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.

Key words: biomass; hydrogen; green chemistry; novel microbial strains; immobilization; nanocatalysis

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 (Kao et al., 2016), 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 ± 12.39 mL hydrogen/g $COD_{removed}$ 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_2-SiO_2-Chitosan-Medium-LaB_6) 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 et al. (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., 2015; Kadier et al., 2016). Accordingly, many workers have been studying innovative experimental bioreactor designs and configurations in view to optimize the biomass-to-hydrogen conversion processes and obtain

better hydrogen production rates and yields. We revisit here some of the recent findings in this aspect of biomass-to-hydrogen production, and highlight the process and operation-related aspects which endow the novel reactor configurations with better performances.

Khan and Kana (2016) demonstrated that designing a novel reactor design is important in providing the efficient mass transfer and improving the hydrogen yield via dark fermentation process. In their study, they have designed a novel baffled design bioreactor with a supporting matrix for cell immobilization using a 3-D filament polylactic acid compound. Here, a stainless steel stand with a mounting angle of 180◦ was designed to provide a sufficient mixing of the bioreactor by increasing the turbulence thereby enhancing the interaction between the immobilized cells and the liquid medium. The hydrogen production performances were then assessed between the standard flask fermentation and novel immobilized cells system and showed an increment in hydrogen yield of 31% when compared to the control standard flask fermentation. In the work of Khan and Kana (2016), the improved performances are achieved by the effective catabolism of glucose and a reduction of the lag phase period. Besides, the formation of a biofilm layer on the surface of the cartridge wall and the observance of rod shaped microorganisms was noticed in this work. In addition, the COD removal efficiency also comparatively better than the shake flash reactor and demonstrated that the designing a novel reactor is important for achieving the stable hydrogen production performances and nutrient removal from the wastewater. del Pilar Rojas et al. (2016) reported the ethanol-type hydrogen fermentation in a novel anaerobic down-flow structured bed reactor (ADSBR) via controlling the operational parameter of organic loading rate for enhancing the hydrogen production performances. Their results demonstrated that the gradual increase in the specific organic loading rate improves the hydrogen production process and microbial attachment into the reactor compartments. Furthermore, the microbial community analysis in this work demonstrated that the presence of active hydrogen and ethanol producing microbes and the major energy production achieved via hydrogen and ethanol production. Ri et al. (2017) designed a novel lab scale horizontal type continuous stirred-tank reactor for efficient separation of gas-solid-liquid, suitable for operation at a low agitation speed. The results obtained from this study showed that operating a novel CSTR with a low agitation speed of 40-50 rpm provided the stable biogas and hydrogen yield from the process. Besides, the agitation speed controlled by computational stimulation process provided the better biomonitoring and kinetic control for stable hydrogen production for scale-up of the process. Bakonyi et al. (2017) integrated the novel gaseous separation membrane with CSTR reactor to intensify the biohydrogen production process. The process used the produced biogas separated via gaseous membrane and sparged into the reactor with a concentrated fraction of CO_2 and H_2 to test its

intensification process. The results showed that sparging the concentrated H_2-sparging negatively affected the hydrogen production, whereas sparging with CO_2 enhanced the hydrogen production rate and it could be viable process for enhancing the hydrogen production. Zhang et al. (2018) tested s combined dark fermentation and photo fermentation process in a pilot scale reactor using the left over corn stover as a feedstock. The integrated process provided a maximum volumetric biogas rate of 87.8 m^3/d with an average H_2 content of 68%. Despite the major variations in terms of biohydrogen production were noticed between the compartments due to the insufficient mixing and this research direction could be further explored for the real time industrial scale applications.

Palomo-Briones et al. (2017) assessed the impact of hydraulic retention time on metabolism and microbial structural changes during a CSTR operation and their outcomes showed that operating a short hydraulic retention time of six hours favored the hydrogen production reactions with the presence of interactive hydrogen producing microbial communities of *Clostridiaceae-Lachnospiraceae-Enterobacteriaceae*, whereas at long HRT the shift of the active hydrogen producing metabolism to lactate fermentation with the observance of *Sporolactobacillaceae-Streptococcaceae.* Elreedy et al. (2016) tested the production of various biofuels from petrochemical wastewater via anaerobic packed bed baffled reactor and showed that anaerobic degradation pathway is directly dependent on the applied organic loading rate. They inferred that operating a low hydraulic retention time of 9 hours favored the hydrogen and ethanol production, whereas the long hydraulic retention time of 27 hours favored the methane production and the developed process could provide a net annual profit over 40% than the traditional single anaerobic bed reactor. Muri et al. (2018) investigated three types of supporting materials for the enhancement of biohydrogen production in an anaerobic packed-bed reactor (APBR) and demonstrated that choice of supporting materials influenced the microbial attachment, distribution of microbial byproducts and biohydrogen production performances. In another report, Anzola-Rojas and Zaiat (2016) tested three different carrier materials with the ADSBR and showed that the biomass carrier with plastic support of polyethylene and polyurethane foam provided better biohydrogen production performances. Although the ceramic matrix provided a higher biomass loading in this work, the hydrogen production was hindered due to the limited flow pattern and inefficient mixing inside the reactor.

Blanco et al. (2017) have developed an anaerobic structured-bed reactor which has shown high capability to produce hydrogen despite some process drawbacks were noted with regards to biomass washout. Besides other interesting findings, Blanco et al. (2017) highlighted that

accumulation of biomass had not significantly affected the average residence time of the novel reactor configuration and this had contributed positively to its improved solids retention capability and overall robustness. Fu et al. (2017) have also designed a new biofilm photobioreactor incorporating a light guide plate serving the purpose of a light guider and support for the microbial biofilm. Fu et al. (2017) tested a number of process optimization scenarios and concluded that a SiO_2-chitosan-medium modified light guide plate was more conducive for the formation of microbial biofilms and as a result their novel bioreactor embodies significant capabilities for enhancing biohydrogen synthesis. Wu et al. (2017) explored the performance of photo-fermentative biohydrogen generating system through the formation of microbial biofilms on the surface of cell carrier in the biofilm reactor. Their results demonstrated that biohydrogen synthesis and substrate utilization efficiency (which increased from 36% to reach 63%) have been considerably enhanced in this specific bioreactor configuration.

