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A review on biohydrogen as a prospective renewable energy

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Abstract

Renewable energy demand is increasing globally. Fossil fuel source depletion and releasing of toxic gases into the environment further increase this response. Renewable energy is of different types; however gaseous biofuels are the promising option. Anaerobic digestion is a well know process for the production of gaseous biofuels. Among the gaseous biofuels, biohydrogen are recently the efficient and high energy yielding gaseous fuel. Therefore, this review article highlights the biohydrogen demand and utility. The review introduces different aspects of anaerobic digestion, dark fermentation, biohydrogen production, compositional of lignocellulosic biomass, factors influencing bioH_2 yield, pre-treatment methods to improve hydrolysis and increasing bioH_2 production, selection of robust microbial flora as an inoculum source for efficient bioH_2 yield are also discussed. The paper highlights ideas and future plans to improve bioH_2 production before gets implemented in industrial scale development.

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Introduction

An option for the future fuel

BioH_2 in the modern age of scientific community gets popularity due to huge demand of energy. Fossil fuel sources (coal, oil and natural gas) are depleting and release extreme quantity of greenhouse gases. Greenhouse gases polluting our environment, increasing urban smog and damaging biodiversity (Saidur *et al.*, 2011). The constant consumption of fossil fuel further generating global warming (Kapdan and Kargi, 2006). Consequently, concentration in the anaerobic fermentation has extended to produce different kinds of environmentally harmless biofuels. Currently biohydrogen is a smart energy option to replace conventional fossil fuels. BioH_2 is energy rich and is ideal for heating, cooking, electricity and can be used vehicles fuel. According to the data recorded by U.S. Energy Information Administration (EIA), the European Environment Agency and International Energy Agency (IEA), oils consumption and price is rising continuously. The data reveal future energy problems and encourage to possible alternative solutions. The energy consumption in 2013 was coal 28.9%, oil 31.1%, natural gas 21.4%, nuclear 4.8%, hydro 2.4%, biofuels and waste 10.2%, and 'other' 1.5% as shown in the (Fig. 1) (Nakićenović *et al.*, 1998; Pérez-Lombard *et al.*, 2008). About 58% of energy are used in transport from the total 80% of energy produced all over the world. The reported value indicates that biofuels productions are not considered as important as it keeps value in the future.

Amongst the other biofuels, H_2 is more suitable as an energy source in the future with the uppermost energy content of 143 GJ ton−1 and energy yields of 122 kJ/g per unit weight amongst the known gaseous fuels which is 2.75 times higher than any conventional fossil fuels (Amon *et al.*, 2007). During combustion it only oxidizes to water is a clean carbon-free fuel, the only pollutant arise is nitrogen oxides, when hydrogen is absent in the air.H_2 can be used in fuel cell easily to generate electricity because it does not discharge CO_2 on burning. H_2 work as a raw material in manufacturing of chemicals and electronic devices, in processing of steel, in refineries for desulfurizing and reformulating gasoline and in food industry for hydrogenation of oils and fats (Weiland, 2006). Bio-H_2 production have many advantages over chemical and electrochemical processes, as they are produced by microorganisms at ambient temperature, pressure and is perceived ideal process for small-scale installations where bio-waste's are abundant to avoid transport expenses.

There are various processes which have been developed for commercial utilization and development phase such as photo biological, photochemical, thermochemical and photoelectro-chemical methods (Momirlan and Veziroglu, 2002). H_2 can be produced by different methods; with light dependant and independent method are the two important methods used for its production. Biophotolysis is a mechanism in which solar energy is used by cyanobacterium and green algae to produce H_2. In this mechanism solar energy is used to split water with an ultimate reduction of ferredoxin, which in turn can reduce nitrogenase or hydrogenase producing hydrogen. Photofermentation is a process used by photosynthetic anaerobic microbes to produce bioH_2 using organic acids as electron donors (Chong *et al.*, 2009). Dark fermentation is an anaerobic digestion of organic compounds by microbes and finally bioH_2 is produced (Hallenbeck and Ghosh, 2009). Amongst the all of methods, dark fermentation is reasonable because it does not need light, oxygen and work at mesophilic 35-40˚C conditions. Moreover, a wide range of carbohydrates feedstock's can be used for bioH_2production (FM Braga *et al.*, 2016). The process is discussed in details below in section (3).

Anaerobicdigestion

In anaerobic digestion (AD), biogas is produced by a syntrophic association between anaerobic archaea. Some of the anaerobic bacteria are involved in the degradation of polymers to their respective monomers such as lipids, fatty acids and glycerol. Some of them ferment these monomers to H_2, CO_2 and acetic acid (Thauer *et al.*, 2008).

Anaerobic digestion produce biogas and can be used as an alternative to fossil fuels for heat generation and a transport fuel (Weiland, 2006). Several groups of enzymes such as lipases, proteases, cellulases, amylases are involved in biological degradation of these complex biomolecules during AD. For effective biodegradation, these biomolecules should be in close vicinity of enzymes (Taherzadeh and Karimi, 2008). In AD, beside of different growth rates, behaviour to pH, microbial consortia work in synchronization and the whole process is interactive i.e. the products formed by one group of microorganism's act as substrate for other microbes. So, as a result, organic matter is transformed principally to a mixture of H_2, CH_4 and CO_2 as shown in (figure 2) (Parawira, 2012). The AD process consisting of the following steps.

Table 1. Lignocellulosic biomass composition adopted from (Sun Ye and Cheng, 2002; Ghimire *et al.*, 2015; G. Kumar *et al.*, 2015).

Substrate	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Paper	40-55	25-35	15-20
Wheat straw	35-40	30-35	15-16
Corn straw	38-45	26	17-20
Corn cob	40-50	20-25	15-17
Paragrass	35-45	25-30	15-20
Grasses	30-40	20-30	20-25
Peanut	40-45	15-17	20-30
Rice straw	38	19	13
Barley straw	37	24	16
Corn stalk	36	26	16
Cornstalk	34	27	21
Lawn grass	30	43	3-5
Sugarcane bagasse	33	23	5
Sweet sorghum	38	21	17

Hydrolysis: During hydrolysis biopolymers proteins, carbohydrates and fats are degraded by extracellular enzymes and broken down to their respective monomers. These new molecules are used by another group of microorganisms in AD and transformed to subsequent products (Stamatelatou *et al.*, 2011). In this step lignin polymer resist to degradation, therefore pre-treatment is performed to enhanced hydrolysis (Deublein and Steinhauser, 2011). Hydrolysis covert complex matrixes to simple to make it easy for enzymatic attack. During hydrolysis of AD, glucose and different products are formed.

Biomass Cellulose + Glucose organic acids + hydrogen + carbon dioxide (a)

Acidogenesis

Acidogenic bacteria breakdown less complex material to a mixture of volatile fatty acids (VFAs), alcohols and other compounds. This step is sometime referred to as fermentation. Production of higher amount of hydrogen accompanied by carbon dioxide is hallmark of acidogenesis. Acids formed in this step are short chain organic acids such as acetic acid, propionic acid, acetate and butyric acid. Production of VFAs in this phase is important for methanogens. But higher amount of VFAs in digester induce microbial stress due to low pH and eventually lower down AD. Therefore, for ideal AD process, concentration of VFAs plays a key role. Efficiency of AD process and their optimum conditions are often measured by examining VFAs (Wang Qunhui *et al.*, 1999).

Table 2. Reported pre-treatment conditions for high yield of H_2.

