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Optimum Production Of Bio Hydrogen During Biogas Production From Organic Waste-A Critical Review.

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Abstract

Bioenergy has an important role as alternative energy in socio economic development of a country. Bioenergy is green, renewable and sustainable. It is a process of methane production by four steps which includes hydrolysis, acidogenesis, acetogenesis and methanogenesis . In batch digestion by following the above four steps it is possible to produce both methane and hydrogen. In continuous process of methane production, one type of bacteria can resist the activities of other species and delay the overall process. The bacteria as well as enzyme are specific to PH and temperature. At low PH, hydrogen gas and volatile fatty acid are produced in the step of acetogenesis while at higher pH (alkaline medium), optimum production of hydrogen gas is possible

Keywords: Fossil fuels, Global warming, Biomass, Anaerobic digestion, Bio methane, Bio hydrogen, Volatile fatty acid

1. Introduction

Economic development of a nation depends on the local availability of energy. In the 19th century, most of the energy demands were fulfilled by fossil fuels i.e. coal, petroleum and natural gas but the use of these fossil fuels was maximum [1].The most people of developing countries like India live without reliable energy source and about 240 million people can not access electricity[2]. Presently 80% of the energy demand is fulfilled by the fossil fuels and there is inadequate knowledge of life span of fossil fuel reserves [3].Energy crisis and the climate changes are the key issues all over the world. Socio-economic development of rapidly growing world depends on the supply of a cleaner, greener, renewable and economically feasible source of energy [4-5]. There will be a severe shortage in energy after 50 years. The current research and future prediction state that the crude oil will continue for s 40-70 years and natural gas will be finished within 50 years [6]. Global average temperature is expected to increase 1.4 to 5.8 degree Centigrade by year 2100 and gradually increase after that [7]. Energy crisis and the climate change are the key issues all over the world . Global warming will lead to change the climate by making flood, drought and melting of ice in the cold zone [8-9]. Decomposition of food waste and other waste and the combustion of fossil fuels like coal, oil and natural gas release natural greenhouse gases (mainly carbon di oxide ,methane and others) in the atmosphere [10] . Ruminant can produce 250 to 500 litres of methane per day [1]. Methane has approximately 21 times greenhouse effect than that of carbon dioxide [11].Renewable energy is politically demanded. Biogas is the efficient and effective alternate renewable source of energy currently available among other energy sources. It is produced through anaerobic digestion processes where the micro-organisms break down the complex organic matter to produce carbon di oxide, methane [12]. The anaerobic digestion process is economically feasible in comparison to other renewable energy sources like hydro, solar and wind energy [13].Biogas can be converted to Compressed Natural Gas after enrichment and bottling. As a renewable source biogas can not only be used as cooking, heating, lighting and production of electricity but also used as fuel for vehicles instead of fossil fuel. By anaerobic digestion the greenhouse gas emission is reduced which is more environment friendly [14].Lignocellulosic organic material are highly accepted for anaerobic digestion because of their abundance. .Agro-waste is a specific type of biomass which is produced as a bye-product from agriculture. Bio mass containing protein, fat, carbohydrate, cellulose and hemicellulose are used as substrate for digestion [15]. The anaerobic digestion occurs in four steps. These are hydrolysis, acidogenesis, acitogenesis and methanogenesis. The hydrolysis of lignocellulosic material is the rate limiting step in anaerobic digestion. The hydrolytic enzymes inhibit the penetration into cellulose and hemicellulose due to presence of lignin [16].Many factors affect the digestion but the presence of high lignin is the most problematic factors to affect the digestion of lignocellulosic organic materials [17].The complex physical and chemical structure of the lignocellulosic substrates cannot be completely biodegraded in anaerobic digestion [18].To get the potential yield of biogas and solve the problem some pre-treatment processes can be applied [19].Bio gas free digestion is sensitive to temperature , digester and pH [20].This indicates that the pre-treatment of substrate needs urgently for further investigation.

