



# Exergy-based performance analysis of a continuous stirred bioreactor for ethanol and acetate fermentation from syngas via Wood–Ljungdahl pathway

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## H I G H L I G H T S

- Exergy analysis as a decision-making tool for sustainability appraisal of continuous ethanol and acetate fermentation.
- Effect of liquid media and syngas flow rates as well as agitation speed on exergetic performance parameters of the bioreactor.
- 450 rpm agitation speed, 0.55 ml/min liquid media flow rate, and 8 ml/min syngas A flow rate as the best operational condition.
- Potential application of the developed approach to facilitate ongoing attempts to improve the performance of bioreactors.

## A R T I C L E I N F O

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## A B S T R A C T

In this work, a thermodynamic framework was proposed to achieve improved process understanding of ethanol and acetate fermentation in a continuous stirred tank bioreactor from syngas through the Wood–Ljungdahl pathway. The bioreactor performance was evaluated using both conventional exergy and eco-exergy principles to identify the effect of different operational parameters i.e. agitation speeds and liquid media flow rates as well as syngas volume flow rates and its composition on the sustainability and renewability of the process. The exergy efficiency of the bioreactor was found to be in the range of 8.14–89.51% and 8.86–89.52% using the conventional exergy and eco-exergy concepts, respectively. The maximum exergetic productivity index was found to be 6.82 and 6.90 using the conventional exergy and eco-exergy concepts, respectively, at agitation speed of 450 rpm, liquid media flow rate of 0.55 ml/min, and syngas volume flow rate of 8 ml/min containing 10% CO<sub>2</sub>, 15% Ar, 20% H<sub>2</sub>, and 55% CO. In general, the exergetic performance parameters computed using both concepts under the studied conditions did not display significant differences because of the low volume of the bioreactor and slow growth rate of the microorganisms. The results of the present study showed that exergy concept and its extensions could undoubtedly play a strategic role in assessing biofuel production pathways with respect to the issues currently of major interest in the renewable energy industry, i.e., sustainability and productively.

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## 1. Introduction

It is anticipated that the rapid depletion of fossil fuel reserves because of increasing global energy utilization accompanied with increasing population and rising life standards will lead to their shortage and higher prices in the near future (Akia et al., 2014). These problems will become even more serious because of the

detrimental environmental impacts of fossil fuels such as global warming, climate changes, acid rain, and stratospheric ozone exhaustion (Rahimnejad et al., 2014; Atabani et al., 2014). Within recent decades, carbon neutral biofuels produced from non-edible feed stocks (second generation biofuels) has been taken into account as one of the substitutes for fossil fuels since they do not compete with the food industry over land and water use (Mohammadi et al., 2014). Amongst the second generation biofuels technologies, lignocellulosic biomass gasification and subsequent Fischer–Tropsch synthesis has been shown to be one of the most applicable techniques for converting the non-food crops to more useful forms of energy and organic materials. Recently, conversion of the produced syngas into biofuels and biomaterials by microbial catalysts has received considerable attention compared to chemical catalysts. These natural catalysts can upgrade syngas components into various desired end-products such as acetate, butyrate, ethanol, and butanol (Elshahed, 2010; Duséaux et al., 2013). Despite the promising nature of such processes, it is still vital for researchers to find the most sustainable and economical pathways for the development of biofuel industries.

Nowadays, thermodynamic analysis, particularly exergy analysis, has attracted extraordinary interests as a key engineering tool for system design, analysis, and optimization of energy conversion systems (Colak and Hepbasli, 2007; Colak et al., 2008; Icier et al., 2010; Hepbasli et al., 2010). In general, exergy refers to the maximum amount of theoretical work that could be generated by a stream of matter, heat or work as it reaches an equilibrium with a reference state (Aghbashlo et al., 2012a, 2012b; Ofari-Boateng et al., 2012a, 2012b, 2012c; Aghbashlo et al., 2015; Aghbashlo, 2015; Dadak et al., 2015; Hosseini et al., 2015). Unlike energy analysis, exergy analysis has been proved to be an efficient and reliable tool for evaluating various biofuels synthesizing routes especially owing to the ability of determining the value of the thermodynamic irreversibilities.

In this sense, a considerable amount of published papers can be found in the literature on the application of exergy concepts for analyzing available and new pathways proposed for ethanol production (Ofori-Boateng and Lee, 2013; Ofori-Boateng and Lee, 2014; Ortiz and de Oliveira, 2014). For instance, Ojeda and Kafarov (2009) applied exergy concept to assess two kinds of enzymatic hydrolysis reactors operating on lignocellulosic biomass for second generation bioethanol production. Later, Ojeda et al. (2011a) applied both energy and exergy analyses along with process integration methodologies for production of bioethanol from acid-pretreated bagasse using different process configurations including sequential hydrolysis and fermentation, simultaneous saccharification and fermentation, and simultaneous saccharification and co-fermentation. In the same year, Dias et al. (2011) used thermoeconomic analysis for calculating exergy-based costs of electricity and ethanol for a traditional Rankine cycle and biomass integrated gasification combined cycle. Ojeda et al. (2011b) also compared four ethanol production chains through the use of the typical daily amount of residual biomass generated by the sugar industry using exergy concept. In a recent study, exergetic life cycle assessment was employed by Ofori-Boateng and Lee (2014) to evaluate thermo-environmental renewability of an oil palm-based biorefinery approaches for mutual production of cellulose ethanol and phytochemicals from oil palm fronds. Moreover, Ortiz and de Oliveira (2014) evaluated four pretreatment technologies including steam explosion, organosolv, liquid hot water, and steam explosion plus liquid hot water via exergy analysis to prepare lignocellulosic biomass for bioethanol production from sugarcane bagasse.