4. Novel microbial strains

There is a very wide spectrum of hydrogen-synthesizing microorganisms which have been assessed for hydrogen production. These microorganisms can be broadly categorized as strict and facultative anaerobes, photosynthetic bacteria, aerobes and photoautotrophic (Kaushik and Sharma, 2016). With time and research, the possibility for isolation of novel strains of bacteria (Azman et al., 2016a,b) and fungal species which can give relatively very high cellulase or hemicellulase turnovers is now also being seen to hold the potential to become one of the drivers in biomass-based hydrogen synthesis. A review of the literature in this specific aspect of hydrogen synthesis using fermentation indicates that there are many research efforts being done to isolate those microbial strains which have superior potency to mediate biochemical reactions which give higher hydrogen generation rates and yields (**Table 1**). *Escherichia coli* (Taifor et al., 2017), *Rhodopseudomonas palustris*, *Clostridium butyricum* (Kao et al., 2016), *Clostridium beijerinskii* (Zagrodnik and Laniecki, 2016), *Rhodobacter sphaeroides* (Hay et al., 2016), *Thermoanaerobacterium* sp. strain PSU-2 (Sompong et al., 2017), *Streptomyces rubiginosus* (SM16) (Sivarajan et al., 2017), *Bacillus licheniformis* AP1 (Srivastava et al., 2017), *Enterobacter aerogenes* (Ramprakash and Muthukumar, 2016) and *Clostridium pasteurianum* (Hsieh et al., 2016) are some of these novel strains which have shown enhanced abilities to use biomass for hydrogen synthesis. Hence, a *sine qua non* condition for the development of fermentative biohydrogen production using the different biomass types resides in the judicious choice (Trchounian et al., 2017) of such bacterial strains which will sustain the biochemical reactions effectively. According to Trchounian et al. (2017), the activities of [Mo]-nitrogenase

and [Ni-Fe]-hydrogenase and [Ni-Fe]-hydrogenases of the photo-fermentative and dark-fermentative bacteria, respectively, have important roles on the kinetics of hydrogen synthesis from biomass sources which have variable carbon contents when used in pure, mixed and co-culture microbial systems. Indeed, a reasonable part of the work of Abreu et al. (2016), Patel et al. (2014) and Sivagurunathan et al. (2014) support the views of Trchounian et al. (2017). Abreu et al. (2016) had studied a two-step coupled dark fermentation and anaerobic digestion route for the production of biohythane (i.e. a mix of methane and hydrogen) using garden waste and reported that the co-culture of *Thermotoga maritima* and *Caldicellulosiruptor saccharolyticus* had given biohydrogen generation yields from cellobiose and xylose, and these yields were higher than those obtained with single microbial cultures. All the more, in this same study, a co-culture of *Caldicellulosiruptor bescii* and *C. saccharolyticus* gave an even higher biohydrogen yield in comparison with the corresponding pure cultures and co-culture of *C. saccharolyticus* and *T. maritima*. Patel et al. (2014) had studied eleven co-cultures consisting of two to four strains, and observed that the synergistic effects of co-cultures consisting of *Enterobacter cloacae* HPC123, *Bacillus cereus* EGU43 and *Klebsiella* sp. HPC793 had produced biohydrogen yields reaching 3.0 moles hydrogen for every gram of glucose. These workers equally noted that co-cultures of *E. cloacae* HPC123 and *B. cereus* EGU43 had allowed for a continuous generation of biohydrogen and had also performed significantly well in achieving enhancement in yields by a factor of 6 in comparison to free bacteria. In their work, Sivagurunathan et al. (2014) reported that the main biohydrogen-synthesizing bacterial strains detected in all the mixed cultures of pig slurry, sewage sludge and cow dung under study were *Clostridium saccharobutylicum, C. butyricum, C. perfringens, C. tertium*. In this same work, the latter strains had offered a new approach to improve hydrogen yields from industrial effluents when used in a mixed-culture utilization scheme.

Progress in the development of new hydrogen-producing strains is indeed providing a potential new direction in the formulation of more economic, process-intensive and efficient hydrogen synthetic routes from biomass. However, the isolation, identification, versatility and detailed assessment of these new microbial species in more reaction milieu with various biomass types will demand more research efforts before afully workable biochemical 'recipe' is obtained. Such a versatile biochemical method for harnessing a wide variety of biomass for biohydrogen production can be essentially based on dark fermentation schemes (Vésteinsdóttir et al., 2011). There are a number of works which indicate the potential for development of the latter schemes. For example, Patel et al. (2015) have reported that *Clostridium* sp. IODB-O3 was able to utilize wheat straw prehydrolysate for biohydrogen generation and could become one of the components of an economic method for sustainable biohydrogen generation. Tian et al. (2015)

also reported that *Clostridium thermocellum* ATCC 27405 was capable of degrading sugarcane bagasse to produce biohydrogen, and that the overall process had been significantly enhanced with calcium carbonate supplements. According to the findings of Tian et al. (2015), the buffering of the carbonate was stimulatory, and its inclusion in biohydrogen production schemes would present a fresh and effective approach for biohydrogen generation from lignocellulosics. Yin and Wang (2016) have isolated a new biohydrogen-synthesizing strain from gamma irradiated sludge, and this novel strain was found to be *Enterococcus faecium* INET2. Yin and Wang (2016) reported that this new strain, when immobilized on polyvinyl alcohol-Na alginate, gave good hydrogen generation performance at 35 °C in a medium with a starting pH of 7 with a substrate concentration of 15 g/L glucose and at 0.1 inoculation ratio. In this specific work, it was found that *E. faecium* INET2 had a peak cumulative hydrogen generation of 0.13 L hydrogen/100 mL and a hydrogen yield of 1.16 mol hydrogen for every mole of glucose when using free cells, and these gas production performances increased by 55.38% and 45.69%, respectively, when using immobilized cells. The work of Yin and Wang (2016) hence indicated that *E. faecium* INET2 holds high promise for biohydrogen synthesis from glucose during fermentative processes. Wu et al. (2017) have used *Enterobacter* sp. CN1 for the production of biohydrogen from galactose-containing biomass. Wu et al. (2017) recorded the maximum biohydrogen yield at 303.2 mL hydrogen for every gram of substrate at a pH of 7.3 and 36 °C. Wu et al. (2017) further explored the performance of this strain in producing biohydrogen using the agar hydrolysate obtained after a saccharification procedure by agarase and neoagarobiose hydrolase. They reported that the combination of the fermentative reactions and enzymatic saccharification gave biohydrogen production rates as high as 5047±228 mL/L when using 50 g/L of agar, and this performance was significantly greater by a factor of 3.86 in contrast with the control runs.

