



## Research paper

# High production of syngas from catalytic steam reforming of biomass glycerol in the presence of methane



Can Huang, Chenghua Xu<sup>\*</sup>, Bin Wang, Xiaodong Hu, Junjie Li, Jiangying Liu, Jie Liu, Chenxi Li

Air Environmental Modeling and Pollution Controlling Key Laboratory of Sichuan Higher Education Institutes, Chengdu University of Information Technology (CUIT), Chengdu 610225, China

## ARTICLE INFO

## Keywords:

Biomass glycerol  
Catalytic steam reforming  
Methanol syngas  
Ni-based catalysts

## ABSTRACT

Ni/Al<sub>2</sub>O<sub>3</sub> catalysts modified with metal oxides for biomass glycerol steam reforming to syngas were prepared by impregnation, and also characterized by XRD, H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD technologies. In order to produce more methanol syngas (H<sub>2</sub>/CO = 2), methane was introduced into biomass glycerol reforming system. The results indicated that Ni/Al<sub>2</sub>O<sub>3</sub> with support modification by Ca-Mg oxides and catalytic active phase adulteration by La-Ce-Zr oxides exhibited an excellent catalytic performance for a high production of syngas. Both CO<sub>2</sub> (< 2.8%) and methane (about 0.07%) contents were very low in the obtained reforming gas with a (H<sub>2</sub>-CO<sub>2</sub>)/(CO + CO<sub>2</sub>) molar ratio of about 2.09, which fitted the feedstock demand for the conventional methanol industry. It was also found that the main function of introduced methane in glycerol steam reforming system was to inhibit CO<sub>2</sub> production through the dry reforming. Under the optimized conditions, methanol syngas yield reaches up to about 87.7% based on glycerol conversion, much higher than that in glycerol steam reforming without methane.

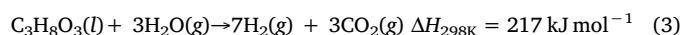
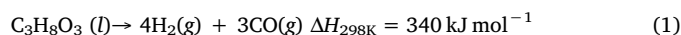
## 1. Introduction

Biodiesel can be used as a fuel for vehicles in its pure form or used as a diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles. Biodiesel is the most common biofuel and produced from domestic, and renewable biomass resources including agricultural oils, recycled cooking oil and animal fats through transesterification with lower alcohols such as methanol. The rapid development of biodiesel production technology has led to the generation of tremendous quantities of glycerol as the main by-product of the process. Stoichiometrically, it has been calculated that for every 100 kg of biodiesel, 10 kg of glycerol are produced. Therefore, the conversion and utilization of these biomass glycerol have attracted more and more interests, will reduce the cost and wastes emissions of biodiesel production.

According to the reported research, glycerol can be used to synthesize the high-value chemicals such as propanediols [1,2], *N*- or *O*-heterocyclic compounds [3–5], and acrolein through hydrogenolysis, cyclocondensation, acetalization and dehydration, respectively. As a kind of oxygenated hydrocarbon, biomass glycerol can also be catalytically converted to H<sub>2</sub> and syngas [6–8], as feedstock for fuel cells, methanol synthesis and Fischer-Tropsch (F-T) reaction, respectively. Therefore, the production of hydrogen and syngas through reforming has been regarded as a good pathway with the highest potential for

consuming biomass glycerol.

1 mole glycerol can theoretically be decomposed (Eq. (1)) to 4 mol of H<sub>2</sub> and 3 mol of CO, resulting in H<sub>2</sub>: CO stoichiometric ratio of 1.33, which is lower than the required H<sub>2</sub>/CO ratio (~2) in syngas to methanol. Meanwhile, it is difficult to stop the glycerol decomposition in this stage due to the easy occurrence of water-gas-shift (WGS as Eq. (2)) reaction especially in the presence of steam [7,8]. The WGS will provide more H<sub>2</sub> along with CO further decrease or complete conversion to CO<sub>2</sub>. Thus 1 mole of glycerol can yield 7 mol of H<sub>2</sub> and 3 mol of CO<sub>2</sub> (Eq. (3)). It means that the presence of WGS is helpful to the production of H<sub>2</sub> as fuel cell feedstock. Although CO<sub>2</sub> generated by this process does not produce a net increase of CO<sub>2</sub> in the atmosphere, carbon resources in biomass glycerol will be wasted. In fact, it has been found from our previous work [8,9] that there are less CH<sub>4</sub> from methanation of CO or CO<sub>2</sub>, besides H<sub>2</sub>, CO and CO<sub>2</sub> through reforming and WGS during GSR.



