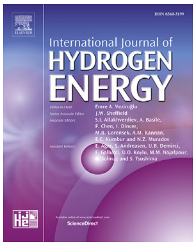
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Thermodynamic analysis of hydrogen-rich syngas production with a mixture of aqueous urea and biodiesel

Horng-Wen Wu*, Ke-Wei Lin

Department of Systems and Naval Mechatronic Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC

A R T I C L E I N F O

Article history:
Received 25 November 2017
Received in revised form
1 February 2018
Accepted 19 February 2018
Available online xxx

Keywords:
Aqueous urea
Adblue
Biodiesel
Syngas production
Autothermal reforming
Thermal neutral temperature

A B S T R A C T

An auxiliary power unit based on a solid oxidation fuel cell for heavy-duty vehicles has been receiving attention for high efficiency, low emissions, and more comfort and safety in vehicles. This study explores hydrogen-rich syngas production via reforming of a mixture of aqueous urea and biodiesel by thermodynamics analysis. The aqueous urea is available from Adblue used in a selective catalyst reduction providing efficient control of nitrogen oxides from heavy-duty vehicles to minimize particulate mass and optimize fuel consumption. The results show that at a reaction temperature of 700 °C, urea/biodiesel ratio = 3, and oxygen/biodiesel ratio = 9, the highest reforming efficiency is 83.78%, H_2 production 30.43 mol, and CO production 12.68 mol. This study verified that aqueous urea could successfully replace the steam in autothermal reforming, which provides heat and increases syngas production, and reforming aqueous urea mixed with biodiesel has ultra-low sulfur, low carbon and little modifying the fuel system.

Introduction

Over the past few decades, many countries have been exploring alternative energy sources and their applications. In the transportation sector, improving energy efficiency and reducing emissions of vehicles are the important issue. All kinds of alternative vehicles, such as electric, hybrid, and fuel cell vehicles, have been developed aggressively to solve the emission and efficiency problem. In addition, biofuels, including ethanol and biodiesel, have been used widely in low emission vehicles based on traditional internal combustion engines. Biodiesel has become the most popular renewable biofuel in the world and is experiencing stable growth. Biodiesel is a Fatty Acid Methyl Ester (FAME) produced from the animal fats or vegetable oils such as soybean, rapeseed, and waste cooking oil, by a transesterification process. Biodiesel can be fueled into traditional diesel engines without modifications, and it has some environmental advantages, such as lower particulate mass, CO_2 emissions, and low carbon footprint of life cycle assessment [1,2]. It also has a lower sulfur content and polycyclic aromatic hydrocarbons compared to fossil diesel [3].

Hydrogen can hold the potential to provide the cleanest energy and the best energy carrier in the world. Thus, many countries have been researching and developing an

---

* Corresponding author.
E-mail address: z7708033@email.ncku.edu.tw (H.-W. Wu).

https://doi.org/10.1016/j.ijhydene.2018.02.126

Please cite this article in press as: Wu H-W, Lin K-W, Thermodynamic analysis of hydrogen-rich syngas production with a mixture of aqueous urea and biodiesel, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.126

application for hydrogen energy. The most important application of hydrogen energy is used as a fuel in fuel cells, which are power devices characterized by high efficiency and low emissions. Therefore, hydrogen energy can be used in a fuel cell vehicles (FCV) to produce electricity and to provide a significant reduction in energy consumption and regulated emissions. Moreover, for heavy-duty diesel engine vehicle applications, Los Alamos National Laboratory has related research on diesel oil reforming for fuel cell-based auxiliary power unit (APU) [4]. More recently, Rechberger et al. [5] developed an APU based on solid oxidation fuel cell (SOFC) in order to provide electricity, to allow drivers to sleep, and to avoid engine emission and noise, as well as to improve fuel economy during engine stops. Lorenzo and Fragiacomo [6] pointed out that SOFC can be operated under high temperature condition, and can be fed not only pure hydrogen but also hydrogen-rich syngas (hydrogen and carbon monoxide). However, the syngas of an SOFC APU requires a reforming process, and in principle, it is dependent on the fuel supply system of the vehicle; as a result, the APU system uses diesel reforming, which has become the most popular technology. The use of on-board diesel reforming can solve the problem of high pressure hydrogen storage and reduce the cost of fill infrastructures.

Diesel reforming involves three reforming processes: steam reforming (SR) [7–9], autothermal reforming (ATR) [10,11] and partial oxidation reforming (POX) [12]. For vehicle on-board applications, SR not only requires adding a water tank to supply steam, but it also needs external heat energy because the process is a strongly endothermic reaction. Therefore, this results in more energy consumption. In contrast, although POX can utilize a fuel supply system, this process is a strongly exothermic reaction; in other words, partial fuel oxidizes and provides the heat for the reaction. However, it has a low reforming efficiency. The advantage of ATR is that it involves neither a strongly exothermic reaction nor an endothermic reaction. The ATR reaction could be conducted by using noble metal oxidation catalysts such as Pt, Ru, and Ph [13,14]. The fuel in the reaction provides heat because of the oxidation reaction, and the heat is supplied for endothermic reaction of water in the reforming process. The reaction could be close to thermal equilibrium by adjusting the oxygen molar and H_2O molar ratio. It has higher reforming efficiency than the partial oxidation reforming processes. However, its main disadvantage is that it still requires a water tank to provide steam, thus making the on-board system more complex.

