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Exergy analysis of biohydrogen production from various carbon sources *via* anaerobic photosynthetic bacteria (*Rhodospirillum rubrum*)

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A B S T R A C T

In this study, exergy analysis of batch biohydrogen production through WGS (water–gas shift) reaction using an anaerobic photosynthetic bacteria *Rhodospirillum rubrum* was carried out for the first time. Various carbon sources including formate, acetate, malate, glucose, fructose, and sucrose were applied to support microbial growth in the presence of CO-rich syngas. The microorganisms utilized carbon monoxide and produced molecular hydrogen concurrently. The process was analyzed based on both conventional exergy and eco-exergy concepts for determining the exergetic parameters i.e., exergy destruction and exergy efficiency. Unlike the exergy efficiency, the exergy destruction based on the eco-exergy concept was remarkably lower than what obtained *via* the conventional exergy theory. Minimum normalized exergy destruction values of 189.67 and 181.40 kJ/kJ H_2 were achieved for acetate as substrate using the exergy and eco-exergy approaches, respectively. In better words, acetate was identified as the most appropriate carbon source for biohydrogen production from the exergy point of view. Finally, the findings of this study confirmed that exergy analysis could be employed as an adaptable framework to determine and compare the renewability of biological hydrogen production using different routes in order to decide on the most suitable approach and conditions.

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1. Introduction

Today, more than 80% of the global energy demands are met by fossil-based fuels. The widespread application of such fuels through combustion processes has led to the emissions of CO_x, SO_x, NO_x, C_xH_y, soot, ash, and organic compounds and has consequently brought about environmental concerns such as global warming [1–4]. In addition to that, the existing fossil fuel resources are depleting and that highlights the importance and urgency to act in haste and further move towards the production and utilization of renewable energies [5–7]. Amongst various renewable energy carriers, hydrogen has been proven promising and is anticipated to play a prominent role in the future of the energy market [8].

In recent years, different routes have been developed for hydrogen production from various renewable and non-renewable feedstocks with their own pros and cons [9,10]. Currently, hydrogen is almost entirely produced *via* natural gas reforming and coal gasification as well as water electrolysis, and thermochemical decomposition [11]. However, to achieve a sustainable and eco-friendly hydrogen production process, hydrogen must be produced from renewable resources instead of employing the depleting non-renewable origins [12]. In addition to biomass gasification [13] and photosynthetic cells [14], renewable hydrogen can also be produced *via* natural biocatalysts using CO-rich synthetic gas through fermentation [15] and waste sludge [8]. In the presence of suitable substrates and process conditions, these microorganisms are capable of simultaneously using carbon

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monoxide and producing hydrogen in a non-thermal way. Overall, biological hydrogen production is regarded as a promising approach for sustainable production of renewable hydrogen energy due to its lower environmental impact as well as smaller capital and operational costs required [15]. Nevertheless, advanced engineering tools should still be employed to assess the sustainability of the biological approaches over the conventional routes. Moreover, these advanced tools could be instrumental in justifying the production of a type of biofuel such as biohydrogen as well as in selecting the most eco-friendly pathway.

Thermodynamic analyses are effective means to obtain more precise and valuable information on the sustainability of renewable energy plans worldwide aimed at dealing with the intensifying climate and energy supply crises. Determining the renewability of an energy resource *via* the traditional energy assessment approaches, which are based on the first law of thermodynamics, has been criticized owing to their debility in identifying the quality of energy flows [16–18]. Therefore, a relatively new version of thermodynamic indicators namely exergy has been increasingly employed to overcome the shortcomings of the conventional energy analysis in terms of assessing the sustainability of renewable energy projects. In fact, exergy is the maximum theoretical available work obtainable from a system as it reaches a complete thermodynamic equilibrium with the reference environment [19–22]. Exergy analysis based on the first and second law of thermodynamics is regarded as a robust tool for determining the energy quantity and quality of a process more precisely than the traditional energy analysis [23].

