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Hydrogen production from catalytic steam reforming of biodiesel byproduct glycerol: Issues and challenges

Binlin Dou^{a,*}, Yongchen Song^a, Chao Wang^a, Haisheng Chen^{b,**}, Yujie Xu^b^a School of Energy and Power Engineering, Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, 116023 Dalian, China^b Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

The objective of this review is to analyze potential technologies and their baseline performance of producing hydrogen from catalytic steam reforming of biodiesel byproduct glycerol. High oxygen content and high impurity level of biodiesel byproduct glycerol, as well as the complex intermediates and high coking potential in its thermal degradation, make the modeling, design, and operation of glycerol steam reforming a challenge. Thermal decomposition characterization of biodiesel byproduct glycerol was covered, and the recent developments and methods for high-purity hydrogen production from glycerol steam reforming were illustrated. The thermodynamics constraint of water gas shift reaction can be overcome by the sorption-enhanced steam reforming process, which integrated catalytic steam reforming, water gas shift reaction and in-situ CO₂ removal at high temperatures in a single stage reactor. The effectiveness of both the enhanced H₂ production and the use of CO₂ sorbents have been demonstrated and discussed. The technical challenges to achieve a stable high-purity hydrogen production by the sorption-enhanced steam reforming process included extending operation time, selecting suitable sorbents, finding a way for continuous reaction-regeneration of catalyst and sorbent mixture and improving process efficiencies. The continuous sorption-enhanced steam reforming of glycerol was designed by a simultaneous flow concept of catalyst and sorbent for continuous reaction-regeneration using two slow moving-bed reactors for high-purity hydrogen production and CO₂ capture, and in this process, catalyst and sorbent were run in nearly fresh state for H₂ production. The sorption-enhanced chemical-looping reforming was also demonstrated. The paper discusses some issues and challenges, along with the possible solutions in order to help in efficient production of hydrogen from catalytic steam reforming of biodiesel byproduct glycerol.

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* Corresponding author. Tel.: +86 41184708460.

** Corresponding author. Tel.: +86 1082543148.

E-mail address: bldou@dlut.edu.cn (B. Dou).

1. Introduction

Due to the environmental concerns, the global demand for hydrogen is expected to increase greatly in the future for the energy and environmental sustainability [1]. Steam reforming, partial oxidation, auto-thermal reforming, and CO₂ reforming have been widely investigated as primary processes for converting hydrocarbons into hydrogen. Steam reforming is still the most dominant route to convert natural gas as a fossil fuel into hydrogen. Currently, over 50% of the world's hydrogen supply is from steam reforming of hydrocarbons [2]. It is now widely acknowledged that CO₂ in the atmosphere as the greenhouse effect is gradually warming the planet [3]. Carbon capture and storage (CCS) is an important part of the strategy for mitigating the risks of climate change, and CO₂ release from H₂ generation from steam reforming should be recognized. Global efforts in reducing greenhouse gas emissions have spurred intense research in sustainable production methods of hydrogen and CO₂ capture [1,4,5]. Conventional H₂ production from steam methane reforming includes in series of a main catalytic reactor operated at 800–1000 °C, one or two water gas shift reactors operated at 300–450 °C, and at the same time, the products stream is fed to a pressure swing adsorption (PSA) unit where all the gases except H₂ get adsorbed in the beds leading to a high purity H₂ product [6]. The drawbacks of this process are the fossil fuel consumption, CO₂ emission, and the high capital costs due to the separation of CO₂ and H₂.

