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Analysis of thermally coupling steam and tri-reforming processes for the production of hydrogen from bio-oil

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ABSTRACT

This paper presents the thermodynamic analysis of thermally coupling steam and tri-reforming processes using a bio-oil aqueous fraction for hydrogen production. The total energy efficiency is investigated to evaluate the overall performance of the proposed system. It is found that the operating temperature, steam-to-bio-oil feed (S/F) ratio and split ratio of waste gas recovery have a positive effect on hydrogen yield; the optimal values are as follows: operating temperature of the steam reforming, 650 °C; tri-reforming operating temperature, 580 °C; S/F ratio, 6; and split ratio, 0.5. However, an increase in such parameters increases the energy requirement for the steam reformer. The new proposed system combining thermally coupled steam and tri-reforming processes with a membrane water gas shift reactor offers higher energy efficiency than a conventional steam reforming process.

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Introduction

Hydrogen is an important chemical that is widely used in the petroleum and chemical industries. It is considered a clean energy carrier and can be employed in fuel cells for electricity generation [1,2]. Presently, hydrogen is produced from fossil fuels, such as natural gas and coal, through thermo-chemical processes. However, due to environmental concerns and the limited availability of fossil fuels, it is advantageous to use renewable resources for hydrogen production, which could also limit greenhouse gas emissions [1–4].

Among the various renewable energy sources that have potential use in hydrogen production, bio-oil obtained from a biomass pyrolysis process has received considerable attention. Bio-oil is derived from plants that use CO_2 for their growth; this has positive effects, including CO_2 balance and the easy transport and storage of liquid fuel. In general, bio-oil

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consists of a complex mixture of oxygenated compounds, depending on the biomass feedstock and the fast pyrolysis technology used. The major components of bio-oil are acid, alcohol, ketone, aldehyde and phenol [5–7]. Bio-oil can be separated into an aqueous fraction and an organic fraction by adding water. The aqueous fraction of bio-oil contains light carbohydrate-derived compounds, including acetic acid, formic acid, hydroxylacetaldehyde, acetol and levoglucosan; these compounds can be easily converted to hydrogen [7]. The organic fraction of bio-oil contains lignin-derived compounds, which cause catalyst deactivation in a steam reforming process [8,9].

To date, hydrogen is primarily produced from a steam reforming process in which steam reacts with fossil fuels or biofuels at high temperatures to produce hydrogen rich gas [10,11]. This process involves a strongly endothermic reaction in the presence of reforming catalysts. For a conventional process, a portion of the fuel is combusted to generate heat for the steam reforming reaction, which requires the use of a huge fired furnace and results in low energy efficiency [12,13]. The use of bio-oil as a fuel for bio-oil combustion in a burner or furnace is not suitable because of bio-oil's high viscosity, high water content, poor volatility and corrosiveness [6,14]. Tzanetakis et al. [15] studied the spray combustion characteristics and emissions of 80% bio-oil blended with 20% ethanol in comparison to conventional fuel oils. They found that a bio-oil blend has a lower combustion efficiency than petroleum fuel oils.

A tri-reforming process is the combination of endothermic steam reforming, dry reforming, and exothermic partial oxidation. The advantage of the tri-reforming process is that heat produced by the exothermic oxidation reaction can be used to supply energy for the steam and dry reforming reactions. As the tri-reforming process utilizes CO_2, some researchers have studied its use with biogas feedstock to produce synthesis gas [16,17]. In addition, the tri-reforming process is a method for reducing CO_2 emissions in flue stack gases [18,19]. Because of the wide range of H_2/CO ratios in synthesis gas produced from a tri-reforming process, many studies have focused on finding the optimum H_2/CO ratios for synthesis of methanol and dimethyl ether via a methane tri-reforming process [19–22]. As the tri-reformer behaves as an exothermic reactor under some operating conditions, it can be integrated with a steam reformer for heat supply and additional hydrogen production [23]. Consequently, the efficiency of bio-oil steam reforming may be improved by using integrating both as reforming and tri-reforming via thermal coupling. Such an integrated process may decrease external heat requirements and result in an enhancement of hydrogen production. In addition, such an approach may also reduce environmental impact by using CO_2 as a co-reactant.

At present, the concept of coupling of endothermic and exothermic reactions has been applied to many processes. Bayat et al. [24] analyzed the two different configurations of exothermic-endothermic heat exchanger reactor for methanol production; the necessary heat for the endothermic methanol synthesis reaction was provided by the catalytic dehydrogenation of cyclohexane. The result revealed that the thermally coupling process increases the methanol production rate in comparison with a conventional process. Karimipourfard et al. [25] studied the integrated thermal coupling of endothermic steam reforming and dehydrogenation reaction, and exothermic methane oxidation for synthesis gas, hydrogen and propylene productions. The results proved that the thermally coupled reactor enhances the process in terms of the production rate, costs and energy efficiency. Bruschi et al. [26] investigated the thermal coupling of ethanol steam reforming and ethanol combustion in a microreformer for hydrogen production and found that the moderately high hydrogen yield was obtained. Mirvakili et al. [27] studied the thermally coupled reactors for styrene production. The results showed that styrene production in the thermally coupled reactor is higher than the conventional reactor (5% increase). Some researchers have applied the tri-reforming process to be a heat source for the thermally coupling reactor. Farniaei et al. [28] investigated a syngas production with thermally coupled reactor of methane dry reforming and tri-reforming. The results indicated that the proposed process can produce two types of syngas with different quality and reduce the energy consumption.

To obtain a higher hydrogen content and a high-purity product, a water gas shift reactor and separation units are added to the hydrogen production process; examples of separation units include pressure swing adsorption (PSA) and cryogenic distillation units [13]. Because the water gas shift reaction is exothermic and reversible, it is a strongly equilibrium-limited reaction when performed at high operating temperatures. One promising method for reducing the complexity of the hydrogen production process is to combine both the generation and separation of hydrogen in a membrane water-gas shift (MWGS) reactor. In addition, the removal of H_2 via a membrane enhances the water gas shift reaction and thus improves both H_2 yield and conversion efficiency [11,29].

The objective of this work is to study the thermodynamic effects of thermally coupling steam and tri-reforming processes with a membrane water-gas shift reactor while using a bio-oil aqueous fraction for hydrogen production. The retentate gas formed from the membrane water-gas shift reactor is recycled to the tri-reformer to improve the overall process efficiency by producing more hydrogen and heat for the steam reformer. The effects of the tri-reformer and steam reformer temperature, the steam-to-feed ratio, and the split ratio of waste gas recovery are investigated to determine the optimal condition of this process. Furthermore, the energy efficiency of thermally coupling steam and tri-reforming processes is investigated and compared with the conventional steam reforming process.

Methodology

Process description

In this work, hydrogen production is studied using the thermal coupling of steam and tri-reforming processes with a membrane water-gas shift reactor. A bio-oil aqueous fraction is used as feedstock for the steam and tri-reforming processes. The physical properties and elemental compositions of the aqueous fraction of bio-oil are shown in Table 1. The main

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