Research paper

Kinetics of hydrogen production by the autothermal reforming of crude glycerol over modified nickel supported catalyst

Ahmad Abdul Ghani[a], Farshid Torabi[b], Hussameldin Ibrahim[a],*

[a] Clean Energy Technologies Research Institute (CETRi), Process Systems Engineering, Faculty of Engineering and Applied Science, University of Regina, 3737 Wascana Parkway, Regina, SK, S4S 0A2, Canada
[b] Petroleum Systems Engineering, Faculty of Engineering and Applied Science, University of Regina, 3737 Wascana Parkway, Regina, SK, S4S 0A2, Canada

ARTICLE INFO

ABSTRACT

In this work, the kinetics of autothermal reforming (ATR) of synthetic crude glycerol (CG) to produce renewable hydrogen was studied over nickel catalyst supported on promoted cerium-zirconium carrier (5% Ni/CeZrCa) in a temperature range of 500–650 °C, steam-to-carbon (S/C) range of 1.6–3.6, oxygen-to-carbon (O/C) range of 0.05–0.2 and weight hourly space range of 0–158.2 gcat min/mol C. Synthetic crude glycerol composed of pure glycerol, methanol, soap, free fatty acids and ashes was used in this work. A kinetic region free of heat and mass transfer limitations was established by varying catalyst particle size and inlet flow rate. The stability of the catalyst was also established in an extended period run for 15 h time on stream experiment. The estimated activation energy of 93.7 kJ/mol with reaction orders of 1, 0.5 and 2 for synthetic crude glycerol, steam and oxygen, respectively, were obtained for this reaction. The developed power law model was

$$-r_A = 2.09 \times 10^{11} e^{\left(-\frac{93700}{8.314T}\right)} P_A^1 P_B^{0.5} P_C^2$$ with 95% predictability.

1. Introduction

It is now very promising that renewable hydrogen from biomass reforming will play a major role in the near future to compensate the dramatic increase of energy demands, concurrent with the tendency of establishing an environment friendly energy system. The international world standards are getting to be zero-emissions from automobiles, industry, residential furnaces and general transportations [1]. The rapid decarbonization of energy sources and mitigation policies to reduce greenhouse gas emissions has become a crucial requirement for maintaining the concentrations of CO_2 in the atmosphere below 580 ppm. Most of mitigation scenarios in place have been prepared to achieve a carbon free energy system by the end of the 21st century [2]. As a clean, abundant and renewable energy carrier, hydrogen can be utilized to supply a significant portion of energy demands in the near future. Technically, taking the carbon out of fossil fuel emissions is not easy especially when considering mobile or small emitters. Burning fossil fuels releases CO_2, CO, NO_x and SO_x to the atmosphere, however hydrogen has no harmful emissions upon combustion.

In a transition period between the current fossil fuels era and the zero-level emissions, biodiesel is expected to be a major energy source for supplying energy demands, since it has low greenhouse gas (GHG) emissions compared to the conventional petro-fuels. Biodiesel emits 41% less GHGs upon combustion than the fossil diesel [3]. A notable decrease in GHG emissions after blending petro-diesel with 2% and 5% biodiesel was revealed in Canada. The net reduction in GHG emissions was found to be 2.6 Mg CO_2 ha^{-1} yr^{-1} in the eastern regions, and 0.94 Mg CO_2 ha^{-1} yr^{-1} in the western regions of the country [4]. On the side of biodiesel industry, transesterification of vegetable oil is the most common technique for biodiesel production. The process yields 1 mol of glycerol for every three moles of biodiesel produced. A sharp diminution in crude glycerol values have been reported due to the flooded market of this product [5]. However, unlike pure glycerol, the high amounts of impurities in the crude glycerol make it unfavorable for commercial purposes. These impurities are usually methanol, ash, soap, water, FFA and FAME residues.