Production of hydrogen is globally thought by scientist and engineers. It is not economically feasible to produce hydrogen.Hydrogen is the cleanest form of energy with huge calorific value and produces pollutant-free products on combustion. Production of hydrogen from organic waste using batch digestion: reduces pollution, as the combustion of hydrogen evolves high energy with water [21].The global hydrogen demand is 70 million tonnes annually, in oil refining and production of ammonia [22].The second generation cellulose containing biomass like straw, corn cob, molasses, barley straw, sweet potato waste and rice straw is used [23]. During the batch digestion of methane production, low cost hydrogen is generated at higher PH. It can also be generated at lower PH in acetogenesis and the hydrogen production depends on the amount of volatile fatty acid produced. Production of hydrogen biologically is termed as bio hydrogen which is an excellent energy carrier to fulfil the future needs of society [24].Research in hydrogen generation is focussed worldwide [25]. It was found that two types of fermentation usually occurs like butyric acid fermentation at $pH > 6$ [26], and ethanol fermentation at $pH < 4.5$ [27]. Acetogenic fermentation, the major products of the process were butyric acid [28].The present study is to enhance the bio hydrogen generation using heat-treated biogas plant slurry as inoculum with kitchen waste by means of pH control. The value of hydrogen as a heating fuel is calculated on the basis of its heat content and the cost of other fuels. The heating value of hydrogen and methane are 141,790 kJ / kg and 55530 kJ / kg respectively [29]. This is comparable biologically generated energy is an alternate to increasing source of fossil fuel [30]. Acetogenic and methanogen bacteria are responsible for the conversion of organic wastes into methane [31].Fermentative hydrogen generation is achieved by anaerobic acid-forming bacteria like Clostridium sp. or facultative anaerobes such as Enterobacter sp.[32-33].Many studies are used the chemicals like glucose and sucrose, starch as substrate for hydrogen generation [34-36].Maintenance of operating conditions for pure cultures of hydrogen generating bacteria is problematic to large scale anaerobic digestion [37]. The main constraint in bio hydrogen generation using mixed bacteria is the coexistence of methanogens [38].

2. Review of Literature

In the second of 19th century, the more systematic and scientific research was started by France to better understand the anaerobic fermentation process. During their investigation, they detected some micro-organisms which are responsible for the fermentation process. Scientific research into the process of digestion was seen in 1930 when the scientists completed numerous studies to better understand the influencing factors of digestion.

2.1 Physico-chemical parameters influencing bio methane production

Certain operating parameters like PH, operating temperature, pre-treatment, C/N ratio, Volatile fatty acid (VFA), retention time, water content, redox potential ete, are needed to be controlled in order to enhance the performance of biogas generation process.

PH

Micro-organisms are very sensitive to change in PH. Buffering is necessary for the control of pH and it is essential step in the overall operating system. Methanogens are very susceptible for variation in pH rather than other micro-organisms in the microbial community Anaerobic digestion is generally performed under optimum PH for the combined culture ranges from 6.8-7.4 [39] .The observed toxicity under low pH is due to un-dissociated Volatile Fatty Acid (VFA) [40] .The methanogenic activity will slow at pH less than 6.3 and >7.8 and this will inhibit the biogas production process [41] .If the pH of the medium drops below 6, the balance is disturbed and the acid producing bacteria dominates the acid consuming bacteria. In addition, the production of strong ammonia during the degradation of protein may inhibit the formation of methane if the pH exceeds 8 .

Operating temperature

Several physico-chemical factors are considered for obtaining optimum biogas production. The most important physical factor is temperature[42] .In the literature, it is reported that the anaerobic digestion takes place in three different ranges of temperature. These are psychrophilic (10-20°C), mesophilic (20-45°C), and thermophilic (45-68°C). For each temperature range different groups of micro-organisms are identified [43] .Methane producing bacteria are very sensitive to sudden thermal changes. So, drastic change in temperature should be carefully avoided so that abrupt decrease in gas production takes place. The anaerobic degradation process is affected by temperature from kinetic and thermodynamic point of view; the rate and the yield are enhanced with the increase in temperature [44].Technically the rate is extremely slow at the ambient temperature i.e. psychrophilic temperature range. While the mesophilic and thermophilic range is interesting. Higher temperature is very effective for eliminating pathogens and virus (e.g., E. coli, Salmonella etc.). Too high temperature will decrease the metabolic rate of decline due to degradation of enzymes which are created by microbes [45].The methanogens mainly contains with maximum production rate in mesophilic (35-40°C) and thermophilic (55°C) temperature[46-47]. However, anaerobic digestion can take place over a large range of temperature from 10-65°C[48-49].