Substrate	H_2 yield ml/gVS	Treatment	Reference
Corn straw	68	10 minutes at 1.5Mpa	(Li Dongmin and Chen, 2007)
Corn Stover	66	200˚C with 1.2 % HCl	(Datar *et al.*, 2007)
Cornstalk	57	NaOH (0.5 %)	(Zhang Mao-Lin *et al.*, 2007)
Cornstalk	150	boiled for 30min with HCl (0.2 %)	(Zhang Mao-Lin *et al.*, 2007)
Grass silage	16	----------	(Karlsson *et al.*, 2008)
Maize leaves	42	30min, 130˚C	(Ivanova *et al.*, 2009)
Sweet sorghum plant	32.4	30min, 130˚C	(Ivanova *et al.*, 2009)
Sugarcane bagasse	19.6	30min, 130˚C	(Ivanova *et al.*, 2009)
Wheat straw	68	microwave heating with 2 % HCl	(Fan Yao-Ting *et al.*, 2006)
Dairy manure	14	boiled for 30min with NaOH (0.2%)	(Xing *et al.*, 2010)
Food waste	196	160 ˚C for 2h	(Li J. *et al.*, 2008)
Cheese whey	290	$NaHCO_3$	(Venetsaneas *et al.*, 2009)
Wheat straw	49	30min at 130˚C	(Ivanova *et al.*, 2009)

Acidogens grow well at pH 5-6; however, fluctuation of pH allows them to live in hostile conditions of AD process. Organic acids accumulation rapidly decreases pH and inhibit digestion process if transformed to other product in the next step of fermentation (Stamatelatou *et al.*, 2011). Overall during these step simple sugars, amino acids and fatty acids are converted into short chain organic acids and alcohols (Gerardi, 2003).

Acetogenesis

In this step, acetogenic bacteria transform VFAs and others metabolites of acidogenesis step into acetic acid, hydrogen and carbon dioxide (Stamatelatou *et al.*, 2011). The Acidogenesis and acetogenesis steps work together, if a significant hydrogen pressure is present then acetate production stops due to inhibition of specific bacterial activity (Chandra *et al.*, 2012). It is known that acetate contributes almost seventy percent towards methane production, the final product of anaerobic digestion (Parawira, 2012).

Acidogenesis and Acetogenesis reaction

Volatile fatty acids acetate or butyrate + carbon dioxide+ hydrogen (b)

Dark-fermentation is promising method for H_2 synthesis

Dark means a process without light, while fermentation is the anaerobic metabolism of bacteria. When external electron acceptors are absent, the extra electrons reduce protons to hydrogen by hydrogenase in anaerobic fermentation of organic substrate (Hallenbeck and Ghosh, 2009). There are a number of different methods for hydrogen production; -i.e. which include electrolysis of water, photofermentation and dark fermentation. Photofermentation can either be direct splitting of water to hydrogen by solar radiation or indirectly by light-driven breakdown of water through cyanobacteria or micro-algae (Nath and Das, 2004). Dark fermentation (DF) has several advantages over other, -i.e. it neither requires sun light nor external heating and can continuously produce hydrogen. Both pure and mix culture can also be used to convert different organic waste for economical biofuels. The production rate of H_2 through (DF) is high from various agricultural residues and waste products compare to others method of hydrogen production (Hallenbeck and Ghosh, 2009). Similarly, H_2 synthesis rates are also higher from several hydrogen producing methods, in comparison to light-dependent H_2 system i.e indirect photolysis, direct photolysis and photo-fermentation, dark-fermentation have uppermost rates of H_2 synthesis. In former methods (light-dependent H_2 system), H_2 synthesis rates are reported below 1 $LH_2/L/h$ (Taguchi *et al.*, 1996).

Table 3. A literature of batch fermentation for H_2 production from simple and complex substrate by microbial culture.

Inoculum	Substrate	H_2 yield	Condition	Reference
Anaerobic sludge	starch	0.92[a]	35°C pH 5.3	(Arooj *et al.*, 2008)
//	starch waste	1.6[a]	37°C pH 5	(Laurinavichene *et al.*, 2010)
//	starch	2.32[a]	55°C pH --	(Akutsu Y. *et al.*, 2008)
//	starch	1.7[a]	55°C pH5	(Akutsu Yohei *et al.*, 2009)
//	starch	2.4[a]	55°C pH5.9	(Cakır *et al.*, 2010)
//	glucose	1.46[a]	pH7.9	(Davila-Vazquez *et al.*, 2008)
Cracked cereals	Sucrose	2.73[f]	35°C pH 5-6	(Zhang Yongfang *et al.*, 2005)
DS	Sucrose	6.12[f]	35°C pH 5	(Zhu and Béland, 2006)
Municipal sludge	starch	9.47[d]	37°C pH 8.5	(Lee Kuo-Shing *et al.*, 2008)
Mesophilic and *thermophilic cultures*	starch	2.8[a]	35 and 55°C pH 5.5	(Akutsu Yohei *et al.*, 2009)
Microflora of rice	Wasted bread	1.3[a]	35°C pH 5.7	(Doi *et al.*, 2009)
Mixed cultures of *Bacillus* sp and *Brevumdimonas* sp	starch	1.04[a]	35°C	(Bao *et al.*, 2012)
Hyperthermophilic *archaeon, Thermococcus onnurineus*	starch	3.13[3]	pH 5-8	(Bae *et al.*, 2011)
C. saccharolyticus and *T. neapolitana*	potato steam peels	2.4-3.8[a]	70-80°C pH 7	(Mars *et al.*, 2010)

DS= digested sludge, *= Cassava starch processing wastewater (CSPW), [a] = mol H_2/mol glucose, [b] = mL H_2/g, [c] = mol H_2/g sub, [d] = mmol/g, [f]mol H_2/mol sucrose.

Thermophilic *Clostridium* are reported with H_2 synthesis rate of 28LH_2/L/h and thermophilic *Caldicellulosiruptor saccharolyticus* with29_LH_2/L/h (Ueno *et al.*, 1996; Van Niel *et al.*, 2002). *Clostridium* sp. is reported up to 72_LH_2/L/h using xylose as a substrate.

Table 4. An overview on biohydrogen production by pure culture.

Strain	Condition	Substrate	H_2 yield	Reference
Bacillus licheniformis JK1	38-40°C pH6	wheat grain	1.5[a]	(Patel Sanjay K. S. *et al.*, 2014)
Bacillus cereus EGU44	37°C pH7	glucose	1.92[a]	(Patel Sanjay K. S. *et al.*, 2011)
*Bacillus thuringiensis*EGU45	37°C pH7	glucose	1.67[a]	(Patel Sanjay K. S. *et al.*, 2011)
Bacillus sp. FS2011	35°C pH6.98	glucose	2.26[a]	(Song Zhao-Xia *et al.*, 2013)
Bacillus licheniformis	Room Temp °C pH 4.3	glucose	8.2[a]	(Kumar A *et al.*, 1995)
Ethanoligenens harbinense B49	----------	glucose	2.26[a]	(Xu *et al.*, 2008)
C. saccharoperbutylacetonicum	pH 5-9	glucose	1.76[a]	(Ferchichi *et al.*, 2005)
Enterobacter cloacae IIT-BT 08	15-45°C pH 4-11	glucose	2.2[a]	(Kumar Narendra and Das, 2000)
Ethanoligenens harbinense B49	36°C pH 6	glucose	2.26[a]	(Xu *et al.*, 2008)
Thermotoga elfii	65°C pH 7.4	glucose	5.1[d]	(Van Niel *et al.*, 2002)
Citrobacter amalonaticus Y19	----------	glucose	8 .7[a]	(Oh Y., 2003)
Enterobacter cloacae IIT-BT	----------	glucose	3.4[a]	(Kumar Narendra *et al.*, 2001)
Rhodopseudomonas palustris P4	30°C	glucose	2.76	(Oh You-Kwan *et al.*, 2004)
Engineered strains *Escherichia coli*	37°C pH 6	glucose	1.37- 1.82[a]	(Mathews and Wang, 2009)
Recombinant *Escherichia coli* BL 2	37°C pH 6	glucose	3.12[a]	(Chittibabu *et al.*, 2006)
Engineered *Escherichia coli*	37°C pH 6	glucose	1.82[a]	(Mathews *et al.*, 2010)
Escherichia coli and *Enterobacter aerogenes*	37-40°C pH 6	glucose	25 and 1.8[a]	(Perego *et al.*, 1998)
mutants Enterobacter aerogenes HU-101	37°C pH 6.3	glucose	0.078[a]	(Rachman *et al.*, 1997)