Kumar et al. (2017) reported that the genus *Clostridium* was successful in producing biohydrogen from acid pretreated de-oiled jatropha waste-derived hydrolysate to the tune of 900 ml/l.day and 86 mL hydrogen/g of reducing sugars added for the peak biohydrogen generation rate and hydrogen yield, respectively. Additionally, Kumar et al. (2017) reported that the immobilized *Clostridium* had had very good stability up to ten cycles. Srivastava et al. (2017) have equally demonstrated that *Clostridium pasteurianum* (MTCC116) could effectively produce biohydrogen from enzyme hydrolyzed rice straw by dark fermentative pathways with a cumulative biohydrogen of 2.58L/L in 144 hours at a peak maximum generation rate of 23.96 ml/L.h in 96 hours. Pang et al. (2017) investigated the feasibility of using new cellulolytic bacterial isolates from bovine rumen in producing biofuel molecules from lignocellulosic biomass, and concluded that these new microbial species (*Escherichia coli*) could

indeed yield up to 4.71 mL/g biohydrogen from corn straw and produce concomitant biodegradation of cellulose and hemicellulose. Poladyan et al. (2017) have concluded that their findings could be much relevant and valuable in the biohydrogen synthesis biotechnology when using a variety of organic substrates derived from wastes feedstocks. The key advance of the work of Poladyan et al. (2017) resided in the formulation of "*E. coli BW25113 wild type strain and hydrogenase (Hyd)-negative mutants*" with gene deletion of those genes which encoded the main subunits of "*Hyd 1–4 (ΔhyaB, ΔhybC, ΔhycE, ΔhyfG)*)", and equally for a "*ΔhyaB ΔhybC double mutant*". Zhao et al. (2017) have studied mycelia pellets as potential biological carrier during the biohydrogen production process from cornstalk hydrolysate, and based on their results and observations, they inferred that mycelia pellets embodied such characteristics which make them ideal biological carriers having the ability to enhance biomass retention in the bioreactors for boosting biohydrogen recovery from lignocellulosic substrates.

TABLE 1 is here

5.0 Integrated fermentative schemes

The integrated fermentative biohydrogen generation approach has been studied in different stages of the photo-fermentative and dark fermentative processes (Ghosh et al., 2018). Some workers have coupled dark fermentation with biocatalysed electrolytic processes for hydrogen production from process residues (Moreno et al., 2015; Dhar et al., 2015; Marone et al., 2017) whereas others have investigated the performance of combined fermentation and heterogeneous catalysis (for example, Wimonsong et al. (2014) and Güell et al. (2015)). Results from studies where sequential dark fermentation and photo-fermentation of biomass have been employed demonstrate the merits of this type of combined operational procedure in terms of the enhanced biohydrogen kinetics. Furthermore, it is observed that the integration of the matching capabilities of bacterial species mediating photo-fermentation and dark fermentation is gradually gathering interest and proving to be a potential route to recover bioenergy with high turnovers, better substrate and energy conversion efficiencies from different types of biomass.

Indeed, Chaubey et al. (2013) have argued that such hybrid biohydrogen production schemes hold very high potentials since they exhaust the bioavailable organic matter to the furthest extent and approach complete conversions. Hitit et al. (2017) have indicated that two-stage systems involving sequential dark and photo-fermentation will allow the optimization and control of microbial culture conditions to be effected separately. Tao et al. (2007) reported that

the combined dark fermentation and photo-fermentation of sucrose gave higher biohydrogen yield. Chen et al. (2008) employed a hybrid dark/photo-fermentation process and demonstrated increased biohydrogen yield which reached 10.02 moles hydrogen for every mole of sucrose. Su et al. (2009) observed a significant increase in biohydrogen yield by a factor of 3.447 from 1.59 moles H_2 per mole. In their work, Zhang et al. (2017b) concluded that a production scheme combining photo-fermentation and dark fermentation had considerably improved the overall energy conversion efficiencies of anaerobic biological treatment plants. When investigating the two-stage dark fermentation and photo-fermentation process of a starch/glucose substrate which was metabolized by *Rhodopseudomonas palustris* and *Clostridium butyricum*, Hitit et al. (2017) reported relatively very high biohydrogen generation and biohydrogen photofermentation yields. Mishra et al. (2016) had studied the biohydrogen generation in a two-stage sequential dark fermentation and photo fermentation process using palm oil mill effluent fermentation under the action of *Clostridium butyricum* LS2 in the first stage and then by *Rhodopseudomonas palustris*. From this work, Mishra et al. (2016) reported that the two-stage fermentation had significantly augmented the total biohydrogen yield from 0.784 ml hydrogen/ml of the effluent obtained during the single stage of dark fermentation to 3.064 ml hydrogen/ml effluent recorded for the dark fermentation-photo-fermentation process.

Chandra et al. (2015) studied a single-stage hybrid system consisting of dark fermentation and photo-fermentation parts and reported that their system had aided in the reaching greater biohydrogen generation with a real distillery wastewater than with dairy waste. One of the crucial inferences from this work and many others where integrated dark and photo-fermentation systems have been used to harness biomass types for biohydrogen is that these systems will give useful data for planning the design and assessment of full scale continuous and cost effective integrated dark-fermentation and photo-fermentation systems. Based on their results, Liu et al. (2015a) have further indicated that their combined integrated dark fermentation and photo-fermentative reactor was both capable of dodging the complex pretreatment steps normally needed in two-stages processes, and also in circumventing the imbalance of bacterial growth and microbial metabolic rate which exists between dark fermentative bacteria and photo-fermentative bacteria. Although there are a number of reports which advocate the complementary merits of integrated photo-fermentation and dark fermentation systems, these integrated biomass processing configurations still have to be optimized, firstly, for a continuous availability and utilization of bioavailable substrates, and secondly, for a more effective control of bacterial successions and pH variations.

