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Review Article

Inhibition of dark fermentative bio-hydrogen production: A review

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ABSTRACT

Dark fermentative bio-hydrogen production is not commercially exploited due to several factors hindering its production, making the process unfeasible on large scale. This study provided an in-depth and critical review of different factors of the dark fermentation process namely H₂-consumers and lactic acid bacteria in mixed microflora, light and heavy metal ions, furan derivatives and phenolic compounds, ammonia and H₂ concentrations and soluble metabolites viz. acetic acid, ethanol, propionic acid and butyric acid that may negatively affect H₂ production. For each of the inhibitors, the mechanism behind process inhibition was explained while strategies for reducing inhibition were outlined. Among the different inhibitors studied, furan derivatives and phenolic compounds suppressed bio-hydrogen production to a larger extent while the most common strategies reviewed for reducing inhibition included inoculum pre-treatment for suppressing H₂-consumers and dilution of reactor contents for decreasing inhibitor concentrations. Although these options are encouraging on small scale, the economic and technical feasibilities of implementing these strategies on larger scale require further investigation.

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Introduction

Fossil fuels have been continuously dominating the world's energy supply for ages. In 2013, fossil fuels accounted for more than 81% of the world's total primary energy supply [1]. However, the negative environmental and health impacts, the unstable prices of fossils as well as the depleting reserves are gradually triggering a shift towards renewable energies [2–4] as confirmed by a mean annual increase rate of 2.5% [5]. Among the renewable energies, bioenergy constitutes the major fraction, representing 76% of total renewable energies in 2011 [6]. With a rise in the world's total primary energy demand over the years, the requirement for bioenergy has continuously increased and this has been partly achieved through an increase in biofuels production from 16 billion litres in 2000 to 110 billion litres in 2013 [7]. Since global energy requirement will continue to increase in the future due to population growth and rise in industrialisation [8], renewable energies in the form of biofuels from biomass will need to be further exploited to prevent any potential energy crisis.

Biofuels are produced from biomass through thermo-chemical or biological processes and can be in the liquid or gaseous state [9]. Several biofuels have been investigated namely bio-methane, bio-ethanol and bio-diesel, amongst others [9]. However, increasing interests now lie towards the production of bio-hydrogen owing to the clean and non-polluting nature of the gas upon combustion as well as its high energy content [10,11]. Bio-hydrogen can be produced through thermo-chemical and biological technologies but owing to the ecological benefits and lower energy requirements over thermo-chemical processes, biological techniques are preferred [12]. Through biological routes, bio-hydrogen can be produced from technologies such as dark fermentation (DF), photo fermentation, direct and indirect biophotolysis and water-gas shift reactions [13,14]. However, the DF process is favoured over the other technologies owing to its more realistic potential to be commercialised in the near future [15].

Currently, the DF process has not been commercially exploited due to the constraints of low H₂ yield and low production rate, making the process unfeasible on large scale [11,16]. The low bio-hydrogen production from DF can be attributed to numerous process parameters that inhibit the process, resulting in low yields. Several studies have reviewed the different operating conditions influencing dark fermentative bio-hydrogen production viz. pH, temperature, hydraulic retention time and organic loading rate, amongst others [17–31]. Although these process parameters are vital for effective bio-hydrogen production, there are other factors which, if neglected, may result in severe process inhibition. As such, the aim of this study is to provide a critical review of the different inhibitors of dark fermentative bio-hydrogen production while proposing some remedial actions to counter their suppressing effects.

Principles of dark fermentation

DF refers to the degradation of organic substrates by anaerobic bacteria in an environment deprived of light and oxygen to produce bio-hydrogen [14,32]. The breakdown and conversion of complex polymers such as carbohydrates into bio-hydrogen takes place through a series of biochemical reactions [33]. Carbohydrates-rich materials are initially hydrolysed into sugar molecules by either biological means or by the use of pre-treatment technologies [15,33]. The resulting sugars (e.g. glucose molecules) then undergo a chain of biochemical reactions as summarised in Table 1. Initially, glucose molecules are degraded by the action of nicotinamide adenine dinucleotide ion (NAD⁺) into pyruvate, H⁺ and nicotinamide adenine dinucleotide (NADH) as depicted in Eq. (1) and this is termed as glycolysis [12]. Pyruvate, which is the main intermediate product of the DF process, is then anaerobically oxidised to acetyl coenzyme A (acetyl-CoA) through two possible routes: the pyruvate:formate lyase (Pfl) pathway or the pyruvate:ferredoxin oxido-reductase (Pfor) pathway [13] depending on the bacterial culture employed [34].

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