Sustainable hydrogen production from crude glycerol reforming has gained its significance due to the high potential of hydrogen yield from this product associated with its cheap prices. The global production of crude glycerol is anticipated to reach 41.9 billion liters by 2020 [6]. The demand on crude glycerol is not expected to grow much due to a flooded market and an unjustifiable purification cost and eventually conversion of the material into other desired products such as hydrogen is becoming more and more feasible [7].

Several techniques have been utilized to extract hydrogen from glycerol, such as steam reforming [8–18], partial oxidation [19] and the

auto-thermal reforming that combines the two processes [20–24]. Other studies have focused on hydrogen peroxide reforming [25], dry reforming [26], dry autothermal reforming [27], and aqueous phase reforming [28–30]. Each technique has its own benefits and drawbacks based on energy efficiency, hydrogen production and stability.

Composition of crude glycerol from biodiesel plants is mainly influenced by production technique, feed, operating conditions and catalyst. A recent characterization analysis has revealed a high matter organic non glycerol (MONG ~70 wt%), but a low glycerol content (12–15 wt%), high ash (~6 wt%) and water (~10 wt%) [31]. In line with that, a study on crude glycerol samples obtained from two different farms in Canada showed a significant difference in free glycerol and soap percentages. Crude glycerol sample 1 had ~30.2 wt% of free glycerol, and ~29.1 wt% soap. Crude glycerol sample 2 had ~15.4 wt % of free glycerol, and ~22.4 wt% soap [32]. In addition, the composition analyses of five samples of crude glycerol obtained from different biodiesel plants have shown a large variation in free glycerol content ranged from 22.9 to 63.0 wt%; and from 20.5 to 31.4 wt% for soap [33].

Kinetic analyses are very significant for optimization and design purposes. Many scholars have studied the kinetics of glycerol reforming reactions, but not that of crude glycerol autothermal reforming. A recent work on the kinetics of crude glycerol fermentation to generate biohydrogen has reported propitious results with respect to hydrogen yield and activation energy. Unlike pure glycerol, crude one was found to be more favorable to produce hydrogen due to a higher yield (0.627 mol H_2/mol glycerol) and lower activation energy (217 kJ/mol). The promoting effect of Na^+ in the process has been experimentally confirmed [34]. In earlier studies, the kinetics of pure glycerol aqueous decomposition over bimetallic Pt-Re/C catalysts to produce synthesis gas was investigated [35]. The study revealed a positive effect of integrating Re into Pt catalyst in increasing the turnover frequency of synthesis gas production. Besides, the kinetics of crude glycerol pyrolysis was also studied [36]. Based on the results of thermogravimetric experiments, four distinct phases in the thermal decomposition of crude glycerol were detected. During the first phase of pyrolysis between 322 and 343 K, mass loss of about 10–15% was observed due to the evaporation of water and methanol present in crude glycerol. Major weight loss (67–69%) occurred during the second phase (322–440 K) due to the removal of more than 95% of free glycerol and liquid nitrate esters. The third phase of crude glycerol pyrolysis (501–774 K) has been attributed to the decomposition of fatty acids methyl esters and a small part of leftover free glycerol, and this contributed to about 10.2–12.7 wt% loss. The fourth phase was found to go between 760 and 1123 K in which less than 5.8% weight loss has been observed with less than 4.5 wt% residue at the end. The activation energies and frequency factors of the four phases at four different heating rates were reported, and as expected, relatively low activation energies were determined for phases 1 and 2 compared with phases 3 and 4.