6. Green biomass pretreatment schemes

Indeed, the significance of the type(s) of biomass being processed via a specific biohydrogen production route and the specific reaction conditions imposed are high since there are different effects on the whole process of biohydrogen synthesis (**Table 1**). In point of fact, several research efforts and findings have demonstrated that when lignocellulosic biomass materials are assessed for their individual biohydrogen production potential, there is practically always the need to perform some singular or combined type of biological, chemical or physical pretreatment (Nguyen et al., 2010; Al Shorgani et al., 2014; Diaz et al., 2015; Ibrahim et al., 2015; Gonzales et al., 2016; Abdul et al., 2016; Sen et al., 2016; Senturk and Buyukgungor, 2017; Eskicioglu et al., 2017; Rafieenia et al., 2017). Hence, by reason of the very complexity, variations in chemical properties and structural morphologies of the different biomass types, imposing some form of pretreatment on the biomass has become extremely important before the optimum kinetics of the intended downstream processing (Ding et al., 2016; Singhal and Singh, 2014).

Of the several pretreatment approaches reported so far in the literature, the feasibility of selecting one single or a mix of pretreatment routes for process intensification and thereafter scale-up seems much to depend on the energy requirements, cost factors and chemoselectivity of the pretreatment effects on hemicellulose, holocelluloses (Monlau et al., 2013) and lignin. In this line of research thinking, and notwithstanding the valuable pool of findings which have been accumulated so far on the pretreatment techniques studied in terms of their merits and demerits which can be reasonably addressed, the trend in the specific field of research and development in biohydrogen production from biomass has been to explore combined physicochemical pretreatment schemes which have a strong connection with the 'green chemistry' elements. This is because there has been a start in the use of microwave-assisted, ultrasound-assisted (Budiman et al., 2017a) and ionic-liquid mediated pretreatments techniques of biomass. So far, the results are in general promising. The key issues which seem to motivate more research in this new branch of biomass pretreatment are the cost factors and process scale-up issues.

Microwave-irradiation assisted biomass pretreatment successfully addresses the issues related to low heating rate and overall thermal efficiency of the process (Merino-Pérez et al., 2015; Li et al., 2016) and anisotropic heating effects, but it concomitantly faces some basic drawbacks related to reactor vessel configuration, sequencing of pretreatment steps and costs. As of date, many of the works completed in the use of microwave irradiation advocate the positive impacts

of microwave heating as a biomass pretreatment technique both at the laboratory scale and pilot-scale. Lin et al. (2015a) reported that microwave-alkali pretreatment had deconstructed the lignocellulose network in water hyacinth, brought about visible swelling of the surfaces and reduced the crystallinity index by 3.0 from 16.0 as a result of cellulose being rendered amorphous. Li et al. (2014a) studied the combined microwave-alkali pretreatment of cornstalk and observed that the disruption of lignin and a subsequent rise in the extent of solubilization made more organic matter available to *Clostridium thermosaccharolyticum* and *Clostridium thermocellum*. The biohydrogen yield achieved was 105.61 mL/g of cornstalk for the following pretreatment conditions: 45 minutes treatment with of 0.12 sodium hydroxide/g of cornstalk, a solid to liquid ratio of 0.02 (g/mL) and a flow rate of 60 mL/s. Li et al. (2014a) found that the hydrogen yield with this pretreatment was 54.8% greater than that with untreated cornstalk, and the corresponding cellulose and hemicellulose degradations rose significantly from about 71.28% and 41%–79.55%, respectively.

One more green form of irradiation which has been continually getting attention in biomass pretreatment for its main advantages in improving the process dynamics is ultrasound irradiation (i.e. sonication). Sonication operates on the heating effects brought about by the cavitational formation, growth and eventually very drastic collapse dynamics of bubbles which induce very strong shear forces and the production of free radicals which significantly aid in the lysis of cell walls and increase the extents of organic matter solubilization (Bundhoo, 2017). As a result of the more pronounced solubilization of organic matter of biomass, fermentative pathways have given better biohydrogen production rates and yields. Martinez-Jimenez et al. (2017) reported that the major positive impact of sonication pretreatment had been on the composition of methane, carbon dioxide and hydrogen when studying the thermophilic anaerobic digestion of sugar production organic residues. Budiman et al. (2017b) have studied the effect of a single cycle sonication pretreatment of *Rhodobacter sphaeroides* on the photo-fermentative biohydrogen synthesis when using different industrial effluents with organic matter contents. As one of their key findings, Budiman et al. (2017b) reported that moderate ultrasonication at a specific energy of 256.33 J/mL had produced the greatest biohydrogen yield amounting to 9.982 mL hydrogen in every millilitre of the medium for a 5.125% light efficiency.

The use of ionic liquids in the biomass pretreatment field is a relatively new area of research and there are relatively few studies which report the different aspects of their performance and mechanisms of pretreatment potential. Ionic liquids are in essence organic salts made up of ions existing in the liquid state and have very low vapour pressures. Ionic liquids have been indeed

gaining much attention in the pretreatment of lignocellulosic biomass for a number of green traits and benign characteristics. The impacts of ionic liquids in the pretreatment of biomass have been the swelling of cellular walls, the dismantling effect in the interactions mediated by hydrogen bonding, and finally a decrease in the cellulosic crystallinity. A survey of the literature shows that ionic liquids are particularly effective in bringing about an appreciable extent of delignification for a very large number of biomass types, and the reactions are relatively moderate to mild in their requirements for time of reaction, temperature and suitability of the handling equipment, as well as an advantageous compatibility with microorganisms needed in the downstream processing steps. Moreover, ionic liquid have equally been observed to be amenable to embody a number of desirable process-specific biological and physicochemical properties, and then also equally benefit from reuse opportunities. Ionic liquids such as imidazolium-based ionic liquids (Socha et al., 2014), 1-(4-sulfobutyl)-3-methylmidazolium hydrogensulfate (Lu et al., 2015), N-methylmorpholine-N-oxide (Cheng et al., 2017) and [Bmim]Oac (Li et al., 2018) have been particularly effective in assisting the fast saccharification of hemicellulose and cellulose (Xia et al., 2014), but their use at larger scales of production faces economic constraints, issues related to recyclability and biomass quality and variability of biomass properties (Perez-Pimienta et al., 2017). Perez-Pimienta et al. (2017) indicated that ionic liquids are well suited for biomass pretreatment because they can improve the access of enzymes to bioavailable matter by decreasing cellulose crystallinity and eliminating lignin. In their work, Xia et al. (2014) attributed, though with some reservation, the pretreatment efficiency of the ionic liquids they used (especially 1-butyl-3-methylimidazolium methanesulfonate ([BMIM][MeSO$_3$]) aqueous solutions) to the H-bond basicity of the anionic component and ionic liquid polarity.