Biodiesel as the biodegradable, non-toxic, near CO₂-neutral and environmentally beneficial fuel has become more attractive recently as alternative diesel fuel to reduce dependency on fossil fuel imports. The transesterification of renewable biological sources such as vegetable oils and animal fat oils with an alcohol using alkaline or acid catalysts is the most common process for biodiesel production. About 10 wt% of glycerol is produced during the production of biodiesel fuel through the catalytic transesterification process [7]. A increase of biodiesel production all over the world from 2000 year has led to great increment of crude glycerol [8]. Catalytic steam reforming of biodiesel by-product glycerol is a new method to renewable energy conversion. The feasibility for hydrogen production by glycerol steam reforming was carried out by different authors [9–20]. The CFD simulation of glycerol steam reforming indicated the parameters including temperature, ratio of steam to carbon (S/C), residence time, inlet gas composition and flow rate should be carefully controlled to maximize H₂ production with minimum coke formation [12,13]. One of the difficulties for the utilization of hydrogen from glycerol steam reforming by catalysts is high CO₂, CO and CH₄ contents. In addition, the demand for high-purity hydrogen production is rapidly growing in the electronics, fine ceramics, and fine chemical industries. Hence, we need a better system to high-purity hydrogen production from renewable resources to decrease fossil energy and control the CO₂, and it is preferred the steam reforming, water gas shift reaction (WGS) and CO₂ removal can be conducted in one single step at a low temperature and pressure. A technology as the sorption-enhanced steam reforming has been proposed and investigated for hydrogen production with simultaneous CO₂ abatement [21–26]. It is based on the concept of combined reaction and separation, which uses a catalyst phase and an adsorbent phase in a reactor. The technology offers a number of advantages including high conversion of hydrocarbons feed, low operating temperature of reforming reactor and enhanced heat transfer of process. In addition, the capital cost can be reduced as the number of processing steps required for subsequently separating CO₂ is decreased. The renewable hydrogen from biomass-derived resources is a major challenge as global energy generation and fuel cell application. This paper gives an overview of the

research progress in catalytic steam reforming of glycerol, and highlights the issues and challenges for high-purity hydrogen production by the sorption-enhanced steam reforming process.

2. Thermal decomposition characterization of biodiesel byproduct glycerol

The thermal decomposition of the fuel was found to play a significant role in the H₂ production and coke formation during catalytic steam reforming process [27]. A typical sample of crude glycerol from biodiesel production mainly consisted of 70–90 wt% glycerol and the average elemental molar formula was $C_{3 \pm 0.2}H_{8.9 \pm 0.4}O_{3.4 \pm 0.2}N_{(5 \pm 2) \times 10^{-3}}$ [28]. The results of GC–MS analysis showed the sample of crude glycerol includes glycerol and methyl esters products of the biodiesel process such as linoleic (C₁₉H₃₄O₂), palmitic (C₁₇H₃₄O₂), oleic (C₁₉H₃₆O₂), and stearic (C₁₉H₃₈O₂) acid methyl esters. Biodiesel byproduct glycerol often contains many impurities and is a very poor fuel used in either petrol or diesel engines [9]. It can be purified and used in the food industry, pharmaceuticals or water treatment for digestion. The work by Yang et al. has successfully converted the crude glycerol by fermentation to obtained up to 1,3-propanediol [29]. However, these processes are very expensive and exhibit a low yield [9]. Glycerol as a potential feedstock via pyrolysis, or gasification to produce H₂, CO or other fuel gases has received considerable research attention [28,30–33]. Valliyappan et al. reported the hydrogen or syngas production from glycerol pyrolysis at high temperatures and the gas products were CO, H₂, CO₂, CH₄ and C₂H₄ [30]. The glycerol pyrolysis was studied in a laminar flow reactor by Stein et al., and the results showed that the initial decomposition products were H₂O, CO, CH₄, CO₂, acetaldehyde and acrolein, and then acetaldehyde and acrolein further were decomposed to produce primarily CO and H₂ [31]. Buhler et al. carried out the thermal decomposition of glycerol in near-critical and supercritical water and they reported the main products include methanol, acetaldehyde, ethanol, CO, CO₂ and H₂ [32]. In fact, it is also very difficult to understand the thermo-chemical characteristics of the crude glycerol from the biodiesel production process. Dou et al. studied the pyrolysis of crude glycerol from a biodiesel biorefinery in dry N₂ by thermogravimetry coupled with fourier transform infrared spectroscopy (TGA–FTIR) [28]. The difference in the mass loss obtained by TGA may be due to the degradation of the different components at different temperatures. The FTIR indicated that the concurrent and dehydration reactions of gas-phase pyrolysis of crude glycerol at low temperatures may lead to the formation of the products such as liquid, gas and coke, and at high temperatures, consecutive thermal cracking reactions were predominant to form H₂, CO, CO₂, CH₄ and carbon [28]. Some species such as H₂CO, HCO and CH₂OO may undergo the decomposition to product CO, CO₂, H₂O and H₂ at high temperatures [34]:



The major drawback of glycerol pyrolysis is carbon formation due to the cracking of some hydrocarbons including CH₄ [30]:



The thermogravimetric experimental data were interpreted by an improved iterative Coats–Redfern method [28]. For the pyrolysis of crude glycerol, a number of forms of the mechanism function were also tested with the experimental data, including: the power law model, the reaction order model, 1–3D diffusion

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