In the last two decades, exergy analysis has been extensively applied to investigate various available and emerging technologies suggested for hydrogen production. Rosen [24] first studied the thermodynamic performance of a water-electrolysis process for hydrogen production. More than a decade later, the performance of hydrogen production *via* steam-methane reforming was assessed using exergy analysis [25]. In another survey, Toonssen et al. [26] applied exergy analysis to compare five different commercial or pilot scale gasification systems for producing hydrogen. Exergetic performance assessment of gasification process followed by steam-methane reforming and shift reactions for hydrogen production from oil palm shell was also carried out by Cohce et al. [27]. In a number of investigations, Modarresi et al. [12,28] applied exergy analysis for hydrogen production from starch and sugar as well as lignocellulosic biomass fermentation *via* thermophilic and photoheterotrophic bacteria. Even though a number of investigations have been published on the photobiological hydrogen production, the purpose of those studies was generally on its feasibility and modeling [29–32]. However, no survey could be found in the published literature on exergy analysis of biological hydrogen production through fermentation of CO-enriched waste syngas using anaerobic photosynthetic bacteria. This approach seems like a very promising methodology to convert environmentally-harmful CO contained in waste gas to a useful energy carrier i.e. biohydrogen.

Therefore, this study was aimed to present exergy analysis of biohydrogen production by means of WGS (water–gas shift) reaction using an anaerobic photosynthetic bacterium (*Rhodospirillum rubrum*) in a batch fermenter for the first time. In this regard, fermentative hydrogen production was analyzed on the basis of both conventional exergy and eco-exergy concepts for evaluating the exergetic and renewability parameters. These analyses were carried out to select the best suitable carbon sources for pilot- and commercial-scale bioreactors. The outcomes of employing such analyses could be of great interest to engineers, designers, and researchers in order to select the most appropriate substrate and process conditions for achieving more economical and eco-friendly biological hydrogen production. In general, exergy analysis can be applied as a decision-making tool for developing new renewable technologies and retrofitting the existing systems from the renewability and sustainability points of view.

2. Materials and methods

2.1. Biohydrogen production as well as liquid and syngas analyses

The WGS reaction involves the reaction of CO with water to produce hydrogen. The other product of this process is CO_2. The process can be represented by the following equation:

$$H_2O + CO \rightarrow H_2 + CO_2 \tag{1}$$

Fig. 1 schematically manifests the biological WGS reaction for hydrogen production using photosynthetic bacteria. These microorganisms conserve metabolic energy through the formation of H_2 while CO serves as the carbon source, electron donor, and energy source. More specifically, CO is oxidized by a monofunctional CO dehydrogenase and the electrons released through the oxidation are transferred to an ECH (energy converting hydrogenase) that reduces protons to molecular hydrogen [33]. In addition, ECH couples the formation of H_2 to the membrane translocation of protons or sodium ions [33]. During the hydrogen production process through the WGS reaction, CO_2 as a greenhouse gas contributor is also produced. Therefore, to improve the environmental aspects of the process, extra measures should be taken in order to mitigate the generated CO_2. These measures could include different methods offered to convert CO_2 into value-added products such as CO_2-to-fuel through thermochemical, photochemical, and electrochemical conversion processes [34].

The detailed information on the biological hydrogen production in a batch fermenter can be found elsewhere [15]. Briefly, *R. rubrum* ATCC 25903 acquired from the American Type Culture Collections was applied in the current survey. This bacterium was incubated at 30 °C in a sealed stoppered serum bottle with a volume of 163 ml after hydrating and growing on malic acid. Serum bottles were filled with 50 ml culture medium under nitrogen gas and were then sterilized at 121 °C for 15 min. Then, 5% (v/v) seed culture was added to each bottle. The pH of the medium was adjusted to 7.5 by adding 0.2 M HCl and base 0.2 M NaOH solutions. The liquid culture media during hydrogen production was similar to the culture media except various carbon sources e.g., malate, acetate, formate, fructose, glucose, and sucrose were employed. Table 1 lists the compositions of the liquid culture media in 1000 ml. Moreover, synthetic gas with 55% CO, 20% H_2, 15% Ar, and 10% CO_2 was used to purge the serum bottles. A 60 W tungsten lamp was used to supply a uniform light intensity of 1000 lux on the surface of the serum bottles. The initial pressure of bioreactor was set to 1 atm. An orbital shaker (B Braun, Germany) was applied to shake the serum bottles at a constant speed of 200 rpm during biohydrogen production.

Experiments were replicated twice and the average values were used in the exergetic calculations. Exergy analysis of the bioreactor was performed by using the data obtained from the experiments conducted by applying various carbon sources as substrate. Generally, the exergy analysis of bioreactors could provide comprehensive and in-depth insights into the process, including the destructed exergy in the fermentation process, optimum operational conditions, appropriate substrate, and etc. The most important feature of the exergy analysis is its capability in the recognition of sustainable methods of using energy sources.

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