O improves conversion, but reduces H<sub>2</sub> yield. Despite involving less catalyst and operating at contact times shorter than those involved in packed-beds, microchannel configuration is capable of operating at higher reactor productivities measured in terms of H<sub>2</sub> yield per unit amount of catalyst. Blank tests carried out in GSR and OGSr conditions give conversions similar to those involving catalyst, which, however, plays a role in shifting product composition in favor of H<sub>2</sub>.

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## 1. Introduction

The efforts in producing renewable fuels that can replace the existing, crude oil-based ones exhibit an increasing trend due to elevated cost of exploration and production of crude oil. Among a number of alternatives, biodiesel turns out to be a promising renewable fuel as its properties allow it to be blended directly with the crude-oil based diesel without creating any issues in the conventional diesel engines [1,2]. Conventional production of biodiesel involves transesterification of animal-based or vegetable oils with methanol (or ethanol). In this route, one mole of glycerol is produced for every three moles of biodiesel [1, 2]. Such a product distribution, however, causes undesirably high supply of glycerol, which increases the cost of biodiesel due to elevated cost of glycerol removal. A potential solution of this problem involves the determination of strategies for efficient valorization of glycerol into value-added products such as H<sub>2</sub>, which is heavily used in important operations of petroleum refining and is a key component for realizing proton-exchange membrane fuel cell operation to provide up to 5 kW power for a number of mobile and residential applications [3].

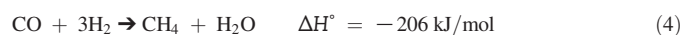
Conversion of glycerol to H<sub>2</sub> is possible by its steam reforming which is a combination of pyrolysis of glycerol (Reaction 1) and WGS (Reaction 2) [4]:



Combination of Reactions (1) and (2) gives the glycerol steam reforming (GSR) reaction:

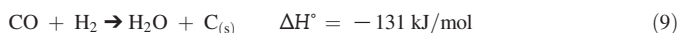
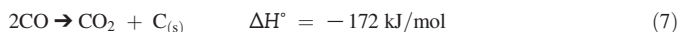
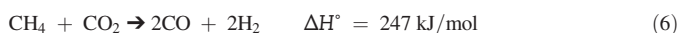


The stoichiometry given above assumes that CO generated by pyrolysis is completely converted by WGS. However, depending on the extent of WGS, CO can be present in the product mixture. GSR is accompanied by a number of possible side reactions such as methanation (Reactions 4 and 5) and dry reforming of methane (Reaction 6). Reactions 7–10 resemble possible routes of carbon formation, which can occur under GSR conditions [4,5]:

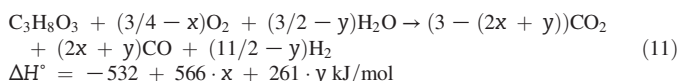


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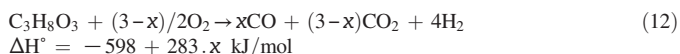
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A possible way to minimize carbon formation is to co-feed sub-stoichiometric quantities of  $\text{O}_2$  with steam to obtain the following stoichiometry, called autothermal reforming (ATR) or oxidative glycerol steam reforming (OGSR) [5]:



As in the case of GSR, degree of WGS and the extents of the side reactions (Reactions 4–10) affect product distribution in OGSR. In general,  $\text{H}_2$  concentration obtained in GSR is higher than that obtained in OGSR, whereas the latter is more suitable for the production of synthesis gas ( $\text{CO} + \text{H}_2$ ) whose composition can be tuned by the respective amounts of  $\text{O}_2$  and  $\text{H}_2\text{O}$  in the feed, which are regulated by the values of  $x$  and  $y$  in Reaction (11), respectively. An alternative route for converting glycerol to  $\text{H}_2$  is catalytic partial oxidation (POX), which involves co-feeding glycerol only with sub-stoichiometric quantities of  $\text{O}_2$ . In this route, the inlet amount of  $\text{O}_2$ , which is dictated by the value of parameter  $x$  in Reaction (12) determines the synthesis gas composition [5]:



Most of the studies in the literature about GSR, OGSR and POX involve testing of different catalysts at specified set of key operating conditions such as temperature, molar inlet steam-to-carbon (S/C) and carbon-to-oxygen (C/O) ratios for the purpose of improving glycerol conversion and  $\text{H}_2$  throughput while reducing/eliminating carbon formation and enhancing catalyst stability. As reviewed in detail by Lin [5], the catalysts involve metals such as Ni, Co, Rh, Pt, Ru and Ir and supports such as alumina, ceria, zirconia, silica and magnesia. Majority of these studies, which provide information about the effect of metals, promoters, support and their interactions, are conducted in packed-bed reactors in which the catalysts are in particulate form [5–8]. However, the number of studies that investigate glycerol conversion and subsequent product distribution on different reactor types such as monolith, foam and microchannel reactors, in which the catalyst is mostly in the form of a layer coated onto the walls of the reactor structure is scarce. Adhikari et al. [9] studied GSR over  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2/\text{Al}_2\text{O}_3$  ceramic foams that involved Rh, Ni, Ru, Ir, Pd and Pt-based catalysts. At 900 °C, S/C of 3 and gas-hourly space velocity (GHSV) of  $1.53 \times 10^4 \text{ h}^{-1}$ , they found that  $\text{Ni}/\text{Al}_2\text{O}_3$  gave glycerol conversion and  $\text{H}_2$  selectivity of 90% and 80%, respectively, which were reported to change to 93% and 71%, respectively, by using  $\text{Rh}/\text{CeO}_2/\text{Al}_2\text{O}_3$  [9]. Comparison of the performances of monolithic, powder and pellet forms of Ni-Sn based catalyst in the context of GSR was carried out by Bobadilla et al. [10]. Even though same activity was recorded for all forms in the first hour of operation, a notable drop in  $\text{H}_2$  selectivity was observed over the particulate catalysts after 5 h. The authors also reported that catalyst morphology affected the extent of coke formation, which was found