*Bacillus firmus*NMBL-03	pH 6.5	starch	22.58 e	(Sinha and Pandey, 2014)
Thermococcus onnurineus	pH 5-8	starch	3.13	(Bae *et al.*, 2011)
Bacillus amyloliquefaciens	pH 5-7.	starch and various other	203.2[g]	(Song Zhao-Xia *et al.*, 2013)
Enterobacter cloacae IIT-BT 08	15-45°C pH 4-11	Potato starch	ng	(Kumar Narendra and Das, 2000)
Thermococcus kodakaraensis	85°C pH 6	starch	14.0[h]	(Kanai *et al.*, 2005)
Caldicellulosiruptor saccharolyticus and *Thermotoga neapolitana*	70-80°C pH 7	potato steam peels	2.4-3.8 [a]	(Mars *et al.*, 2010)
Clostridium acetobutylicum	36°C pH7	(CPW) *	2.41 [a]	(Cappelletti *et al.*, 2012)
Clostridium butyricum	30°C pH5.6	starch	2.0 [a]	(Masset *et al.*, 2010)
Clostridium butyricum	30°C pH6.5	starch	1.9 [a]	(Goering and Van Soest, 1975)
Rhodobactersp M-19	30°C pH 6.5	starch	3.6 [a]	(Goering and Van Soest, 1975)
*Clostridium butyricum*CGS2	37°C pH6.5	starch hydrolysate	2.03 [a]	(Chen *et al.*, 2008)
Clostridium tyrobutyricum	37°C pH6	Cassava starch	3.2 [a]	(Jiang *et al.*, 2013)
Caldicellulosiruptor saccharolyticus	70°C pH7	Pre-treated wheat straw	3.8 [a]	(Panagiotopoulos *et al.*, 2010)
Caldicellulosiruptor saccharolyticus	70°C pH7	Pre-treated barely straw	nr	(de Vrije *et al.*, 2009)
Caldicellulosiruptor saccharolyticus	70°C pH7	Carrot pulp hydrolysate	2.8 [a]	(Claassen *et al.*, 2010)
*Thermoanaerobacterium thermosaccharolyticum*W16	60°C pH7	hydrolysed corn stove	2.24 [a]	(Cao *et al.*, 2009)
*Clostridium thermocellum*7072	55°C pH7.5	Corn stalk	17.8 [a]	(Cheng Xi-Yu and Liu, 2011)
Clostridium thermocellum ATCC2740	55°C pH6.5	delignified wood fibres	1.6 [a]	(Levin D. *et al.*, 2006)

*= Cassava starch processing wastewater (CSPW), [1] = mol H_2/molglucose,[d]= mmol/g, [e]= mmol H_2/L,[g] = ml/g, [h]=mmol gdw−1 h−1, ng=negligible, nr =not reported.

The highest synthesis rates are obtained using mesophilic mixed culture ranging from 221-414 H_2/L/h (Morvan *et al.*, 1996;Lay, 2001;Chang Jo-Shu *et al.*, 2002).

The mechanism of organic substrate to biofuels is well-known. High energy electron acceptors are utilized to pass in to lower energetically favourable reactions if electron acceptors (nitrate, oxygen, iron (III), sulfate and CO_2) are available. Therefore, an anaerobic reaction lacking O_2/H_2O electron couple, the organic substrate reduces thermodynamically from aerobic respiration of -78.3 kJ/mol to +23.5 kJ/mol through methanogenesis. DF becomes thermodynamically unfavorable when H_2 yield start increasing which decrease pH, thus maintainace of both is vital for large scale application. Theoretically, the complete conversion of 1 mole of glucose ($C_6H_{12}O_6$) could produce 12 mol of H_2 as shown in the equation (a) $C_6H_{12}O_6 + 6\ H_2O \rightarrow 12H_2 + 6CO_2$. So far the highest fermentative yield of H_2 11.6 H_2/mol with 96.7% conversion efficiency is reported (Woodward *et al.*, 2000) by combining hydrogenases from *Pyrococcus furiosus* and enzymes of the oxidative pentose phosphate cycle under optimized in vitro conditions.

But definitely, the complete oxidation of glucose into H_2 and CO_2 is not possible in bacterial fermentation because corresponding reaction (a) with positive ΔGo of +3.2 kJ is thermodynamically not feasible. Theoretically a conversion efficiency of 33% (4 mol H_2/mol glucose) is possible in laboratory from glucose fermentation (Logan *et al.*, 2002). During DF hydrogen are directly generated after hydrolysis in the acetogenic and acidogenic phases. The acetogenic bacteria convert the substrate into H_2, CO_2 and organic acids i.e butyric and acetic acid (Shin *et al.*, 2004). In acetate pathway 4 mol H_2/mol glucose and 2 mol H_2/mol glucose in butyrate pathway are simultaneously produced -i.e. $C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2C_2H_4O_2$ and $C_6H_{12}O_6 \rightarrow 2H_2 + 2CO_2 + C_4H_8O_2$. In dark-fermentation of mixed culture both acetic and butyric acids are produced frequently, in this case the highest H_2 yield is reported up to 2.5 mol H_2/mol glucose (Hallenbeck and Benemann, 2002). H_2 yield depends on the end products of the fermentation, 1mol H_2/mol glucose is produced when propionic acid is the end product -i.e. $C_6H_{12}O_6 \rightarrow H_2 + CO_2 + C_3H_6O_2$, whereas, no hydrogen is produced when lactic acid is the end product of fermentation by bacterial species *Lactobacillus paracasei* or *Enterococcus durans*, i.e. $C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$.

In addition, lactic acid bacteria *Enterococcus durans* or *Lactobacillus paracasei* could generate toxic or inhibitory intermediates for hydrogen producing bacteria (Noike *et al.*, 2002). In short, maximum H_2 yields is link to acetate and butyrate production while low H_2 yields are connected with propionate and negligible amount or no H_2 yields when alcohols and lactic acid are generated. These finding propose to find out high acetate producing bacterial strains for bioH_2 production through DF as shown in the (Figure 3).

Hydrogenases: H_2 production is carried out by metalloenzymes, namely hydrogenases and nitrogenases. In nitrogen fixation, nitrogenases discharge H_2 as a by-product whereas hydrogenases convert protons to hydrogen in a simple reaction i.e. $2H^+ + 2e^- \leftrightarrow H_2$. The reaction direction depends on reduction status of the main component interacting with enzyme. Hydrogenases are divided in to 3 main classes (1) nickel-iron ([NiFe] hydrogenases (2) iron-only ([FeFe] hydrogenases and (3) metal-free hydrogenases.

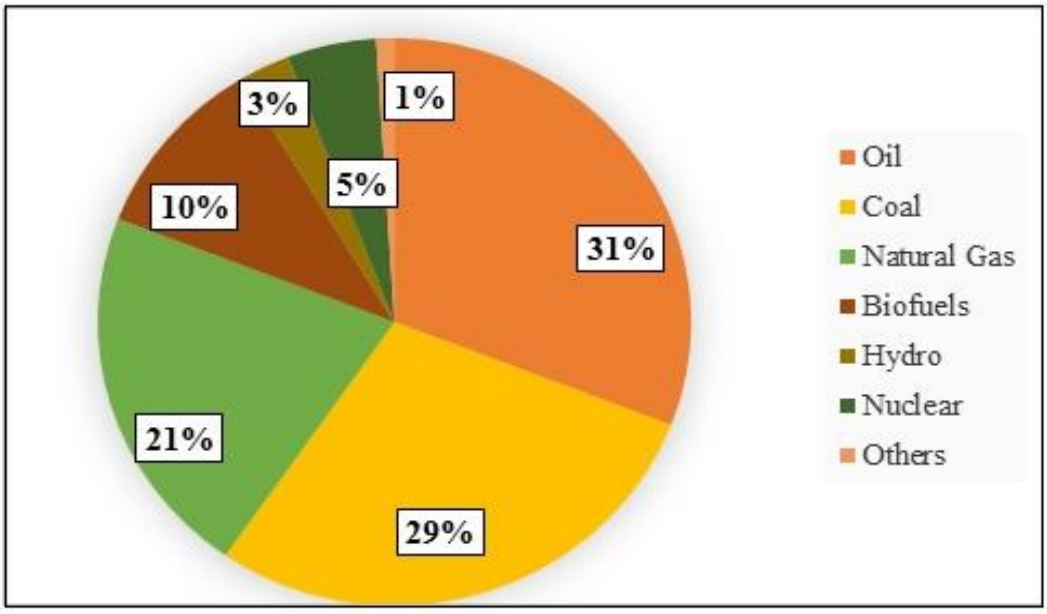

Fig. 1. The data presented here is according to the European Environment Agency and International Energy Agency (IEA) in 2013 for the total primary energy supply in the world.