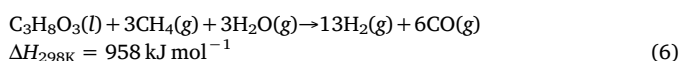
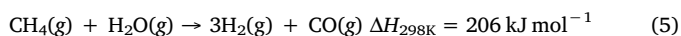
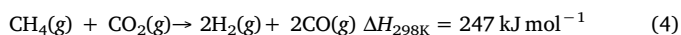
It is not difficult to find that it is very important for the high production of methanol syngas (containing H<sub>2</sub> and CO with molar ratio of

<sup>\*</sup> Corresponding author.

E-mail address: [xch@cuit.edu.cn](mailto:xch@cuit.edu.cn) (C. Xu).

2) from GSR to inhibit or prevent WGS and methanation. Our previous work [8,9] has reported that the modification of Mo and La can improve the production of methanol syngas and inhibit methanation over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Even so, about 50–60% of carbon species in glycerol are converted to CO<sub>2</sub> and only 40–50% methanol syngas is produced in reforming gas. That is to say it is very difficult to completely convert glycerol to CO and H<sub>2</sub>, and the production of much CO<sub>2</sub> is not avoided [7,10].

Meanwhile, biomass methane (CH<sub>4</sub>) can be obtained from biogas produced by the fermentation of biological straw and aquaculture wastewater, and the biogas engineering has wide application in the southwest region of China. CH<sub>4</sub> can react with CO<sub>2</sub> to H<sub>2</sub>-CO with a molar ratio of 1: 1 through dry reforming described as Eq. (4) [11,12], and also gives rise to the production of H<sub>2</sub>-rich methanol syngas through steam reforming (Eq. (5)). If CH<sub>4</sub> is introduced into GSR system, the formed CO<sub>2</sub> will possibly continue to react with CH<sub>4</sub> through dry reforming. And the presence of CH<sub>4</sub> can also inhibit the methanation of CO or CO<sub>2</sub> thermodynamically. Thus, GSR in the presence of CH<sub>4</sub> will probably carry out according to the total reforming procedure described as Eq. (6). Theoretically, it can give rise to the production of syngas with a H<sub>2</sub>/CO molar ratio of about 2.16, meeting the feedstock demand of conventional methanol manufacture. Moreover, almost all carbons in glycerol molecules are converted to syngas, resulting in a greatly higher yield of methanol syngas than that during glycerol steam reforming (only 40–50%) reported in our previous work [8,9].



Thermodynamically, all reforming processes to syngas are endothermic. From Eqs (4) and (5), production of per mole methanol syngas (calculated as CO) will need about 128 kJ and 206 kJ of energy through two conventional manufacturing technologies including methane dry reforming and steam reforming, respectively. Glycerol steam reforming in the presence of methane (Eq. (6)) needs about 160 kJ for production of 1 mol syngas, showing that it is a relative energy-saving procedure for methanol syngas production. And even more important, it will provide a rational approach for conversion of biomass glycerol to another clean fuel methanol. Therefore, the present work lays special stress on the steam reforming of glycerol in the presence of CH<sub>4</sub> over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts modified transition metals and/or alkali earth metal oxides prepared by impregnation. And the effects of reforming temperature, CH<sub>4</sub> and steam amounts, gas hourly space velocity (GHSV) on syngas production over Ni-based catalysts are investigated in details. It aims to search proper reforming parameters and catalysts for conversion of glycerol to methanol syngas in the presence of methane. A possible route is hoped to be provided for conversion of biodiesel by-product glycerol to a clean fuel methanol.

## 2. Experimental

### 2.1. Catalysts preparation

Ni/Al<sub>2</sub>O<sub>3</sub> catalysts modified by metal oxides were prepared by the incipient wetness impregnation according to our previous work [8]. Typically, the dried commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $S_{\text{BET}} = 226 \text{ m}^2 \text{ g}^{-1}$ , particle size 0.8–1.2 mm, Chengdu Kelong Chem Co., China) was first impregnated in the aqueous solution containing Ca<sup>2+</sup> and Mg<sup>2+</sup> at room temperature for 4 h, and then dried overnight at 100 °C and calcined at 800 °C for 6 h in air to obtain the CaO-MgO-modified Al<sub>2</sub>O<sub>3</sub> supports (CMA). The impregnation of active phase Ni or/and promoters La, Ce, Zr oxides on supports such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CMA were also carried out to

obtain Ni-based catalysts such as Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/CMA and NiLaCeZr/CMA according to the similar procedure, respectively. The precursors of the introduced Ni, Ca, Mg, La and Ce were their corresponding nitrates except Zr from ZrCO<sub>3</sub>, and all these materials were also purchased from Chengdu Kelong Chem Co., China. The impregnated amounts of metal Ni was 10 wt% relative to the weight of supports such  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or CMA, the modified contents of Ca, Mg, La, Ce or Zr oxides were 10 wt% also relative to supports  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

