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A comparative study of experimental investigation and response surface optimization of steam reforming of glycerol over nickel nano-catalysts

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ARTICLE INFO

Article history:

Received 6 March 2016

Received in revised form

24 April 2016

Accepted 7 May 2016

Available online 28 May 2016

Keywords:

Steam reforming

Glycerol

Response surface methodology

Nanocatalysts

ABSTRACT

A Box-Behnken design of response surface methodology (RSM) was applied to examine the glycerol steam reforming over Ni/Al₂O₃ nanocatalysts. The catalysts were synthesized by impregnation method and characterized by XRD, BET, and TPR techniques. The results of XRD analysis revealed the crystalline sizes of 5.1 nm and 17.2 nm for the Al₂O₃ and 15 wt % Ni/Al₂O₃ catalyst, respectively. The effects of the process independent variables namely gas hourly space velocity (GHSV), temperature (°C) and feed ratio (water to glycerol ratio) on glycerol conversion to gaseous products (H₂, CH₄, CO₂ and CO) were investigated and 3D surface plots were obtained in order to visualize the interactive effects of variables. For most of the responses, experimental results showed the adequacy of fitted data into first and second-order polynomial models. Ultimately the process was optimized and the optimum conditions for the glycerol steam reforming were: GHSV (36,787 mL g⁻¹ h⁻¹), temperature (671.8 °C) and feed ratio (9). At the optimized conditions glycerol conversion, H₂, CH₄, CO₂ and CO production were found to be 97.53%, 74.40%, 0.15%, 23.87% and 1.55%, respectively.

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Introduction

Energy crisis in past decades caused that most of the scientists seek for new energy alternatives as replacement for fossil fuels. Among various alternatives, hydrogen has gained in importance especially as clean energy source since hydrogen combustion is cleaner compared to fossil fuels. Almost 95% of hydrogen is produced via non-renewable resources. Recently,

hydrogen production by means of biomass due to renewability and more environmental friendly characteristics raised attentions. Typically, biodiesels produced from vegetables and seeds. Glycerol is byproduct of process of fatty acids and alcohols trans-esterification of biodiesels. The produced glycerol as a valuable source can be used for production of desirable products. Among various methods of hydrogen production, steam reforming is one of the most popular methods [1–5].

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<http://dx.doi.org/10.1016/j.ijhydene.2016.05.047>

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In the steam reforming of glycerol the most important products are hydrogen and carbon dioxide in high concentrations and carbon monoxide and methane at low concentrations. However, other liquid products and alkanes can be produced via this process. The major reactions in glycerol steam reforming process are shown in Table 1.

The aim of application of catalysts in the process of reforming is providing more active reactions, which results in increasing the hydrogen generation from reactants which in turn leads to increasing the desired product selectivity.

Typically, supported nickel catalysts used in the process of glycerol steam reforming, because they have high activity in breaking C–C bonds and C–H and O–H in the process of steam reforming of glycerol [6–8]. Compared to noble metals, low cost and high approach of nickel catalyst led to its prevalent use in the preparation of the catalyst for steam reforming of glycerol, although the most important drawback of this type of catalysts is the accumulation substances on the surface of nickel catalyst, which in turn leads to the production of coke [9].

Glycerol steam reforming over Ni based catalysts have attracted a lot of interests, because these catalysts have shown promising results. Also, from economical viewpoint, they are much profitable in comparison with noble metal based catalysts [9,10]. Numerous works have been made in improving the catalytic performance of glycerol reforming process, including the addition of Ce, Co, La, Cu, Zr, Mg or Sn into Ni-based catalysts [10–17]. Iriando et al. [16] reported that the modifiers favor the hydrogen selectivity in the process. It is suggested that different decoration of Ni phases by promoters changes the catalytic activities of Ni/Al₂O₃ catalyst.

Sanchez et al. [11] was applied 5.8wt.%Ni/Al₂O₃ catalyst in glycerol steam reforming. They achieved maximum hydrogen selectivity of 99.7% at 650 °C and also 99.4% for glycerol conversion at 700 °C. Sanchez et al. [12] was studied 4Ni/Al₂O₃, 4Co–4Ni/Al₂O₃, and 12Co–4Ni/Al₂O₃ catalysts for glycerol steam reforming. As temperature declines, cobalt modifier

favors hydrogen and decreases CO₂ production. At low Co loading, maximum hydrogen was produced.