The [NiFe] hydrogenases are found to catalyze both H_2 production and uptake using cytochrome *c*3 as electron donors or acceptors, and are bound to either cytoplasm, periplasm or to cytoplasmic membrane. Likewise,3 families of Fe-hydrogenases are known namely, - soluble, cytoplasmic and monomeric Fe-hydrogenases.

They are highly sensitive to O_2 and are often reported in strict anaerobic bacteria *Megasphaera elsdenii* and *Clostridium pasteurianum*. Both types of these enzymes have nearly mutual structures, each has few Fe-S clusters and an active site with metallocluster synchronized by CO and CN ligands (Hedderich, 2004). The activity of hydrogenase is affected mainly by pH of the medium.

A low activity in the cells of *Clostridium beijerinckii* are reported at a pH lower than 5.2, whereas pH 5.8 in *Clostridium acetobutylicum* and very interestingly a different growth pattern and activity in two *Bacillus* spp is recently reported in our study (Valdez-Vazquez and Poggi-Varaldo, 2009; Shah *et al.*, 2016).

The optimum pH is around 5.5 and optimal temperature is 50°C for hydrogenase activity and no much difference for other factors (Valdez-Vazquez and Poggi-Varaldo, 2009), however, the production of bioH_2 by dark fermentation could be influenced by metabolism of the applied microorganisms.

Two stage anaerobic method: Anaerobic digestion could be either single stage anaerobic digestion or two-stage anaerobic process.

The single stage anaerobic digestion is normally simple dark fermentation, while the two-stage anaerobic is divided into (a) hydrolysis/Acidogenesis and (b) acetogenesis/methanogenesis process operated in separate bioreactors.

Beside traditional biogas process for CH_4 production the two stage anaerobic digestion could yield both H_2 and CH_4 simultaneously, in this process organic rich substrate are converted to H_2, CO_2 and fatty acids, which is then converted to CH_4 by methanogens (Benemann, 1996).

To acquire profitable output bioenergy (Biohydrogen and Biomethane), the dark fermentation must be coupled to the second phase of the anaerobic digestion, this process could be ideally separated as microorganisms of both stages has significant differences in terms of nutritional needs, physiology, pH sensitivity and sensitivity to others environmental conditions. A methane gas of 270 ml/h and 119 ml/h hydrogen is reported using a two-stage anaerobic digestion system (Zhu *et al.*, 2008).

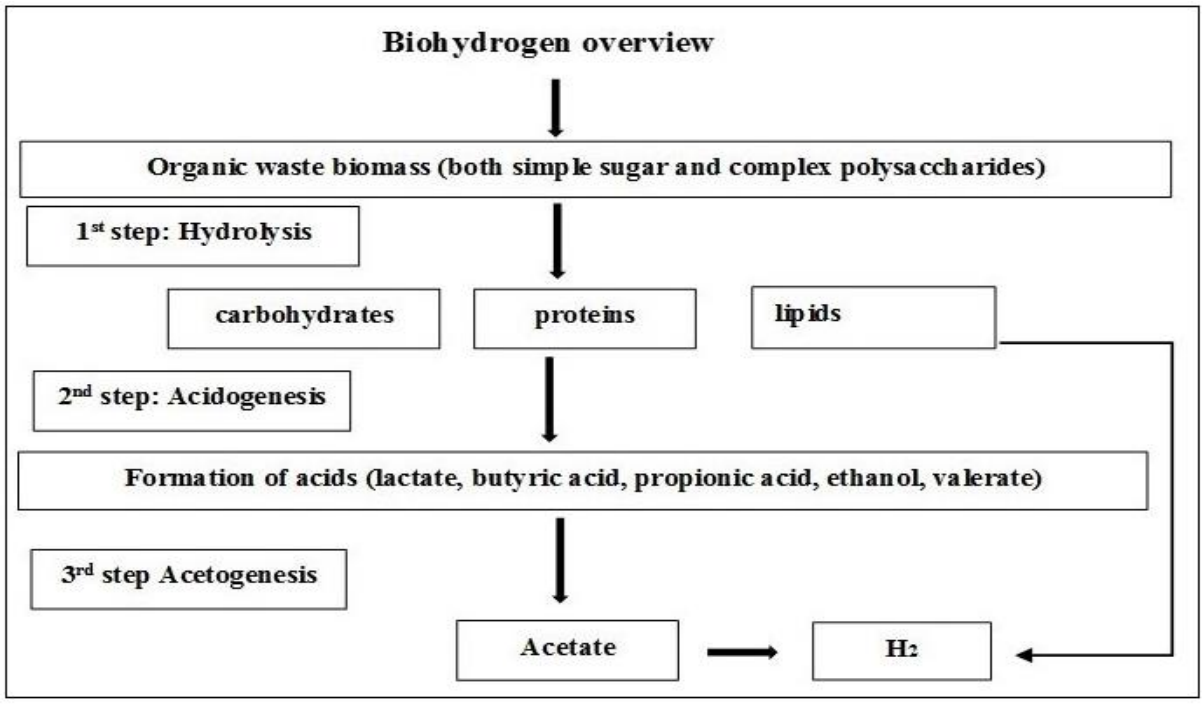

Fig. 2. Pathways and processing steps involved in the biodegradation of waste biomass for bioH_2 production (Ghimire *et al.*, 2015).

In future the two stage anaerobic fermentation process could be considered more feasible than others processes for bioH_2 and CH_4 production as shown in the (figure 4) (De Bere, 2000; Hawkes *et al.*, 2007).

Abundance and recalcitrance of lignocellulosic biomass

The demand of cheap bio-hydrogen fermentation could be meet with lignocellulosic feedstock as substrate. The main hurdle is the recalcitrant structure of lignocellulosic biomass that resist in digestion to microbial consortia and enzymatic hydrolysis.

Prior fermentation it requires pre-treatment to remove the barrier lignin and inhibitors producing component (hemicellulose) from feedstock. Pre-treatment also swollen surface morphology and increase enzymes accessibility to fermentable sugars and cellulosic biomass (Cui *et al.*, 2009; Ma *et al.*, 2011). Cellulose and sugars can be used for the production of hydrogen, ethanol, and other high-value chemicals by using a wide range of enzymes (exoglucanase, b-glucosidase, xylanase and endoglucanase) from bacterial and fungal strains. The major challenges in pre-treatment process are demand for high energy, use of harmful chemicals

and large amount of costly enzymes for hydrolysis which rises the production cost and restricting its commercial applications significantly (Jin *et al.*, 2008; Xu *et al.*, 2008). Energy crops and organic waste biomass (soft wood, hardwood, grasses, forestry and agricultural residues) are the most favored input materials due to their high potential of H_2 yield. Solid waste is produced more than 220 billion tons approximately annually throughout world. Among the waste about 50% is organic and expected to increase up to 2.23 billion tons in 2025 (Yang *et al.*, 2015).