### 2.2. Catalysts characterization

Powder X-ray diffraction (XRD) analysis was introduced to verify the crystalline structure of the prepared catalysts, and these experiments were performed on a DX-2700 powder X-ray diffractometer (Dandong Fangyuan Co., China) operated at 30 kV and 20 mA, using Cu K $\alpha$  radiation. Temperature-programmed reduction by H<sub>2</sub> (TPR) and temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) were performed with a TP-5080 adsorption instrument (Tianjing Xianquan Co., China) equipped with a thermal conductivity detector (TCD). In a typical TPR experiment, 100 mg samples was first degassed in a quartz tube under a 30 ml min<sup>-1</sup> of N<sub>2</sub> flow at 300 °C for 30 min. After cooling, the sample was heated from room temperature to 950 °C under a 30 ml min<sup>-1</sup> of 5% H<sub>2</sub>-N<sub>2</sub> mixture gas, and the heating rate was 10 °C·min<sup>-1</sup>. For NH<sub>3</sub>-TPD, 200 mg catalysts were pretreated in He at 400 °C for 30 min, and then NH<sub>3</sub> adsorption was carried at 50 °C in 30 ml min<sup>-1</sup> of He carrier gas containing 10 vol% NH<sub>3</sub> for another 30 min. Subsequently the physisorbed NH<sub>3</sub> molecules over samples were removed at 50 °C by He flow for 2 h. The TPD of the obtained sample was heated in 30 ml min<sup>-1</sup> of He at a rate of 10 °C·min<sup>-1</sup> from 50 °C to 700 °C for NH<sub>3</sub> desorption.

### 2.3. Catalytic reforming

GSR in presence of CH<sub>4</sub> was conducted in a vertical fixed-bed quartz reactor (15 mm diameter and 600 mm length). Prior to the catalytic test, 6 g catalysts (apparent volume about 7.5 ml) were sandwiched with quartz sands and reduced in a 30 ml min<sup>-1</sup> of H<sub>2</sub> flow at 700 °C for 2 h. Then the temperature was adjusted to a desired value and 30 ml min<sup>-1</sup> of N<sub>2</sub> as balance carrier gas was introduced. After the residual H<sub>2</sub> was completely removed, a desired flow rate (typically 1 ml min<sup>-1</sup>) of glycerol aqueous solution was injected by a HPLC-pump and CH<sub>4</sub> flow was passed through the catalyst bed to start reforming. The reaction mixture was cooled by cool trap and separated. The volume of the produced gaseous mixture was monitored by wet-type gas flowmeter, and the composition of gas products including H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> was analyzed by on-line gas chromatograph (GC-2000, Chongqing, China) equipped with a TDX-01 (carbon molecular sieves, 3 m × 3 mm) packed column and TCD. The residual glycerol was certified according to the GC analysis of the collected liquid products on another GC-2000 gas chromatograph equipped with a KB-Wax capillary column (30 m × 0.32 mm × 0.5  $\mu$ m, Kromat Co., USA) and a flame ionization detector (FID). Conversions toward glycerol and CH<sub>4</sub> were calculated by their residual amount in the inlet feedstock, outlet gases or liquid.

## 3. Results and discussions

### 3.1. Catalysts selection

From XRD patterns of three catalysts and two supports (Fig. 1), it is found that Ni/Al<sub>2</sub>O<sub>3</sub> mainly exhibits distinct characteristic signals of support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase (Pdf. 29–63) at  $2\theta = 37.5^\circ$ ,  $45.5^\circ$  and  $66.6^\circ$ , and a weak diffraction peak of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase (Pdf. 3–1033) at  $2\theta = 43.8^\circ$ . But there are no obvious NiO signals. It indicates that support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gives a part phase transformation, and also easily interacts with introduced Ni species to form NiAl<sub>2</sub>O<sub>4</sub> spinel phase during the catalysts

Download English Version:

<https://daneshyari.com/en/article/11027911>

Download Persian Version:

<https://daneshyari.com/article/11027911>

[Daneshyari.com](https://daneshyari.com)