7. Inhibitor effects and detoxification

Whilst most of the pretreatments routes are a mix of enzymatic, chemical, acid/base and other emerging techniques falling under the umbrella of green chemistry and have been mostly effective in bringing improvements in biomass-based hydrogen production performance, these pretreatments are much comparable for their cost-effectiveness with respect to energy production intensity, and have also been found to suffer from severe inhibitor formation, which then impede the overall process efficiency. A survey of the literature shows that the levels and partitioning of the inhibitors is influenced by a number of factors. These factors include the actual type(s) and combinations of pretreatments and the stringency of the pretreatment conditions, and the variability in chemical composition of the biomass types being pretreated. The principle mechanism of inhibition on the hydrogen synthesizing anaerobic microbial species equally appears to consist in unionized configurations of weak acids permeating

through the microbial cell walls and reducing the pH within the cells and finally inducing unfavourable conditions for hydrogen synthesis. Moreover, a close inspection of the relevant literature on hydrogen production under inhibitory conditions shows that phenolic species and furan derivatives are the most damaging inhibitors. The main inhibitors are furfural and 5-hydroxymethylfurfural which are synthesized from C_5 and C_6 sugars present in the cellulose and hemicellulose portions, methanoic acid, acetic acid, levulinic acid and a variety of phenolic moieties and aldehydes. These inhibitors have been reported to severely induce unfavourable effects on the overall kinetics of microbial fermentative processes through decreases in the growth rates of cells, reductions in the permeability of the cell membranes and enhanced formation of oxygen species which are reactive (Koopman et al., 2010; Quéméneur et al., 2012; Cantarella et al., 2004; Allen et al., 2010). It has also been found that the levels of some of these inhibitors depend on the strains of the microorganisms seeded for mediating the hydrogen biochemical reactions to occur (Gao et al., 2010; Liu et al., 2015b; Barakat et al., 2015; Lin et al., 2016a; Akobi et al., 2016). When studying the generation dynamics of biohydrogen from glucose in continuous system, Haroun et al. (2016) have found that the initial biohydrogen yield of 2.27 mol H_2/mol glucose rose by 6% and 17% for furfural levels of 0.5g/L and 0.25, respectively, but then experienced a decline by 62%, 29% and 21% for furfural concentrations of 4 g/L, 2 g/L and 1 g/L, respectively. Akobi et al. (2016) equally evaluated the effects of furfural on the biohydrogen generation rates and yields in batch operated systems using synthetic substrates made up of lignocellulosic hydrolysate. The interesting finding of Akobi et al. (2016) was that for furfural concentrations reaching up to 1 g/L, an improvement in biohydrogen generation was recorded with yields being higher by 19% with respect to the control systems.

The core aim of detoxification methods resides in segregating the non-sugar molecules from the pretreatment hydrolysates with a minimum possible loss of the fermentable sugars (Deng and Aita, 2018). Various detoxification approaches which include biological and physicochemical methods have been assessed and these have consisted in techniques based on flocculation, evaporation, adsorption using activated carbon, overliming, use of laccases and ion exchange resins (Moreno et al., 2012; Carter et al., 2011; Mateo et al., 2013; Lee et al., 2011; Vallejos et al., 2016; Den and Aita, 2018). In view to curb the severe impacts of furfural and 5-hydroxymethylfurfural on the overall biohydrogen production performance, a number of studies have been conducted in this specific branch of research, and a few have shown interesting promise. Kumar et al. (2015) reported that only 5-hydroxymethylfurfural (5-HMF) could be removed from red algal hydrolysate which had been pretreated with dilute sulphuric acid using hybrid immobilized cells but the whole process was accompanied by a net decrease

in the biohydrogen generation dynamics. Vedrenne et al. (2015) have studied the effects of photo-Fenton on the extent of furfural detoxification during the pretreatment involving corncob prehydrolyzates, and found that an optimal dose of peroxide-to-iron in the ratio 112 had produced a final furfural concentration of 0.35±0.23 g/L whereas the levels of xylose and mannose was decreased to 4.00±0.29 g/L. Vedrenne et al. (2015) concluded that photo-Fenton reactions for effecting the detoxification pretreatment of prehydrolyzates needed sufficient dose which could eventually minimize chemical use and equally aid in the degradation of mannose and xylose, and all the same ensuring adequate biological compatibility with the strain of microorganisms being used for mediating the biochemical biohydrogen-producing reactions. Lin et al. (2015b) have assessed the use of sodium borohydride in its ability to detoxify aldehydes inhibitors during biohydrogen generation in fermentation reactions. They reported relatively very high extents of detoxification of furfural and 5-hydroxymethylfurfural with 30 mmol/L sodium borohydride to the tune of 96.7% and 91.7%, respectively. Lin et al. (2015b) also observed that the sodium borohydride had brought about adequate reduction potential for the reduction of the aldehyde inhibitors. The key outcome from this promising work was that there had been a notable recovery in the yields of biohydrogen yield at 99.3% and 64.6% recovery of the maximum biohydrogen generation rate. Lin et al. (2017) have developed a novel and very effective approach for producing biohydrogen from real textile desizing effluents. Their method consisted in conducting a coagulation-pretreatment and it led not only to significantly enhanced biohydrogen generation (3.9 L hydrogen/L.day and biohydrogen yield reaching up to 1.52 mol hydrogen/mol hexose) but also followed much seemingly the butyrate-type fermentative pathways and assisted in the removal of some toxic moieties which would otherwise have inhibited the overall process performance. Yee et al. (2018) reported the ability of recombinant manganese peroxidase synthesized from *Pichia pastoris* in degrading furfural and HMF. Yee et al. (2018) found that recombinant manganese peroxidase had reduced the furfural and HMF levels and that the extent of degradation was dependent on the dose of the recombinant manganese peroxidase added. Growth assays performed by Yee et al. (2018) using *Saccharomyces cerevisiae* demonstrated that recombinant manganese peroxidase had decreased the toxic and inhibitory characteristics of furfural and HMF, and as a result these outcomes could be harnessed for optimizing the growth patterns and kinetics of microorganisms during fermentative processes involving biomass.

