



## A review of research trends in the enhancement of biomass-to-hydrogen conversion



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### ABSTRACT

Different types of biomass are being examined for their optimum hydrogen production potentials and actual hydrogen yields in different experimental set-ups and through different chemical synthetic routes. In this review, the observations emanating from research findings on the assessment of hydrogen synthesis kinetics during fermentation and gasification of different types of biomass substrates have been concisely surveyed from selected publications. This review revisits the recent progress reported in biomass-based hydrogen synthesis in the associated disciplines of microbial cell immobilization, bioreactor design and analysis, ultrasound-assisted, microwave-assisted and ionic liquid-assisted biomass pretreatments, development of new microbial strains, integrated production schemes, applications of nanocatalysis, subcritical and supercritical water processing, use of algae-based substrates and lastly inhibitor detoxification. The main observations from this review are that cell immobilization assists in optimizing the biomass fermentation performance by enhancing bead size, providing for adequate cell loading and improving mass transfer; there are novel and more potent bacterial and fungal strains which improve the fermentation process and impact on hydrogen yields positively; application of microwave irradiation and sonication and the use of ionic liquids in biomass pretreatment bring about enhanced delignification, and that supercritical water biomass processing and dosing with metal-based nanoparticles also assist in enhancing the kinetics of hydrogen synthesis. The research areas discussed in this work and their respective impacts on hydrogen synthesis from biomass are arguably standalone. Thence, further work is still required to explore the possibilities and techno-economic implications of combining these areas for developing robust and integrated biomass-to-hydrogen synthetic schemes.

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## 1. Introduction

The increasing need for clean energy generation and its usage have both mobilized considerable research efforts in exploring the integration of key green chemistry and green engineering principles for the comprehensive assessment of the biomass types in their respective potential to yield hydrogen (Çelik and Yıldız, 2017). Hydrogen generation by fermentative routes using biomass has several key advantages. The main advantages are that there are no greenhouse gas emissions and there is a high potential to reuse wastes biomass as renewable feedstocks. Therefore, the switch to a future hydrogen fuel biotechnology regime holds a good share of promise. A quick survey of the available literature will show that there are very many different types of original research works and reviews that have been reported on biomass utilization for hydrogen production, and which have provided useful information on the diverse technical, biochemical, mechanistic, economic and energy-related considerations (Dasgupta et al., 2010; Mattos et al., 2012; Lin et al., 2012; Christopher and Dimitrios, 2012; Ghimire et al., 2015; Azwar et al. 2014; Parthasarathy and Narayanan, 2014; Trchounian, 2015; Lee, 2016; Sivagurunathan et al., 2016; Elbeshbishy et al., 2017; Rezania et al., 2017; Boodhun et al., 2017; Liu et al., 2018). In this review, we discuss some recent trends in research on hydrogen production from various biomass types specifically in relation to reaction environments where (i) different microbial cell immobilization techniques and bioreactor configurations have been assessed, (ii) different biomass pretreatment routes involving microwave waves, ultrasound waves and ionic liquid have been assessed, (iii) novel microbial strains have been developed, (iv) applications of metal-based nanocatalysis have been made, (v) subcritical and supercritical water processing conditions have been tested for biomass gasification, and (vi) finally, where different inhibitor detoxification options have been studied.

## 2. Cell immobilization

Hydrogen synthesis using continuous systems based on the suspended cells design configuration have also been gaining attention, but have unfortunately been found to fail in certain circumstance because of process limitations emanating from short hydraulic retention times and cell wash-out (Zhao et al., 2017; Chandolias et al., 2016; Yeshanew et al., 2016; Zagrodnik et al., 2015; Mohammadi et al., 2014). To address these biomass-based hydrogen production technical issues, many useful immobilization strategies have been therefore formulated. Cell immobilization, which can be broadly classified as natural immobilization and artificial immobilization, ensures that larger concentrations of biomass are utilized and as a result the reactor sizing requirements decrease and processes can be run over longer durations (Sagir et al., 2017b). Indeed, many of the most commonly used biocell immobilization techniques have significantly improved hydrogen generation rates (Zhang et al., 2017a) and enhanced the overall process yields and equally brought useful insights into how to tackle issues related to reaching stable hydrogen operational modes (Mohan et al., 2008) and production schemes.

The main cell immobilization techniques which have been assessed and have brought net positive contributions to enhance

the biomass-based hydrogen generation kinetics are adsorption-based and attachment type immobilizations (Basile et al., 2010; Wu et al., 2012; Reungsang et al., 2013), encapsulation-based immobilization (Sekoai et al., 2018), polymer-based immobilization (Ismail et al., 2011), and immobilization on nanoparticles (Shuttleworth et al., 2014; Seelert et al., 2015). These techniques have been widely studied and a number of attempts have been reasonably successful in optimizing the overall performance with respect to the process and design parameters namely bead size and cell loading, mass transfer coefficient, pH and immobilized biomass ratio support materials, types of microorganisms immobilized, supplements, temperature (Satar et al., 2017), the bioavailability of organic portions of the biomass, and in exploring the possibility to integrate the synergistic influence of co-immobilization and using nanoparticles. Kerčmar and Pintar (2017) have demonstrated that the type of support material has a pivotal influence on the properties and behaviour of the attached biomass during anaerobic processes. Salem et al. (2017) have reported that amendment with hematite nanoparticles had improved the hydrogen production rate from 3.87 L hydrogen/L.d to 5.9 L hydrogen/L.d when hydrogen generation from a sucrose wastewater was investigated. Nasr et al. (2015) reported that an enhanced hydrogen yield reaching  $104.75 \pm 12.39$  mL hydrogen/g COD<sub>removed</sub> had been obtained in an anaerobic baffled reactor which was inoculated with sludge immobilized on maghemite nanoparticles.

Pansook et al. (2016) have studied biohydrogen synthesis by *Aphanothece halophytica* cells immobilized in alginate beads, and their results indicated that such immobilization conditions gave better process performance with respect to conditions where there were free cells within the reaction control volume. Li et al. (2017) have developed a new photothermal biomaterial (GeO<sub>2</sub>-SiO<sub>2</sub>-Chitosan-Medium-LaB<sub>6</sub>) which they tested as a support for photosynthetic bacteria in its influence on biohydrogen generation using. The results from Li et al. (2017) demonstrated the high capability of this new biomaterial in enhancing biohydrogen production since the hydrogen production rate increased by a factor of 4.1 and the mean biofilm growth rate was boosted by a factor of 3.4 in contrast to the control experiments with no biomaterial support. The essential inference from the work of Li et al. (2017) supported the potential of such biomaterial in assisting in the design of more effective and efficient photobioreactors for biohydrogen synthesis. Following the discussions put forward by Gokfiliz and Karapinar (2017) and Ma et al. (2017) in regards to the influence a specific type of support material can exert on the kinetics of hydrogen synthesis, the optimization of the specific process parameters in relation to the type of biomass used and the interaction of the physical process conditions is then needed. As a consequence, further research will be needed before a unified design approach may be formulated for the use of such biomaterial supports in photo-mediated biochemical reactions for hydrogen synthesis.

## 3. Novel reactor configurations

The type of reactor and its configuration are also closely linked to and influence the hydrogen generation process (Mudhoo et al., 2011; Kumar et al., 2015a; Kadier et al., 2016). Accordingly, many workers have been studying innovative experimental bioreactor

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