Other scholars studied the kinetics of glycerol steam reforming over Ni/CeO$_2$ catalysts [37]. A power law model of the form has been fitted to illustrate the change of reaction rate with respect to reforming temperature and glycerol concentration. The activation energy and reaction order were determined to be 103.4 kJ/mol and 0.233, respectively. The results showed a fair agreement between experimental and predicted conversions with an average absolute deviation of about 6.7%. In line with this work, a more recent work investigated the kinetics of glycerol steam reforming over Pt/C catalyst in a temperature range between 623 and 673 K [38]. The kinetic data was again collected in a fixed bed reactor by varying inlet flow (space velocity) and reaction temperature. The reaction was found to have an order of one with respect to glycerol with a good comparison between experimental and predicted conversions. Using a bimetallic Co-Ni catalyst supported on alumina carrier, the kinetics of glycerol steam reforming was studied in a temperature range between 773 and 823 K [39]. A power law model of the form $-r_{GSR} = A\exp(-E_A/RT)[P_{glycerol}]^{\beta}[P_{steam}]^{\gamma}$ was

proposed. The results showed a reaction order of 0.36 with respect to steam and 0.25 with respect to glycerol beside 63.3 kJ/mol activation energy. In this work, the kinetics of synthetic CG auto-thermal reforming process was investigated in a Packed Bed Tubular Reactor using nickel catalyst supported over promoted cerium-ziconium carrier. The corresponding results are illustrated and discussed in this paper.

2. Experimental

2.1. Catalyst

Calcium promoted cerium-zirconium support loaded with 5 wt% nickel catalyst (5 wt% Ni/CeZrCa) was developed and characterized in-house for the autothermal reforming of synthetic crude glycerol. The support was prepared in help with the surfactant assisted technique followed the wet impregnation of the active metal. The low-priced developed catalyst exhibited excellent performance with respect to stability and hydrogen yield. In general, the performance of a catalytic process is the outcome of complex interactions among the several chemical and structural properties of the utilized catalyst, alongside with the applied operating conditions. Before screening the performance of synthesized catalysts on the ATR of CG, a comprehensive experimental work was performed to characterize the developed catalysts. The techniques used include thermogravimetric analysis, N_2 physisorption, temperature-programmed oxidation, temperature programmed reduction and x-ray diffraction. The enhanced performance of the 5Ni/CeZrCa catalyst in the ATR of CG can be attributed to the reducibility, nickel dispersion, pore volume to surface area (PV/SA) ratio and hammet basicity properties. More details about catalyst preparation, characterization, experimental work and expected reactions are given elsewhere [40,41].

2.2. Feedstock

The synthetic crude glycerol used in this study was prepared in our laboratory by premixing specific amounts of ingredients (methanol, ash, soap, water, free fatty acid and fatty acid methyl esters residues) that are typically found in industrial crude glycerol generated during the biodiesel production process. The composition of the synthetic crude was based on the composition of crude glycerol samples collected from Milligan Biofuels Inc., a major biodiesel producer in Saskatchewan Canada. The synthetic crude glycerol used in this study had weight percentage composition of 45.6% pure glycerol, 11.2% methanol, 8.3% water, 29.1% soap, 3.8% free fatty acid (oleic acid), and 2.0% ashes (sodium and potassium chlorides).

2.3. Experimental setup

The experimental setup utilized in this work was composed of several units as shown in Fig. 1. The different units are:

- Packed Bed Tubular Reactor (Inconel 0.5″ ID, Homemde at UofR)
- Electric Tubular Furnace (ZCP 386, Zesta Engineering Ltd.)
- Two K-type thermocouples (1.6 mm × 18″, Zesta Engineering Ltd.)
- Thermal Mass Flow Controller (DFC26, Aalborg Instruments)
- Mass Flow Meter (GFM 17, Aalborg Instruments)
- Syringe Pump (100 ml Stainless Steel, KD Scientific)
- Gas Chromatograph (GC-TCD, HP 6890, Agilent Technologies)
- Pure Nitrogen Cylinder (UHP 5.0,Praxair)
- Compressed Air Cylinder (Praxair)
- Hydrogen-Nitrogen Cylinder (5% H_2-balance N_2, Praxair)
- Condenser (Water-cooled, Homemade at UofR)
- Condensate Collector (Ice-cooled, Homemade at UofR)