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Energetic, exergetic and environmental life cycle assessment analyses as tools for optimization of hydrogen production by autothermal reforming of bioethanol

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ABSTRACT

This paper proposes a methodology devoted to finding and selecting more accurate conditions for sustainable hydrogen production via autothermal reforming of bioethanol. This methodology implies entire hydrogen production process design and simulation, energetic, exergetic and environmental life cycle assessment analysis studies and parametric (intuitive and design of experiment based methods) investigations.

A base-case process operating under conditions recommended by simple investigation of chemical reactions was thoroughly studied. The results show that this base case process suffers from low performance. This is because the energetic, exergetic and environmental performances are comparatively lower than similar findings previously reported by other researchers for other reformates. The parametric investigation indicates that the process performances could be ensured by a proper and rational combination of the reactor temperature and the steam-to-carbon ratio. A key outcome of this research lies in establishing of second order mathematical models. These models can rapidly estimate the process performances (energetic, exergetic and environmental) based on temperature and the steam-to-carbon ratio.

This paper recommends a reforming a temperature of 800 °C and a steam-to-carbon ratio of 4 as the most accurate conditions for autothermal reforming of bioethanol. Such conditions ensure not only the lowest consumption of energy to generate a given amount of hydrogen but also the best environmental performance of the entire system.

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Introduction

Dependence on fossil hydrocarbon fuels as the main energy sources has led not only serious energy crisis but also environmental pollutions. The only way to resolve these problems is to move towards alternative, renewable, efficient and cost-effective energy sources with less environmental impacts. Hydrogen is, currently, considered as one of the leading candidates in the search for an alternative to fossil fuels (FF). Nevertheless, H_2 is only an energy carrier like electricity and not a primary energy source. It can be produced from a wide variety of energy sources, such as natural gas, coal, biomass, solar (thermal and photovoltaic), etc [1]. Despite all the effort made, 96% of the produced H_2 in the world comes from FF, with a non-negligible amount of CO_2 produced emissions in these processes [2]. FF-to- H_2 system appears to have limited horizons, and the development and implementation of new methods for eco-friendly H_2 production, especially from bio-renewable feedstocks, are absolutely required. Therefore, there has been, recently, a significant amount of research going on to produce H_2 efficiently at low cost and minimum environmental impact from renewable sources.

Among various renewable feedstock alternatives for H_2 production, bioethanol has attracted much attention because of its relatively high H_2 content, availability, ease of storage, handling and safety, including its low comparative toxicity [3]. Moreover, bioethanol can be produced renewably from several biomass sources such as (i) sugar or starch crops (sugar beet, sugar cane, corn and wheat, etc.), (ii) lignocellulosic biomass, and (iii) algae biomass [4]. It should be noted that using H_2 from bioethanol is more efficient than bioethanol used directly in internal combustion engines and/or blended with gasoline [5]. The upgrading of raw bioethanol (crude bioethanol) requires various purification steps prior to be blended with gasoline or supplied to an internal combustion engine [5]. In fact, fuel grade bioethanol needs to be water-free. Thus the purification requires distillation beyond the azeotropic point, and this is one of the major production costs of fuel-grade ethanol, consuming almost 3/4 of the energy used in the bioethanol production process [6–8]. Therefore, the use of raw bioethanol as a feedstock in H_2 production will minimize the heat consumption during the distillation process.

Several catalytic processes have been developed in recent years to convert bioethanol-to- H_2 by different routes, such as catalytic steam reforming (SR) [9,10], partial oxidation (POX) [11,12], autothermal reforming (ATR) [13,14], CO_2 reforming [15,16], etc. Among these reforming processes, the ATR has received much attention in research during the recent years as a viable process for H_2 generation for fuel cell systems [13,17,18]. ATR or, more generally denoted oxidative steam reforming, is a combination of SR and POX reactions. This combination is considered as one of the most attractive options for the on-board reforming of complex hydrocarbons. ATR process offers advantages of lower operational temperature and small unit size, easier startup and other dynamic response times [19,20]. Moreover, it has a higher energy efficiency compared to SR or POX. For these reasons, many efforts have been made to improve H_2 productivity in the ATR of

ethanol. However, most of the efforts in this field have been focused on thermodynamic investigations of the bioethanol ATR reaction [21,22] and/or researching catalysis in this system [23,24], but little attention has been devoted to the energetic and environmental performances of an entire system that includes all of the steps involved in the production of H_2 via ATR of bioethanol.

In recent decades, there has been an increasing interest in using both energy and exergy analysis modeling techniques for energy-utilization assessments. The energy analysis is the basic method of a process investigation. It is based on the first law of thermodynamics, which expresses the principle of the conservation of energy. Energy analysis has some inherent limitations, such as not accounting for degradation of the quality of energy through dissipative processes, and does not characterize the irreversibility of operations within the process [25]. The exergy analysis is a modern thermodynamic method used as an advanced tool for process evaluation [26]. Based on both the first and the second laws of thermodynamics, exergy analysis compensates for the inability of the energy analysis to reveal the losses of energy due to its thermodynamic imperfections, and it plays unique roles in revealing the reasons for, location of and direction of improvement for losses. Therefore, exergy analysis has been widely used in recent years in assessing the performance of various bioenergy production processes [27–31]. For example, Modarresi and colleagues [32] applied exergy analysis to a novel process for biological production of H_2 from biomass employing thermophilic and photo-heterotrophic bacteria. The authors obtained a chemical exergetic efficiency of 36–45% without considering any heat and process integration. In another study, Li and co-workers [33] established a theoretical framework for the exergy analysis and advanced exergy analysis of a real biomass boiler. They showed that the maximum exergy destruction occurs in the combustion process, followed by the water walls and radiant superheater and the low temperature superheater. Most recently, Karellas and Braimakis [34] have performed an energy–exergy analysis and economic investigation of a cogeneration and trigeneration ORC–VCC hybrid system utilizing biomass fuel and solar power. Their results showed that, in the base case scenario, the net electric efficiency is 2.38%, with an electricity output equal to 1.42 kW_e and a heating output of 53.5 kW_{th} .

One of the most important criteria to inform decision-makers on the most sustainable options for process design is the evaluation of the environmental impacts. In this context, Life Cycle Assessment (LCA) methodology could be used in parallel with the process design for finding and assessing technical solutions that could be adopted in the production process for reducing the environmental impacts [35]. LCA is a holistic method that assesses the impact of a product by considering all stages of its life cycle. LCA is considered as a “cradle to grave” method of assessing resource use and emissions to the environment from the extraction of resources through manufacturing, transportation, operation and recycling or final disposal [36]. LCA has been extensively applied as a design-support tool for highlighting environmental criticalities and improvement solutions in the life cycle of bio-based energy systems such as H_2 [35,37–39],

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