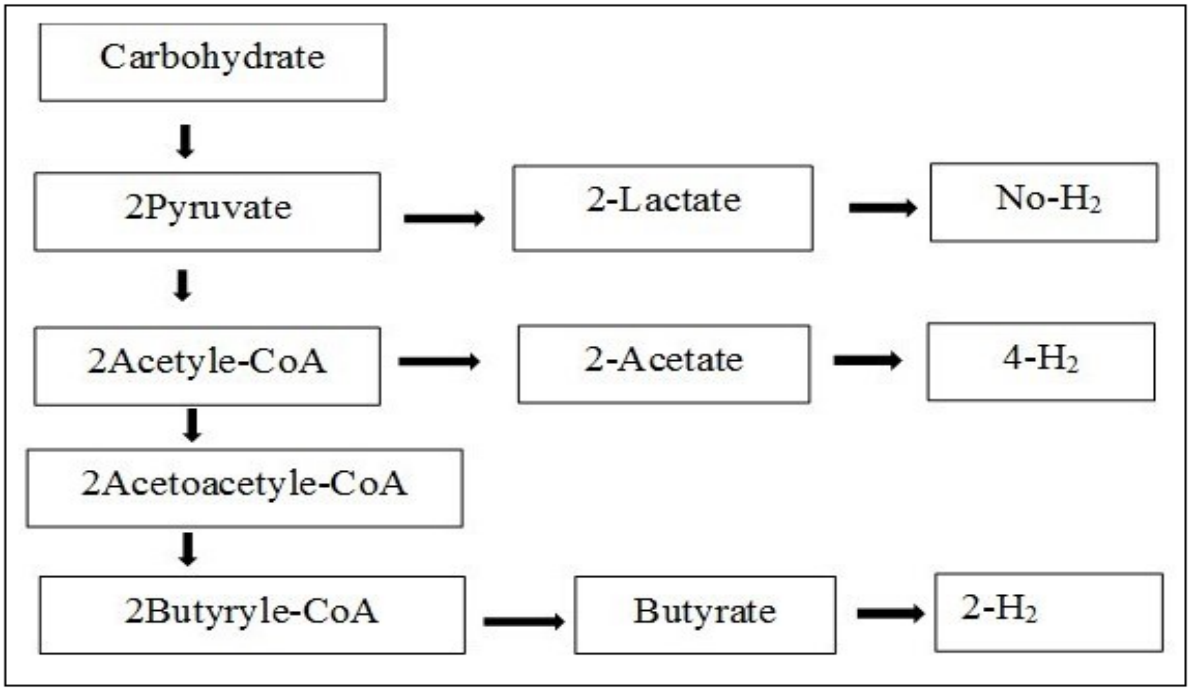

Fig. 3. H_2 yields in the metabolism of diverse group of bacteria through dark fermentation.

Plants materials compositions are difficult to hydrolyse and the biofuels production is not reported beyond 40-50% practically. The lack of efficient pre-treatment method for suitable degradation is one of the major limitation in term of utilization of these biomasses in anaerobic digestion for the production of biofuels. Therefore, researchers studied multiple pre-treatment methods, aiming to increase solubilisation of complex lignocelluloses to free sugar (Azman *et al.*, 2015). Lignocellulosic biomass consists of 40-50% cellulose, 25-30% hemicellulose and 20% lignin and other extractable components (Kumar G. *et al.*, 2015). However, the composition of the substrate can vary significantly for lignin, hemicellulose, cellulose and other content depending on its source (Sun Ye and Cheng, 2002). Cellulose is a long chain of homo-polysaccharides composed of β1-4linke D-glucose units. It is bound by lignin and hemicellulose rings. Cellulose contains inter and intra hydrogen bonds plus vander-waals forces.

Hemicellulose binds lignin and cellulose and it cover the surface of cellulose limit the excess of cellulases to hydrolyse in to glucose (Pérez *et al.*, 2002). The third main component of plants materials are lignin. Lignin are the most complex hydrocarbon polymer contain three phenylpropane units (Rubin, 2008), such as guaiacyl (G), p-hydroxyphenyl (H) and sinapyl (S) units linked by C–C bonds or aryl ether bonds. The amorphous hydrophobic nature of lignin strengthens the phenylpropane units and cellulose–hemicellulose fibrils by cross-linking between them to build the lignocellulosic biomass structure recalcitrant to microbial and enzyme degradation. Lignin also exhibit glass transition at 90 and 170°C melting temperature proving as thermoplastic polymer (John and Thomas, 2008). It is well established that the most recalcitrant component of the plant biomass is lignin, thus disruption and degradation of its chemical bonds is compulsory in demand to increase the bioavailability of cellulose for enzymatic diffusion and improved activity (Van Wyk, 2001).

Type of Pre-treatment that promote biohydrogen production from lignocellulosic biomass Pre-treatment are used to disrupt cellulose, lignin crystallinity and hemicellulose content. A wide range of pre-treatment methods have been tested, including physical, hydrothermal, chemical and biological. The best pre-treatment method must have properties like (a) require less chemical (b) maximum carbohydrate recovery (c) very limited amount of by-products (d) cost-effective for large scale application (e) applicable for different kinds of biomass feedstock's and (f) reduce the amount of enzymes required for substrate hydrolysis (Biswas *et al.*, 2015). Generally, the above mentioned properties are the key limitations of most pre-treatment methods, in viewing to these points we are briefly describing the ideal methods for the pre-treatment of different biomass types.

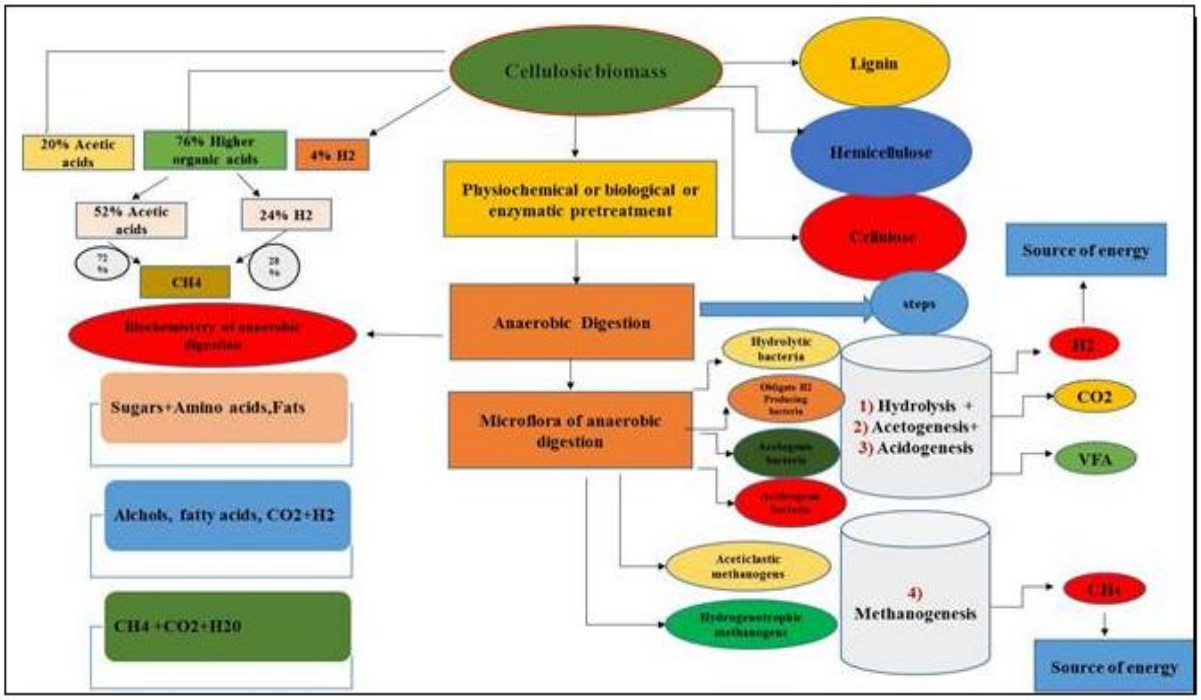

Fig. 4. The figure show process and biochemistry of anaerobic digestion and integration of two different biogas reactors for bioenergy production.

Mechanical pre-treatment

Mechanical pre-treatment makes solid particles of the feedstock coarse, increasing the specific surface area and break them down into small size particles with low water, easy implementation and a moderate energy consumption in initial pre-treatment process. A variety of mechanical pre-treatment methods -i.e piston press, high-pressure Homogenizer, bead mill, sonication and grinding are reported.