8. Subcritical and supercritical water processing

Hydrothermal technologies are defined as the transformation and/or conversion of biomass using water at high temperature and pressure (Peterson et al., 2008). The application of water

as a non-toxic, non-flammable solvent is favourable over conventional processes in being a promising and green alternative for biomass (Déniel et al., 2016) since it does not generate effluents that need treatment. Water as a reaction medium, in a subcritical and supercritical state, is an efficient reaction medium for the production of chemical products, biofuels and the generation of gases such as hydrogen (Yanik et al., 2007). The water in subcritical state is at a temperature range of 100 to 374 °C using pressures higher than the vapor pressure avoiding the phase change. In turn, under supercritical conditions, the temperature conditions are higher than those of its critical point (critical temperature of 374.15 °C and 22.1 MPa) (Lachos-Perez et al., 2017; Mayanga-Torres et al., 2017). Under these conditions, water is a highly reactive solvent, and this is due to such interesting changes in its properties (namely density, dielectric constant, ionization constant and viscosity) due to the progressive increase in temperature and pressure (Brunner, 2009; Kruse and Dahmen, 2015; Kruse and Dinjus, 2007; Möller et al., 2011; Yu et al., 2007) which are appropriate for effective hydrothermal biomass processing.

In subcritical conditions water is an excellent medium for ionic type reactions that favour the depolymerization and hydrolysis of biomass (cellulose, hemicellulose and lignin) resulting in the production of low formulaic molecular mass organic species (e.g. sugars, furanic aldehydes and acids organic) (Reddy et al., 2014; Sasaki et al., 1998; Watchararuji et al., 2008). In the supercritical state, the conversion of organic products into gases is favoured by means of free-radical type reactions which are very important for the production of hydrogen through the gasification process (Kruse and Dinjus, 2007). This occurs because in normal conditions of temperature the water presents hydrogen bonds very well grouped, which in the supercritical state break, reducing the value of its dielectric constant. The high diffusivity improves the transfer of mass in the process of gasification in conditions existing in supercritical water, and can easily be accessed through the porosity of the biomass, allowing quick reaction time in the gasification process (Guo et al., 2015). The gasification of model molecules namely glucose and cellulose in supercritical water provides information of the reaction mechanisms through a series of complex chemical reactions that react with each other. This gives a deeper insight in view of the conversion of the real biomass (Behnia et al., 2016; Correa and Kruse, 2018). But, the use of complex biomass types, and the interactions amongst their different components are usually different because the variable operating conditions of the process such as pressure (Safari et al., 2018), temperature (Amrullah and Matsumura, 2018; Safari et al., 2018), type of cooling regime (Zhang and Zhang, 2017), residence time (Safari et al., 2018), catalyst (Rana et al., 2018) and concentration can alter the composition of the gas and lead to the formation of solids (Calzavara et al., 2005; Yanik et al., 2007).

Moreover, in the subcritical/supercritical state, the polymerization and consequently hydrolysis of the lignocellulosic material generates monomers namely pentose (C_5) and hexoses (C_6), and the lignin is degraded in its respective phenolic compounds and acidic compounds that are formed in parallel by the thermal effect (Prado et al., 2014; Sasaki et al., 1998). The transformation of the biomass for bio-hydrogen has been studied applying different operational conditions, but it is known that the application of high temperature favors the hydrogen yield (Kruse and Dahmen, 2015) in the gasification process with supercritical water. In the gasification process with supercritical water, the sugars and water-soluble materials are converted into gases, whose majority composition is in hydrogen. Some research findings such as those from Guan et al. (2014) and Molino et al. (2017) suggest using metal-based catalysts to improve the hydrogen generation yields using average temperatures during the gasification process. The advantage of supercritical water gasification is that the reactions that are developed favour the production of a hydrogen-rich gas (Behnia et al., 2016; Castello et al., 2013; Guo et al., 2010; Kruse, 2008; Molino et al., 2014; Zhang et al., 2011). The reaction mechanism for the generation of hydrogen using water as a reaction medium or reactant is developed in part by steam reforming (Equation 1) and vapour-water displacement (Equation 2):

$$CH_4 + H_2O \rightarrow H_2 + CO \qquad \text{(Equation 1)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(Equation 2)}$$
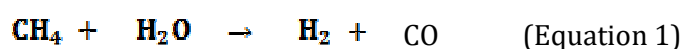
It verifies that the consumption of water is essential at high temperatures, thus minimizing energy costs in additional processes such as drying (Reddy et al., 2014; Zhang et al., 2011). Excess water as a reaction agent in combination with carbon monoxide, are responsible for half the hydrogen formed in the synthesis gas (H_2 and CO_2) produced at temperatures equal to or less than 500 °C and reducing the carbon monoxide content with the use of catalysts leads to an increase in the production of hydrogen (Equation 2) (Yanik et al., 2007).

Different types of interesting investigations have been based on supercritical water gasification studies in the last five years using different reaction conditions and the results on the hydrogen production hold out good promise for proceeding to the next sequel of scaling-up the processes for further optimization of the core green chemical engineering process metrics which are renewability, recyclability, scalability, robustness, controllability and clean-up. Hence, the application of supercritical water technology for the conversion of biomass into hydrogen guarantees the development of sustainable energy and its use becomes more competitive for the production of biofuels. To this is the added advantage of an efficient use of catalysts in

supercritical water to increase the conversion of biomass into soluble polar organic compounds which in the supercritical state result in high yields of synthesis gas at moderate temperatures (Azadi and Farnood, 2011; Dimitriadis and Bezergianni, 2017; Peng et al., 2017; Safari et al., 2018; Yanik et al., 2007). A proposal that is advantageous for the process of gasification in supercritical water is the generation of two phases which originate as a result of the depressurization of the system (a synthesis gas phase and an aqueous phase with the polar organic compounds that were not gasified). The synthesis gas can be purified and hydrogen thus isolated for application in clean fuel cells, while the aqueous phase can be recirculated to the process for conversion to gas.