to be minimized over monolithic catalyst. Autothermal reforming (ATR) of glycerol over Pt and Rh/Pt dual-layer monolithic catalysts was studied by Liu et al. [11] at a GHSV of  $1.5 \times 10^4 \text{ h}^{-1}$ . Their parametric study involved exploration of the effects of feed temperature, steam-to-carbon and carbon-to-oxygen ratios in the ranges of 300–700 °C, 0.4–1.5 and 1.67–2.5, respectively, on glycerol conversion and product distribution. They demonstrated almost complete conversion with  $\text{H}_2$  and CO yields of 75% and 48%, respectively, with negligible coke deposition, and reported that product concentrations were close to their equilibrium counterparts [11]. Liu and Lawal [12] also studied the kinetics of glycerol ATR with negligible heat and mass transfer resistances over their monolithic catalyst structure and reported activation energy of 130.7 kJ/mol. Glycerol ATR was also studied by Liu and Lin [13] on monoliths coated with  $\text{LaMnO}_3$  and  $\text{LaNiO}_3$  perovskites. While  $\text{LaMnO}_3$  was reported to favor combustion into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ,  $\text{LaNiO}_3$  promoted  $\text{H}_2$  production. However, addition of Pt over  $\text{LaMnO}_3$  was found to improve  $\text{H}_2$  and CO selectivities up to ca. 60% and 40%, respectively [14]. Sadykov et al. [15,16] investigated glycerol ATR over Ni-Ru based structured reactors and reported that the microchannel substrate made from a heat-conducting material and offered transport limitation free operation led to synthesis gas yields that are close to equilibrium. The same authors also demonstrated the possibility of minimizing coke formation and improving the stability of the operation by adding optimized amounts of oxygen into the feed [16]. Dauenhauer et al. [17] studied glycerol POX and ATR over Rh-Ce/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts washcoated on  $\alpha$ - $\text{Al}_2\text{O}_3$  foam at GHSVs in the order of  $10^5 \text{ h}^{-1}$ , and in the temperature and molar inlet carbon-to-oxygen ratio (C/O) ranges of 900–1200 °C and 0.8–1.6, respectively. They found maximum  $\text{H}_2$  selectivity of 56% at (C/O) of 1.2 and CO selectivity of ~80% at all C/O ratios, and reported further increase in  $\text{H}_2$  selectivity up to 79% upon addition of steam to obtain S/C = 4.5 in the feed mixture. The authors reported synthesis gas composition, i.e.  $\text{H}_2/\text{CO}$  ratio of 1.7 at 825 °C, and at C/O and S/C ratios of 1.2 and 4.5, respectively. Rennard et al. [18] carried out a similar study in which the possibility of obtaining desired  $\text{H}_2/\text{CO}$  ratio by tuning feed composition through C/O and S/C ratios over Pt-coated ceramic foams was demonstrated.

The studies summarized above show the importance of reactor geometry on the extent of glycerol reforming. At this point microchannel reactors can be considered as promising candidates for improving the efficiency of the glycerol reforming process. Microchannel reactors are typically composed of straight, parallel channels each of which has a dimension (e.g. diameter, height, width) in the order of micrometers. The channels are separated by solid walls, which are usually made of a thermally conductive material. As in the case of monolith reactors, the porous catalyst is usually introduced in the form of a thin layer that is coated onto the inner wall of each channel [19,20]. Due to the high share of channels in the solid reactor block, microchannel units can offer surface area-to-volume ratios which are up to  $\sim 10^2$  orders of magnitude higher than those of the conventional units and can operate with negligible pressure drop. Moreover, small channel diameters ( $d_h$ ) in the order of micrometers lead to the evolution of laminar flow at which Nusselt number ( $Nu = h \cdot d_h/k$ ) is constant at a channel-shape specific asymptotic value, and the resulting heat transfer coefficients ( $h$ ) are much higher than those involved in the conventional reactors [19–21]. These properties significantly improve the rate of heat transfer over the porous catalyst layer and allow its efficient utilization by enabling it to operate at the desired temperature. Apart from a few studies [15, 16,22], the use of microchannel reactors in glycerol reforming is not investigated extensively in the literature. The objective of this study is to investigate non-oxidative and oxidative steam reforming of glycerol in a  $\text{Ni}/\text{Al}_2\text{O}_3$  coated microchannel reactor and explore the impact of reaction temperature, feed composition (i.e. S/C and C/O ratios), catalyst loading and feed flow rate on glycerol conversion and product distribution. Description of the experimental techniques and microchannel reactor is provided in Section 2. Outcomes of the catalytic tests and their discussion are given in Section 3.

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