Thermal pre-treatment

Amongst the pre-treatment methods, thermal treatment is extensively used at industrial scale for pathogen removal. This treatment let down the viscosity of the digestate and solubilized organic compounds. Thermal treatment includes temperatures ranges from 100-160°C with shorter or longer treatment time depending on limiting loss of volatile organics, solubilisation of proteins and carbohydrates.

Chemical pre-treatment

Chemical pretreatments have been extensively used to improve the biodegradability of cellulose by removing lignin and hemicellulose. Concentrated and diluted acids are involved to break the rigid structure of the lignocellulosic material. The most commonly used acid is dilute sulphuric acid (0.5-1% w/v) hydrolyzing the hemicellulose portion of lignocellulosic biomass to simple sugars minimizing the production of fermentation inhibitors during anaerobic digestion (Lenihan *et al.*, 2010). Alkali treatment remove the lignin and left over relatively pure cellulose from agricultural waste biomass.

The most extensively used alkaline pretreatment bases are potassium hydroxide, sodium hydroxide and calcium hydroxide (Yan *et al.*, 2015) to degrade the lignin of the feedstock and to maximize the accessibility of enzymes to cellulose (Song Zilin *et al.*, 2014). It is tough to categorise the most suitable pre-treatment method for all types of lignocellulosic biomass (Hahn-Hägerdal *et al.*, 2006). However, the appropriate pre-treatment method should increase porosity of the substrate and minimize the development of inhibitors (Hahn-Hägerdal *et al.*, 2006). Literature study and review on lignocellulosic chemistry (Hu and Ragauskas, 2012) makes it clear that alkaline pre-treatment can be performed at low temperatures so that very little of the saccharide fractions of cellulose is solubilized (Lin *et al.*, 2010) which is necessary benefit for bioenergy production from energy-rich components of lignocellulose.

Sodium hydroxide, potassium hydroxide and calcium hydroxide are the most extensively studied alkali which degrade lignocellulose principally in the same manner; however, sodium hydroxide has a higher reaction rate (Gupta and Lee, 2010) compared to calcium hydroxide, but the main problem is high expenses on large scale implementation. Among the alkaline bases, calcium hydroxide is one of the inexpensive alkali for pretreatment of lignocellulosic feedstock (Kootstra *et al.*, 2009). Therefore, the researchers need to use raw materials as less expensive substrate and cost-effective chemical pre-treatment method for increasing yield of biofuels production from solid waste biomass through anaerobic fermentation.

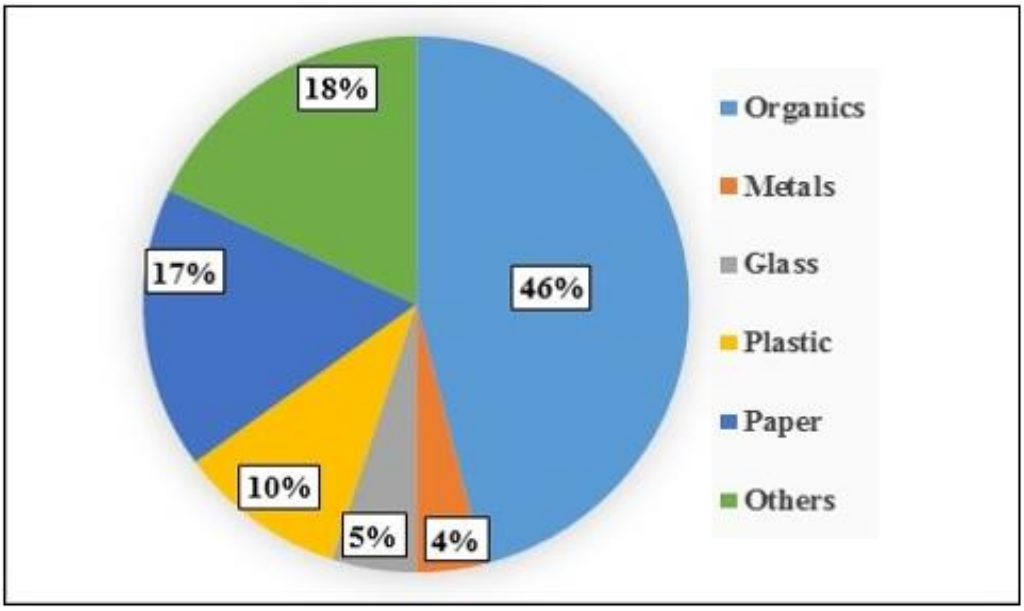

Fig. 5. The data present an estimation of annual percentage of global waste.

Biological pre-treatment

Biological pre-treatment with microbial consortia or addition of specific enzymes such as laccases, xylanases, lignin peroxidases, peptidases, endoglucanases and other hydrolases to the lignocellulosic substrate. Saccharification process is an alternative cheap method to chemical pre-treatment. Biological pre-treatment can be performed by enzymatic Saccharification, composting or micro-aeration to obtain a maximum hydrolysis of complex substrates prior to biofuel production.

A wide range of fungal strains *Pleurotus ostreatus, Trametes versicolor, Ceriporiopsis subvermispora, Phanerochaete chrysosporium* and a number of bacterial spp are reported foroxidative biodegradation of lignin from agricultural wastes to increases the enzymatic hydrolysis efficacy. Biological pre-treatment consumed less energy, environmentally non-toxic and require no chemicals treatments. However, slow treatment rate, growth conditions and requirement of bulky space are the only limitations of the biological process (Cheng Chieh-Lun *et al.*, 2011).

Thermophile *Anaerocellum thermophilum* and other *Clostridiums* spp can degrade lignin (Chang Jui-Jen *et al.*, 2008; Chang Tinghong and Yao, 2011). Brown-rot fungi principally hydrolysed cellulose, while white fungi degrade both lignin and cellulose (Galbe and Zacchi, 2007). These microbes utilize their ligninolytic enzymes such as manganese peroxidase, lignin peroxidase, laccase and versatile peroxidase (Lee J *et al.*, 2007). *Stereum hirsutum (*white-rot fungi) is reported with 14.5 % and 7.8 % *degradation* of the lignin from the wood (Lee J *et al.*, 2007). In a 20 days of incubation, *Coniochaet ligniaria* fungus degrade 75 % of pepper plant residues. Similarly, *Pleurotus florida* degrade 45 % lignin during 60 days incubation from corn straw (Zhong *et al.*, 2013). In a result of pre-treatment increase in bioH_2 yield is noticed. A 2% Enzyme mixtures Vicozyme L (cellulase, arabinase, hemicellulase , β-glucanase,and xylanase) increased bioH_2 yield from 15.04 to 44.92 mL H2 g-1-dry poplar leaves(Cui *et al.*, 2010). *Bacillus amyloliquefaciens* improved energy production from 0.18 to 0.78 MJ kg-1 VS equal to 333% increase (Ivanova *et al.*, 2009). Mutual acid-enzymatic pre-treatments also enhanced bioH_2 yield from 37-125 LH2 kg-1VS from wheat (Nasirian *et al.*, 2011). These studies proposed that biological treatment is economical pre-treatment method amongst the all for inexpensive biofuels productions.

