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# A thermo-environmental study of hydrogen production from the steam reforming of bioethanol

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ABSTRACT

The main objective of this study is to accurately report the conditions for sustainable hydrogen production via steam reforming of bioethanol. To this end, various engineering assessment tools are simultaneously applied (energetic and exergetic analyses and life cycle assessment). The process operating parameters were also varied to illustrate the energetic, exergetic and environmental sensitivity and to provide guidance for where research and development efforts should focus for process improvement. A base-case process operating under conditions recommended by simple investigation of chemical reactions was thoroughly investigated. The results show that this base case 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 performance could be improved by a proper and rational combination of the reactor temperature and the steam-to-carbon ratio. A reforming a temperature of 800 °C and a steam-to-carbon ratio of 5 are recommended as the best conditions for the conversion of bioethanol-to-hydrogen. 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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## 1. Introduction

Our current dependence on fossil fuels (FF) as an energy source has caused serious environmental problems, i.e., air pollution and greenhouse gas (GHG) emissions as well as natural resource depletion. However, development of renewable and clean energy resources is necessary for reducing pollution levels caused by those conventional fuels. At the international level, $H_2$ is considered as a major vector that could contribute to the reduction of the global dependence upon FF and to the reduction of atmospheric pollution [1]. $H_2$ is, also, considered as one of the most promising fuels for generalized use in the future, mainly because it is low-polluting, versatile and energy-efficient. $H_2$ is a high-quality energy carrier, which can be used with a high efficiency and zero or near-zero emissions at the point of use [2]. So far, $H_2$ is produced almost entirely from FF (96%), such as natural gas (48%), heavy oils and naphtha (30%), etc. [3]. In the present case, the same amount of $CO_2$ as that formed by combustion of those fuels is released during $H_2$ production. However, the transition to an $H_2$ economy requires it to be produced from renewable resources and with ecofriendly processes to build a sustainable energy system. Thus, in the last decade, there has been a significant amount of research into the production of $H_2$ from renewable sources efficiently at low cost and with minimum environmental impact.

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 [4,5]. 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 [6]. 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 [7]. The upgrading of raw bioethanol (crude bioethanol) requires various purification steps prior to be blended with gasoline or supplied to an internal combustion engine [7]. In fact, fuel grade bioethanol needs to be water-free, thus the purification requires distillation beyond the

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## Nomenclature

Notation

| | |
|---|---|
| ADP | Abiotic depletion potential |
| AP | Acidification potential |
| ATR | Autothermal reforming |
| CCD | Central composite design |
| COPROX | CO preferential oxidation reactors |
| D | Total molar flow rate |
| DOE | Design of experiments |
| EP | Eutrophication potential |
| Ex | Exergy |
| FAETP | Fresh water aquatic ecotoxicity potential |
| FF | Fossil fuels |
| FU | Functional unit |
| GHG | Greenhouse gas |
| GWP100 | Global warming potential for time horizon 100 years |
| H | Molar enthalpy |
| HTP | Human toxicity potential |
| HT-WGS | High temperature shift reactor |
| LCA | Life cycle assessment |
| LCI | Life cycle inventory |
| LCIA | Life cycle impact assessment |
| LHV | Lower heating value |
| LT-WGS | Low temperature shift reactor |
| m | Mass flow |
| MAETP | Marine aquatic ecotoxicity potential |
| n | Number of chemical species in the material stream |
| ODP | Stratospheric ozone depletion potential |
| P | Pressure |
| PEMFC | Proton exchange membrane fuel cell |
| POCP | Photochemical ozone creation potential |
| POX | Partial oxidation |
| PSA | Pressure swing adsorption |
| Q | Heat transferred |
| RS | Model response surface model |
| S | Molar entropy |
| SB | System boundaries |
| SG | Synthesis gas |
| SMR | Steam methane reforming |
| SR | Steam reforming |
| SRK | Soave-Redlich-Kwong equation of state |
| T | Temperature |
| t.km | Ton.kilometers |
| TEP | Terrestrial ecotoxicity potential |
| W | Mechanical work |
| WGS | Water–gas shift |
| Y | Predicted response |
| Z | Factor (variable) |

Subscripts

| | |
|---|---|
| M | Material stream |
| mix | Mixing part |
| Q | Heat transfer |
| phy | Physical part |
| W | Work exchange |
| chem | Chemical part |
| 0 | Reference conditions |

Superscripts

| | |
|---|---|
| l | Liquid phase |
| v | Vapor phase |
| 0 | Pure component properties at standard conditions at $T_0$, $P_0$ |

Greek letters

| | |
|---|---|
| ε | Molar standard chemical exergy |
| h | Efficiency |
| β | Axial level (“star point”) |
| α | Stoichiometric coefficient of water |

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[8–10]. Therefore, the use of raw bioethanol as a feedstock in $H_2$ production will minimize the heat consumed 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) [11–13], partial oxidation (POX) [14,15], autothermal reforming (ATR) [16–18], $CO_2$ reforming [19,20], etc. Among these reforming processes, SR of ethanol has a higher efficiency for $H_2$ production than the other reforming processes [21]. For this reason, many efforts have been made to improve the $H_2$ productivity (mole $H_2$ produced per mole of ethanol used in feed) in the SR of ethanol. However, most of the efforts in this field have been focused on chemical reaction investigations of the bioethanol SR [21–23] and/or researching catalysis in this system [11,12,24]. 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 SR of bioethanol.

Hence, an SR system is considered efficient when the $H_2$ productivity of the system is high. This approach does not emphasize total energy consumption, i.e., the energy required to generate a given amount of $H_2$. In an entire bioethanol-to-$H_2$ plant with heaters, reactors, steam generators, and so forth, the overall energy balance could be very endothermic, and $H_2$ production becomes energy intensive. Therefore, an energy analysis should be established to quantify the energy consumption and thereby the energetic performance of such a process. Moreover, in most bioethanol-to-$H_2$ studies no importance was given to the environmental impacts caused by the use of raw materials, material and energy (electrical, heat, etc.) within the entire system of $H_2$ production via bioethanol reforming. Manifestly, the design of an eco-friendly $H_2$ production system from bioethanol should include all environmental impacts generated by its entire life cycle.

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, Soltani et al. [29] applied exergy analysis to an externally-fired combined-cycle power plant integrated with biomass gasification. The authors showed that interactions between the components are not very strong and concluded that the focus for improving cycle performance should be on the heat exchanger and not the

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