Although a large number of reports have been published on the production of various biofuels from syngas via natural catalysts (Kundiyan et al., 2010; Maddipati et al., 2011; Liu et al., 2012,

2014), the exergetic performance of such bioreactors has not yet been investigated, to the best of our knowledge. Therefore, the aim of current survey was to conduct the exergy analysis of a continuous ethanol and acetate fermentation from syngas through the Wood–Ljungdahl pathway at different agitation speeds and liquid media flow rates as well as syngas volume flow rates and its compositions to achieve the optimal conditions. This was the first time that an exergy analysis was performed on a continuous bioreactor used for liquid fuel production from syngas using microbial catalysts. The findings of such a study would be beneficial to policy makers and researchers for identifying the most appropriate conditions to achieve an eco-benign and highly efficient route for biofuels production. In general, exergy analysis could aid to develop strategies and guidelines for more sustainable and effective biofuel production using various routes.

## 2. Materials and methods

### 2.1. Microorganism, culture media, and syngas

The detailed information on the continuous ethanol and acetate fermentation via *Clostridium ljungdahlii* can be found in our previous publications (Younesi et al., 2005; Mohammadi et al., 2012). A pure culture of the bacteria *C. ljungdahlii* ATCC 55383 used for acetate and ethanol fermentation from syngas was obtained from the American Type Culture Collection (USA). The microbes were grown in a rich ATCC media in an incubator shaker (Barnstead/Lab-Line, MaxQ 4000, USA) at 37 °C anaerobically. For the growth stage, the microbial culture prepared was transferred into Wheaton serum bottles made of Borosilicate glass, containing 50 ml liquid medium of the following compounds: NH<sub>4</sub>Cl (1 g/L), KCl (0.1 g/L), MgSO<sub>4</sub>·7H<sub>2</sub>O (0.2 g/L), NaCl (0.8 g/L), KH<sub>2</sub>PO<sub>4</sub> (0.1 g/L), CaCl<sub>2</sub>·2H<sub>2</sub>O (0.02 g/L), yeast extract (1 g/L), NaHCO<sub>3</sub> (2 g/L) and fructose (5 g/L). The trace element solution was prepared by mixing the following chemicals (10 mL): Nitroloacetic acid (2 g), MnSO<sub>4</sub>·H<sub>2</sub>O (1 g), NaCl (1 g), (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.8 g), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.18 g), ZnSO<sub>4</sub>·7H<sub>2</sub>O (0.2 g), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.1 g), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.01 g), CuSO<sub>4</sub>·5H<sub>2</sub>O (0.01 g), Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.01 g), Na<sub>2</sub>SeO<sub>4</sub> (3 mg) and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (3 mg). Vitamin solution (10 ml) included: biotin (2 mg), folic acid (2 mg), pyridoxine-HCl (10 mg), thiamine-HCl (5 mg), riboflavin (5 mg), nicotinic acid (5 mg), calcium D-(+) pantothenate (5 mg), cyanocobalamin (0.1 mg), p-aminobenzoic acid (5 mg) and thioctic acid (5 mg). Also, reducing agent was prepared in 100 ml distilled water: NaOH (0.9 g), cysteine HCl (4 g) and Na<sub>2</sub>S·9H<sub>2</sub>O (4 g). The reducing agent and fructose were separately autoclaved and added into the media solution.

Fig. 1 schematically represents the experimental set up applied for acetate and ethanol fermentation with automatic temperature and pH controls. The defined medium containing vitamin solution, trace metals, sodium bicarbonate and reducing agent was used to prepare the inocula and for cultivation of the cells in the bioreactor. The medium was reduced by adding 10 mL of Na<sub>2</sub>S·9H<sub>2</sub>O solution (10% w/v). Moreover, the bioreactor temperature was kept at a constant temperature of 37 °C. Fig. 2A shows the continuous bioreactor operation at various fresh liquid flow rates and agitation speeds while Fig. 2B shows the variations applied in syngas volume flow rates and its compositions throughout the ethanol and acetate fermentation process. It must be noted that three different compositions of syngas blended for industrial applications (Air Products, Malaysia) were used in this study. The syngas A consisted of 10% CO<sub>2</sub>, 15% Ar, 20% H<sub>2</sub>, and 55% CO. While the syngas B composed of 15% Ar, 15% H<sub>2</sub>, and 70% CO. Furthermore, the syngas C was pure CO. To simulate the industrial bioethanol production plants equipped with gasification units, three types of

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