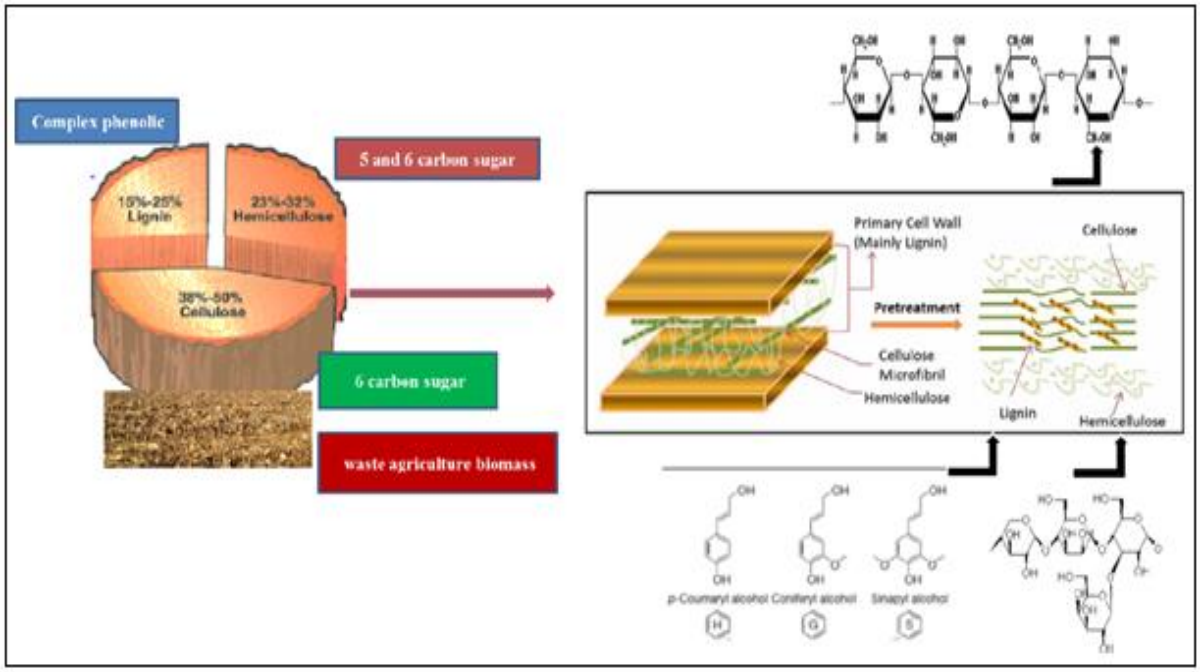

Fig. 6. Lignocellulosic biomass and pre-treatment effect.

Roadmap to improve bioH_2 yield

There are several pre-treatment methods (chemical, thermal, physical and biological) that have been used for conversion of biomass to biofuels (Hahn-Hägerdal *et al.*, 2006). However, none of the method is considered suitable to remove lignin and hemicellulose for anaerobic digestion of solid waste biomass (Lenihan *et al.*, 2010). So far diluted acids and alkali treatments are considered methods of choice to remove lignin and to left over relatively pure cellulose from agricultural waste biomass (Kootstra *et al.*, 2009).

One of the best process is to utilize a non-stringent dark fermentation process for various kinds of bio-waste including simple sugars (xylose, arabinose, glucose) and polysaccharides polymers (starch and cellulose) to produce bioH_2 (Wang Yi *et al.*, 2008). Two pathways are involved in H_2 production through dark fermentation-i.e. acetate pathway or butyrate pathway. Hypothetically and theoretically, one mole of glucose can yield up to 4 moles of hydrogen through acetate pathway and two moles of hydrogen by butyrate pathway using pure culture. Similarly, one mole of xylose can produce 3.33 moles of hydrogen through acetate pathway and 1.67 moles by the butyrate pathway (Kongjan *et al.*, 2009).

Thus quantitatively more hydrogen is expected by acetate and less by butyrate during substrate metabolism in a fermentation system (Hawkes *et al.*, 2007). For the efficient and high yield of H_2 by dark fermentation, *Enterobacter,* Bacillus and anaerobic *Clostridium* species are the best competent microorganisms amongst heterotrophic bacteria that can be used as a pure, mixed or co-culture to produce hydrogen (Ntaikou *et al.*, 2010). *Bacillus*, *Enterobacter,* and *Clostridium* are the most widely investigated hydrogen-producing bacteria species. *Clostridium* sp. are reported to produce hydrogen yield 2 mol H_2/mol glucose comparatively higher hydrogen yield 1 mol H_2/mol glucose of *Enterobacter* sp (Girbal *et al.*, 1995; Yokoi *et al.*, 1995). *Clostridium thermocellum*is reported with hydrogen yield of 1.6 mol H_2/mol glucose from lignocellulosic biomass (Levin D. *et al.*, 2006). Similarly, *Caldicellulosiruptor saccharolyticus* is reported with 2.09 mol H_2/kg by from wheat straw (Ivanova *et al.*, 2009). A slightly higher bioH_2 yield of 3.6 mol H_2/mol is observed for pure culture of *Clostridium acetobutylicum* from cellulose. While the highest bioH_2 yield 8.1 mol H_2/ mol cellulose is obtained using co-cultures of *Ethanoligenens harbinense* and *Clostridium acetobutylicum* (Yokoi *et al.*, 2001;Wang Yi *et al.*, 2008).

However, improvement with pure culture is difficult and require aseptic conditions, beside this mix culture can be a good option to consume different waste biomass for hydrogen yield (Li Jianzheng *et al.*, 2007; Ntaikou *et al.*, 2010). Although, mixed microbial cultures has some drawbacks, there are hydrogen consuming, hydrogen suppressing and non-hydrogen producing species (homoacetogens, methanogens, and lactic acid bacteria) involved in consumption of hydrogen or inhibition of hydrogen through by-products (ethanol propionate, lactate) production (Guo *et al.*, 2010; Ntaikou *et al.*, 2010). Researchers used heat treatment (80-110°C for 15 min), acid/alkali pre-treatment, chemical inhibitors such as acetylene, bromoethanesulfonate and chloroform to remove non-spore-forming microorganisms like *Methanogenic archaea* and to left behind the hydrogen producers (Fang *et al.*, 2006;Argun *et al.*, 2008; Guo *et al.*, 2010; Ntaikou *et al.*, 2010).

Different chemical and biological pretreatment studies reported high bioH_2 production compare to untreated substrates. A 126.22 and 141.29 mL H_2 is produced from cornstalk after 0.6% HCl (90°C,2 h) and *Trichoderma viride* cellulases (50°C,72 h, pH 4.8) inoculated with heat-pre-treated anaerobic sludge (Wang Xiaoyi *et al.*, 2007;Wang Jianlong and Wan, 2009; Wang Yu *et al.*, 2010). In a similar study, cornstalk pre-treatment with microbial consortia for 15days produced 176 mL of H_2 with aerated microbial consortium fermentation (Fan Y. *et al.*, 2008). Similar high H_2 yield is observed in acid, alkali or enzyme pre-treated substrate -i.e. Lawn grass, Soybean straw, Poplar leaves, Sugarcane bagasse, Reed canary grass, Rice straw and Sweet sorghum bagasse with single enriched or mix consortia (Pattra *et al.*, 2008;Cui *et al.*, 2009; Claassen *et al.*, 2010; Nguyen *et al.*, 2010; Panagiotopoulos *et al.*, 2010; Wei *et al.*, 2010;Lakaniemi *et al.*, 2011;Cui and Shen, 2012; Han *et al.*, 2012). Correspondingly higher amount of H_2yield was produced from glucose and arabinose from the least producer of hydrogen (Li J. *et al.*, 2008). A literature review showed that H_2 yield can be produced from rotten dates in sequential three stages fermentation involving facultative and strict anaerobes. It is observed that hydrogen can be produced from rotten dates by dark as well as photo fermentation and sucrose supplementation to dates enhance H_2 production (Abd-Alla *et al.*, 2011). In another study it is also observed that dark fermentation followed by photo fermentation of sucrose increased biohydrogen production (Tao *et al.*, 2007). Recently indigenous microflora of vegetables is also evaluated for H_2 production (Marone *et al.*, 2014). In our study, two *Bacillus* sp. strains showed 61 mL of H_2 g/vs from organic fraction of municipal solid waste (OFMSW). These strains could be considered decent candidates for industrially applications (Shah *et al.*, 2016).