9. Metal-based nanoparticulate catalysis

The development of the processes which metabolize organic matter in the various biomass forms to produce biohydrogen has been continually advanced with better engineered catalytic transformations. The different techniques for catalyst synthesis and catalyst usage have all been geared towards improving the general and certain specific properties of the catalysts themselves, and as a result, enhancing the overall performance of the catalytic biomass conversion systems. Such enhancements in catalytic properties can be relatively well achieved by selecting and thereafter tailoring suitable combinations of metals, and any other green component(s) or conditions such as nanoparticles (**Table 2**), ionic liquids, zeolites and subcritical/supercritical conditions, respectively, as evidenced by many published data. For the sake of conciseness, this part of the review has revisited selected research articles and highlighted the key outcomes of studies addressing the issue of improvement in biohydrogen synthesis under catalytic conditions using nanoparticles.

Figure 1 depicts the main interactions and reactions mediated during the dark fermentative synthesis of hydrogen in the presence of metal based nanoparticles. Data in **Figure 1** show that nanoparticles (NPs) do not invigorate the enzymatic catalytic action of hydrogenase but instead indicates the potential enhancement brought about by NPs in the degradation process of the substrate (in this case, glucose). Here, it is assumed that electric streams could move throughout the metal NPs *via* conductivity effects, and thus accordingly interceding exchange of electrons in the periplasm. Step I involves the degradation of biomass-based carbohydrates to form pyruvate and this leads to the formation of acetyl-coA from the degradation by means of ferredoxin oxidoreductase (Fd_{ox}) in the cytoplasm where it is related to the function of reducing the surroundings. In Step II, there is a formation of iron-sulphur proteins namely ferredoxin

(Fd_{re}) occurring *via* ferredoxin oxidoreductase thereby occasioning the exchange of electrons to the hydrogenase from the NPs where Fd_{rd} is further reoxidized by the production of H_2 in the periplamic layer, it comprises Step III. As a result, Fd_{rd} mediates the electron transfer process, and NPs-Fe can upgrade the electron exchange between Fd_{rd} and hydrogenase and this enhances the productivity of biohydrogen (Hsieh et al., 2016).

TABLE 2 IS HERE

FIGURE 1 IS HERE

One advantage of the metal-based nanocatalysis in biohydrogen production from biomass is that the concomitant use of ionic liquid solvents ultimately increases the turnover number of the catalyst. Metal-based nanoparticulate components which have been adequately stabilized in solvents such as ionic liquids have proven to be interesting and chemically attractive catalysts for biomass conversions to various types of bioenergy, namely biomethane, bioethanol and biohydrogen. Cheng et al. (2017) have treated residues of cassava in N-methylmorpholine-N-oxide as the ionic liquid medium and reported an improved overall kinetics and a combined biohythane production with a net bioconversion which had escalated to 21.4–27.9%. In addition to other interesting results in this work, Cheng et al. (2017) also reported that the enzymolyzed cassava residues pretreated with N-methylmorpholine-N-oxide had produced biohydrogen with a yield which had escalated from 92.3 to 126 mL/g TVS. Taherdanak et al. (2016) compared the effects of Fe^0 and Ni^0 nanoparticles, Fe^{2+} and Ni^{2+} on H_2 production from dark fermentation of glucose and obtained higher H_2 yield for Ni^{2+} followed by Fe^0 nanoparticle, Fe^{2+} and Ni^0 nanoparticles. In fact, there are a few but initial successful studies which advocate the merits of nanocatalysis in biohydrogen production. They have adapted the selective H_2 producers to improve biohydrogen throughout the fermentative route. In addition, these NPs were effectual at some point in the biomass pretreatment and immobilization of the entire cells as well which were utilized. It has been found that the integration of dark-fermentation with photo fermentation is a more effectual for improving the development of economy. Seif et al. (2016) were compared the use of three catalysts namely MnO_2, CuO and Co_3O_4 on hydrothermal gasification of industrial wastewaters and stated that Co_3O_4 was the best, followed by CuO and MnO_2 catalysts for H_2 production. Li et al. (2014b) investigated the effects of Fe as catalyst for methane decomposition using three porous supports namely HBETA zeolite, HZSM-5 zeolite and Al_2O_3 and reported highest H_2 production with 20 wt% Fe using Al_2O_3 as support. Mostafa et al. (2016) reported that the addition of magnetite/graphene oxide (MGO) enhanced

biohydrogen production from dark fermentation of gelatinaceous wastewater and is due to change from the propionic metabolic pathway to the butyric reaction path. On the other hand, the conversion procedure of magnetite/graphene oxide nano composite is almost of the given dosage dependent. Le and Nitisoravut (2015) compared the use of different hydrotalcites and reported a maximum increase in bio-hydrogen production using Ni-Mg-Al hydrotalcite (HT). Likewise, Wimonsong et al. (2013) studied the influence of different hydrotalcites on biohydrogen generation and inferred that Mg-Al hydrotalcite gave the highest H_2 yield. However, the same authors later reported that Zn-Mg-Al hydrotalcite supported Au catalyst yield a higher amount of bio-hydrogen (Wimonsong et al., 2014).

The main attributes to the improvement in the yield of so catalyzed bioprocesses are the large surface-to-volume ratio of the nano-based catalysts, the superior hydrothermal resistance and stability of these types of catalysts and their related acidity control properties. An ability to control the acidity of the reaction medium would most reasonably enable a more robust control of the pH and buffering capacity of the biomass to bioenergy conversion process. A restricted number of previous work have demonstrated that the metal nanoparticulate components significantly determine the type of catalytic transformations whereas the subsequent use of the ionic liquid aids much in defining the active sites and porosity distributions within the catalysts and hence influencing the overall chemistry and surface reactivity of the metal-based nanoparticles. Lu et al. (2016) observed that the use of the electrocatalyst NiFe layered double hydroxide enhanced H_2 production rates and recovery from wastewater in microbial electrolysis cells. Wang et al. (2016) studied the effects of Ni/MgO catalyst on steam reforming of butanol and reported highest H_2 yield with $Ni0._{12}$/MgO. Lervolino et al. (2016) compared commercial TiO_2 with home-prepared TiO_2 both modified with Fe-Pt and reported a higher photocatalytic H_2 production with the home-prepared catalyst. Hsieh et al. (2016) found that Fe nanoparticles could enhance biohydrogen production while nanoTiO_2 addition had no significant effects on H_2 production. Jafari and Zilouei (2016) reported an enhancement in biohydrogen production of 127 % for bagasse pretreated with nanoTiO_2 (1 g/L), ultraviolet irradiation (120 min) followed by acid hydrolysis (30 min) as opposed to bagasse subjected to only acid hydrolysis (30 min). Dolly et al. (2015) also obtained enhanced biohydrogen production with Fe-nanoparticle as supplement. Similarly, the addition of γ-Fe_2O_3 nanoparticle was reported to have enhanced biohydrogen synthesis from glucose (Lin et al., 2016b). Zhao et al. (2011) compared ferrous ions with Fe_3O_4 nanoparticle for enhancing H_2 production and reported higher H_2 yield was higher with Fe_3O_4 nanoparticle. Similarly, Beckers et al. (2013) studied the effects of lead, silver, copper, palladium and iron oxide nanoparticles encapsulated