Fossil diesel contains sulfur that will poison the reformer catalyst, whereas biodiesel has almost no sulfur content and low amounts of polycyclic aromatic hydrocarbons, so it is better than fossil diesel for reforming. Nevertheless, there have been few studies focusing on biodiesel reforming. Most of them have put an emphasis on SR and ATR. Tsolakis and Megaritis [15] conducted on-board H_2 production by exhaust gas fuel reforming of diesel and biodiesel into a diesel engine through exhaust gas recirculation (EGR) to reduce smoke and NOx emissions. They also discussed fuel economy when operating the engine. Nahar [16] used the Gibbs free energy minimization method to analyze chemical thermodynamics of FAME under an ATR process for an SOFC application. The composition of FAME with molecular formula $C_{19}H_{36}O_2$ was calculated in the analysis. The control parameters included water-biodiesel molar feed ratios (WBFRs) set between 3 and 12 and Oxygen-biodiesel molar feed ratios (OxBFRs) that ranged from 0 to 4.8, and the reaction temperature was set between 300 and 800 °C under atmospheric pressure. He found that the best operational parameters were WBFR $\geqq 9$ and OxBFR = 4.8 at a reaction temperature of 800 °C, where the H_2 production rate was 68.8%, and the CO production rate was 91.66%. Martin et al. [17] compared the on-board autothermal and steam reforming of biodiesel. For the thermodynamic analysis, a maximum reforming efficiency of 74.1% was obtained for autothermal reforming of biodiesel at steam-to-carbonate ratio = 2 and air ratio = 0.36 when it reacted with heat integration.

Nahar et al. [18] also assessed the feasibility of biodiesel steam reforming using Ni/Ca-Al and Ni/Ce-Zr catalysts. The experiment was carried out under vaporization of the biodiesel at 190–365 °C, where the reaction temperature was between 600 and 800 °C. The weight hourly space velocity (WHSV) was 3.18/h and H_2O/C ratio = 3, where H_2 production rate was 91% for the Ni/Ca-Al, and H_2 production rate was 94% for the Ni/Ce-Zr catalyst. Under this operational condition, carbon deposited on the catalyst accounted for 3.6% and 1.3% of the fuel feed. Martin et al. [19] utilized a Rh/Al_2O_3 catalyst to conduct steam reforming using ultra-low sulfur diesel (ULSD) and biodiesel (B7) as fuel. Their experimental results showed that ULSD could obtain reforming efficiency up to 97.6%, and B7 could obtain reforming efficiency up to 98.7% for the inlet temperature of the catalyst at 800 °C with H_2O/C ratio = 5 and the gas hourly space velocity (GHSV) between 2200 and 2500/h. Noureddine et al. [20] evaluated the syngas production of waste frying oils (WFOs) with molecular formula $C_{56.28}H_{99.62}O_6$ using steam and autothermal reforming through the Gibbs free energy minimization method, under control parameters including reaction temperatures ranging from 400 to 1200 °C, H_2O/C ratio between 1 and 15, O_2/C ratio between 0 and 2, and atmospheric pressure. Their results displayed that the best SR operating condition was at reaction temperatures between 650 and 850 °C as well as H_2O/C ratio = 5, and H_2 yield was 169.83 mol H_2 per kg WFO. The best ATR reaction temperature was between 600 and 800 °C, where H_2O/C ratio ranged from 3 to 5; O_2/C ratio ranged from 0 to 0.5, and H_2 yield was 146.45 mol per kg-WFO. Kraaij et al. [21] assessed the feasibility of biodiesel reforming combined with a polymer electrolyte membrane fuel cell. They designed a 10 kW prototype reformer that produced syngas with CO proportions of less than 10 ppm, and system efficiency was found to reach 87%. Lin et al. [22,23] started a series of studies based on SOFC applications by using biodiesel and biodiesel blended with different ratios of fossil diesel. They discussed the influence of the reforming efficiency under reaction temperature, the steam/carbon ratio, and the oxygen/carbon ratio, as well as the biodiesel/diesel blending ratio.

Nowadays, heavy-duty diesel engine vehicles complying with the Euro 5 emission regulations almost equip with a SCR system. The system uses AdBlue as a solution in a fixed proportion of 32.5 wt% urea and 67.5 wt% deionized water. It reacts with NOx emissions in the tailpipe of a diesel engine on the catalyst to become N_2 and CO_2. The molecular formula of

Please cite this article in press as: Wu H-W, Lin K-W, Thermodynamic analysis of hydrogen-rich syngas production with a mixture of aqueous urea and biodiesel, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.126