Screening of robust strain for increasing bioH_2 production

H_2 productions are conceded usually at ambient temperatures with minimum energy consumption. An enormous number of microbial species like *Methylotrophs*, Cyanobacteria, *Clostridia*, rumen

bacteria, methanogenic bacteria, *archaea*, *Escherichia coli*, *Enterobacter*, *Alcaligenes* and *Bacillus* spp and some other mesophilic and thermophilic microbial flora has been isolated and cultivated for H_2 production (Show *et al.*, 2012). There are several examples of different strains isolated from different kinds of sources like sludge, waste water, anaerobic digester and animals dung. Considering the isolation process, *Clostridium* species are reported from sludge under strict anaerobic conditions (Pan *et al.*, 2008) and from heat (90°C) or alkali treated food waste (Kim *et al.*, 2009). Similarly, *Enterobacter cloacae* is isolated from sugar refinery sludge (Sun Lili *et al.*, 2015). A small number of *Clostridium* species from heat treated (100°C for 15 minutes) activated sludge (Wang Xiaoyi *et al.*, 2007). *Clostridium papyrosolvens* from highly acidic pH (Jin *et al.*, 2008) and *Clostridium bifermentans* is isolated from sludge after autoclaving at 121°*C* for 30 minutes (Wang CC *et al.*, 2003). *Clostridium* and *Bacillus* species from municipal biosolids (Duangmanee *et al.*, 2002) and recently three strains of Enterobacteriaceae from vegetables as an indigenous microflora without any treatment (Marone *et al.*, 2012).

Most of the literature is focusing on using both mix and pure cultures of bacteria for fermentative H_2 production using simple carbon source (glucose, xylose, maltose etc) to a wide range of complex feedstock. The list of microbial spp utilizing simple to complex microbial consortia and their H_2 yield at given conditions are enlisted in the (Table 2, 3 and 4) using dark fermentation system for H_2 production. The rate of H_2 production may vary from the same substrate fermented either by pure culture or mixed microbial consortia but in practical sense it is reported low compare to the theoretically expected levels. Mix microbial culture are reported with high H_2 yield. *Bacillus* sp. and *Clostridium* sp. mixed culture are reported with H_2 yield of 1.52 mol H2/mol sucrose. Similarly, co-culture of *Rhodobacter* sp. and *C. butyricum* were observed with highest 4.5 mol/mol glucose of H2 yields. A mixed culture of *Rhodobacter sphaeroides* and *E. aerogenes* produced 3.15 mol H2/mol glucose (Yokoi *et al.*, 1998; Kotay and Das, 2007; Vipin Chandra and Purohit, 2008).

Beside this anaerobic sludge, pre-treated cow dung, digested sludge and municipal sludge are studied in a mesophilic condition to convert organic substrate into H2 as shown in the (Table 3).

The potential H2 producers are the facultative anaerobes such as *Campylobacter, Aeromonas, Alcaligenes, Salmonella, Citrobacter, Serratia, Bacillus, Enterobacter, Klebsiella, Thermotoga, Streptococcus* and aerobic *Azotobacter* etc listed in the (Table 3 and 4). In our recent study, a total of 120 bacterial strains were isolated from heat-treated granular sludge and only two *Bacillus* sp. strains were found good H_2 producers from glucose, starch and organic fraction of municipal solid waste (OFMSW) (Shah *et al.*, 2016). Modern science needs to focus on the genetic manipulation and metabolic modification of the H_2 producing bacterial sp. and utilization of their hydrogenases activity. Presently, metabolic engineering and genetic engineering has well established tools, but very less effort is applied to bioH2 production. Numerous possibilities can be tracked in the upcoming years in efforts to overwhelm the thermodynamic/metabolic obstacles to efficient H_2 yields. In this concern, introduction of thermodynamically bearable NAD (P)H dependent hydrogenases/pathways was tested for maximizing H_2 yields (Veit *et al.*, 2008). However, the author recommended probability of increasing the hydrogenase expression activity. So metabolic engineering can help in increasing the H_2 production by increasing cellular NAD (P) H level (Lozupone and Knight, 2007; Hallenbeck and Ghosh, 2009).

The genetic tools for probing unique H_2 producers has been exploited. Certain fascinating H_2 isolates, *Desulfitobacterium dehalogenans, Wolinella succinogenes, Novosphingobium aromaticiviorans* and *Burkholderia fungorum* were identified.

These interesting H_2 producers display distinctive characteristics, i.e. remediation of contaminated soil, degradation of chlorinated phenols, ethenes, plant root colonization and degradation of industrial wastewaters etc. plus they grow in a varied kind of environments including fresh waters, soil, marine life and can use bio-waste's as feed.

Therefore, genetic mining can further identify robust H_2 producers (Kalia Vipin C *et al.*, 2003; Kalia Vipin Chandra and Purohit, 2008).

Factors influencing H_2 production

H_2 production by dark fermentation is a very complex process and effected by many factors such as substrate, reactor type, inoculum, nitrogen, metal ion, phosphate, pH and temperature. Here is a summary for better understanding even through with disagreements on the optimal condition for each factor about yield of H_2 production. Beside of chemical and heat pre-treatment methods a hollow fiber or vacum suction pipe is reported for enriching hydrogen-producing bacteria as an inoculum source (Liang *et al.*, 2002).

The pH is particularly a vital factor for continuous H_2 yield. As pH gets low due to high yield of H_2 concentrations, the H_2 production drop down in result of reduced substrates accumulation and change in metabolic pathways of the system. Similarly, concentration of carbon dioxide also effects H_2synthesis (Das and Veziroğlu, 2001).

Ideally a strict anaerobic conditions are requiring, sparging N_2 gas in the reactor is necessary to limits the production of CO which inhibits hydrogenase.

A mix bacterial cultures is a good choice rather than pure for utilization of wide range of feedstock (Wang Jianlong and Wan, 2009).

In a dark fermentation, a high yield of H_2 is reported from simple substrates comparatively to complex organic wastes (Wang Jianlong and Wan, 2009).

For optimum sharing literature studies support the use of continuous stirred tank reactor (CSTR) to enhance the capability of H_2 producing bacteria (Wang Jianlong and Wan, 2009).

Among the micronutrients, high concentration of any nutrient can negatively affect the performance of H_2 producing bacteria while among the metal ions only Fe^{2+} increase H_2level (Wang Jianlong and Wan, 2009).

Despite of the literature disagreement it has been established that optimum temperature is around 37-50°*C* and pH range from 4-6 generally (Wang Jianlong and Wan, 2009).

Future perceptions and strategy for increasing H_2 production

Current industries facing problems for economical processing of solid waste (industrial, municipal, construction, agricultural or biomedical waste) for efficient biofuel production. Therefore, a proper waste management strategy for storage, transport, collection and disposal is necessary to keep the environment safe. In this respect anaerobic digestion of waste is the only better option to produce environmentally hygienic biofuels. The expertise and technologies for H_2 production are in different phases of progress. Overall, research is concentrated on operations, maintenance of costs and reduction of capital equipment as well as refining the efficacy of H_2 production technologies. Numerous studies reported efficient microbial consortia for H_2 using different biomass. Metabolic pathways of microbial strains have been assessed to shifting microbial metabolism from butyrate to acetic acid for maximum H_2 yield. Recombinant DNA, cloning, Over-expression techniques has been tested for metabolic engineering and shifting carbon pathways to preferred end-products (Levin David B *et al.*, 2009; Levin David B and Chahine, 2010). To increase H_2 production, a large scale experimentation and collection of data is necessary to build an ideal situation for large scale bioreactor fermentation. This requires online computer based reactor to monitor critical conditions, mathematical and statistical tools. Similarly, inoculum development and culture immobilization further improve the digestion process (Singh and Rathore, 2016). Optimization of parameters for fermentation process, exclusion of hostile reactions, isolation and selection of thermophilic strains for high H_2 yield, cloning and genetic engineering of more active hydrogenases are necessary. Inhibition of H_2 consumer and boosting of H_2 producers is the real requirement for commercial scale application (Kalia Vipin Chandra and Purohit, 2008; Kotay and Das,

2008; Chong *et al.*, 2009; Dong *et al.*, 2009; Hallenbeck and Ghosh, 2009; Levin David B *et al.*, 2009; Guo *et al.*, 2010; Patel Sanjay KS *et al.*, 2010; Singh Lakhveer and Wahid, 2015; Kumar G. *et al.*, 2015).

Conclusion

The article suggest that up-to-date knowledge is required for alternative biofuels, i.e. hydrogen and methane production. Cheap lignocellulosic residues and innovative pre-treatment strategies are the primary focus. The best pre-treatment conditions that can improve hydrogen and methane production to be well identified before industrial scale. Optimization of the working conditions and continuous utilization of by-products (VFAs) could further improve H_2/CH_4 process.

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