in porous SiO_2 (silica) and found that iron oxide nanoparticle exhibited the highest H_2 yield. Mullai et al. (2013) obtained an improvement in biohydrogen production by 22.7% by means of maximum H_2 production yield of 2.54 mol/mol glucose by anaerobic sludge with the addition of 5.7 mg/L Ni nanoparticles under the thermophilic condition (55 ^{o}C). One green trait with respect to the use of iron oxide NPs is that they can easily be removed and recycled as they have magnetic properties. At this time, the difference in the yields of H_2 production might be related to the variation in the structural composition of the feedstock.

10. Algae-based hydrogen production

Our survey also indicates that the bioconversion of algal biomass for hydrogen production is also an active area of biomass-to-bioenergy research. However, when compared to the other biomass-to-bioenergy systems such as biodiesel production, algae-based biomass-to-bioenergy transformation is not fully developed and much still remains to be worked on before it may be echeloned to viable full-scale implementation. Amongst the several important aspects and issues discussed by Show et al. (2018), the design and optimization of the most suitable bioreactor configuration(s), the control of light intensity from sunlight and the integration of beneficial transformations resulting from metabolic and genetic engineering in biomass conversion routes are key research areas which will assist in the development of mature algae-based hydrogen production systems. Kumar et al. (2016) have surveyed that very few studies have reported the use of mixed microbial cultures for the fermentation of microalgae when compared to the more frequent use of single cultures. Shobana et al. (2017) indicated one more research bottleneck in this specific area wherein the mechanisms of catalytic action of enzymes are yet to be fully spelt out, following which process optimization may here be undertaken. These latter workers also indicate that biohydrogen synthesis using microalgae by biophotolysis, photofermentation and microbial electrolysis schemes is outsmarted by dark fermentation. Shobana et al. (2017) have summarized the main merits of such systems and these are, inter alia, greater generation rates of biohydrogen, more concentrated but variable concentrations of carbohydrates, lipids and proteins in micro-algae and macro-algae, no requirement for land for cultivation, the possibility to utilize a variety of process effluents for growing the algae by harnessing the nutrient contents of these growth media, enhanced possibility to meet up with greenhouse gas emissions mitigation, possibility to produce by a series of side reactions many value-added chemicals which have significant economic value, and finally the versatility of algae-based biohydrogen production schemes in a very large number of countries. Besides the latter favourable traits of algal biomass for biohydrogen

production, Chen et al. (2016) have equally stressed that the absence of lignin in microalgal cellulose structures renders saccharification reactions of these biomass species significantly easier than would be the kinetics observed with lignocellulosic biomass.

11. Conclusions and Research Outlooks

To conclude, there is definitely an extensive panoply of research work being conducted worldwide in pursuit to study and refine the biomass-to-hydrogen production processes. As a result, hydrogen produced from biomass places itself as a promising green biofuel in the future energy mix. The research trends in the synthesis of hydrogen from a variety of biomass substrates under different reaction conditions have been reviewed, and the main observations are:

- Cell immobilization and the use of nanoparticles have been found to considerably enhance biomass-to-hydrogen generation rates and yields.
- The fabrication of novel and more potent microbial strains has given higher cellulase turnovers which improve hydrogen synthesis
- Furthermore, microwave irradiation, ultrasonication and the use of ionic liquids all unanimously, and in their own respective specificities, have proven to be useful and green biomass pretreatments
- Biological detoxification methods have been found to lower inhibitor levels significantly and thus promote yield recovery.
- The gradual rise in research of integrated photo- and dark fermentation systems also holds promise in enhancing biomass-to-hydrogen production.
- Algae-based biomass-to-hydrogen production is still in its early stages of research and deeper process analysis is much required

Notwithstanding the rich pool of data already compiled in the literature on hydrogen production from biomass, the following future works can be planned and undertaken to further improve the biomass-to-hydrogen production routes and assist in the leapfrogging of the bench-scale systems to ones having full-scale implementation potential:

- Conducting more elaborate techno-economic analysis of novel hydrogen production schemes which may integrate one or more of the following green process enhancement component: cell immobilization, better bioreactor design features, green biomass pretreatment regimes, new and more potent microbial strains, use of metal nanocatalyst,

subcritical or supercritical water reaction conditions and workable inhibitor detoxification methods

- Undertaking mathematical modeling and simulation of those potentially scalable bench-scale biomass-to-hydrogen production schemes for process optimization
- Optimizing bench-scale biomass-to-hydrogen production schemes with respect to the key process metrics of biomass and energy conversion efficiency, controllability, yield, safety and hazard control and recyclability within the scaled-up scheme
- Devoting more attention to sort out the techno-economic and socioeconomic sustainability issues related to the acquisition, handling and conditioning of biomass for hydrogen production
- In addition, addressing potential technical and operational issues which could crop up in relation to selectivity towards hydrogen synthesis, poisoning and probable deactivation of metal-based catalysts and equally the fouling of bioreactor piping networks due to char formation
- Exploring the implications of innovative integrated biomass-to-hydrogen production schemes such as combined fermentation-gasification processes
- Last but not the least, pursuant to the above points, allocating research resources in further improving those hydrogen production routes which qualify for potential full-scale implementation by conducting risk assessment and lifecycle impact analysis

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