Valliyappan et al. [14] investigated the Ni/Al₂O₃ performance in glycerol steam reforming and reported that for catalyst loading of 0.2 g and steam/glycerol ratio of 25/75, maximum hydrogen selectivity of 68.4 mol % was obtained. Czernik et al. [18,19] employed a fluidized bed reactor and a commercial Ni catalyst for catalytic steam reforming of byproducts obtained from biomass thermoconversion process. Dou et al. [20] was investigated crude glycerol by-product steam reforming with CO₂ using a fixed bed reactor in temperature range of 400 °C and 700 °C. In this study, glycerol conversions were very similar and for temperatures more than 600 °C, no CH₄ was observed. Profeti et al. [17] applied Ni/CeO₂–Al₂O₃ catalyst for glycerol and ethanol steam reforming. They suggested that dispersed CeO₂ on alumina prevents inactive nickel aluminate formation.

Recently, Bobadilla et al. [21] investigated the steam reforming of glycerol on bi-metallic NiSn/CeO₂–MgO–Al₂O₃ catalysts. Bobadilla and coworkers concluded that activity of bimetallic NiSn/Al₂O₃ catalysts enhanced by addition of MgO or CeO₂ promoters and coke formation also decreased. This research team reported that temperature increment, feed concentration and space velocity diminishing, resulted in more hydrogen production and glycerol conversion. Thyssen et al. [22] also reported that addition of La₂O₃ to nickel catalyst supported on SiO₂, enhanced the gaseous hydrogen and carbon dioxide production and declined the formation of carbon during the reaction.

In this paper, an experimental and modeling study on steam reforming of glycerol over Ni/Al₂O₃ nanocatalyst were carried out at different operational conditions. The catalysts were characterized by XRD, BET and TPR techniques. Compared to similar studies which Ni-based catalysts have been applied, temperature and feed ratio were more practical for industrial applications and also the selected GHSV was significantly higher than those reported in other published papers. The response surface methodology (RSM) was applied for mathematical modeling of glycerol steam reforming over Ni/Al₂O₃ nanocatalyst. Moreover, this study was examined the suitability of RSM for steam reforming optimization of glycerol. A three-level, three variables (temperature, feed ratio and GHSV) Box–Behnken design was selected in order to investigate mutual relation and subsequent effects of independent variables on five responses. All of the models were evaluated by statistical methods. Finally the steam reforming of glycerol process were also studied at optimum conditions.

Table 1 – The major reactions in glycerol steam reforming process.

Name of reaction	Reaction	ΔG_{298K}^R (Kj.mol ⁻¹)
Steam reforming of glycerol	$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2$	-128
Glycerol decomposition	$C_3H_8O_3 \leftrightarrow 3CO + 4H_2$	250
Water gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	-41
CO disproportionation reaction	$2CO \leftrightarrow CO_2 + C_{(s)}$	-172
Methanation of CO	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206
Methanation of CO ₂	$CO_2 + 4H_2 \leftrightarrow CH_4 + H_2O$	-165
Methane dry reforming	$CO_2 + CH_4 \leftrightarrow 2H_2 + C_{(s)}$	247
Methane decomposition	$CH_4 \leftrightarrow 2H_2 + C_{(s)}$	76
Methane Oxidative reforming	$CH_4 + 0.5O_2 \leftrightarrow 2H_2 + CO$	-38
Carbon gasification	$C_{(s)} + 2H_2O \leftrightarrow 2H_2 + CO_2$	90

Experimental

Catalyst synthesis

15 wt.% Ni/Al₂O₃ catalysts were prepared by means of impregnation method. The preparation method of catalyst support was described in our previous work [23]. In summary, aluminum tri isopropylate (98% purity, Merck, Germany) was dissolved in double distilled water at 80–85 °C under vigorous stirring for 1 h. In order to adjust the HNO₃/Al molar ratio to 1, a HNO₃ solution was slightly added to the prepared solution.

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