C/N ratio

The carbon/nitrogen (C/N) ratio represents the relationship between the amount of carbon and nitrogen present in waste materials. Material with different C/N ratios differs widely for the yield of biogas production [50]. Nitrogen present in the feedstock has two benefits: (a) It provide essential element for the production of the amino acid, proteins and nucleic acids and (b) ammonia is produced which is a strong base to neutralise the VFA produced by the fermentative bacteria. If C/N ratio is too high there will not be sufficient N for microbial growth, while if C/N ratio is too low there will be excessive production of ammonia which may result inhibition of methanogens or toxic effect [51-52].For optimum degradation recommended C/N ratio is between 20 and 30 [53-55].

Volatile fatty acids

.High concentrations of VFA such as acetate, propionate and butyrate may lead to inhibition of the methanogens due to its toxicity effects[56-57]. VFA are not only formed through bacterial metabolism during degradation, they are already present in considerable amounts in the influent depending on the type of feedstock. The initial concentration of VFA varies with the type of slurry. Lipids cause problems in anaerobic digestion because of their tendency to promote floating scum and due to possible accumulation of inhibiting degradation intermediates like long chain fatty acids [58].

Retention time

Retention time is the average time needed to complete the decomposition of organic materials. The retention time depends on the type of feed stocks, environmental conditions and waste composition [59].The retention time of waste treated in mesosphilic digester is required15-30 days and 12-14 days for thermophilic digester. The longer substrate is kept in a particular reaction condition, the more complete its degradation will be. The rate of reaction decreases with longer retention time indicates that in an optimum retention will achieve the benefits of digestion in a cost effective way.

Water content

Bacteria collect the available substrates in dissolved form. Therefore, biogas production and water content are depended on each other. Very trace amount of biogas is produced when the water content is below 20% by weight. Biogas production is enhanced with the increase of water content and it becomes optimum at 91-98% water content by weight.

Anaerobic digestion

Anaerobic digestion is a biochemical process in which micro-organisms breakdown biodegradable organic material in the absence of oxygen to produce biogas for energy conversion [60-63].Biogas production is the possible low cost solution to treat the waste [64] .Biogas can be produced in psychrophilic, mesophilic and thermophilic range of temperature [65-67]. Biogas is mixture of methane and carbon dioxide [68] with trace amount of other compounds which can be used to generate heat and/or electricity.. The energy content of biogas with 60% methane content is about 600Btu /cubic ft. while natural gas is 1000Btu / cubic ft .Biogas which produces bioenergy from biomass has advantages over other renewable energies [69-70].Key bye products of anaerobic digestion are solid and liquid bio fertilizers [71-73]. The available nitrogen remains in the treated sludge [74-75]. About 97% pathogens are destroyed in anaerobic digestion. The use of anaerobic digestion during waste management the volume of waste is reduced [76-77] with reduction of odour [78-79] as well as reduction of greenhouse gas emission by methane and carbon dioxide [80]; with the less leakage of nutrient salt to ground and surface water. There are four basic steps involved in anaerobic digestion process which relies on different groups of microbes where complex organic material converts into methane and carbon dioxide [81]. They are hydrolysis, acidogenesis, acetogenesis and methanogenesis .

Hydrolysis

Hydrolysis or depolymerisation is the first step of solubilisation of in soluble organic materials in the anaerobic digestion process [82-83]. Polymeric materials such as lipids, proteins, carbohydrates, lignin, cellulose are hydrolysed into organic molecules such as fatty acids, glycerol, amino acids, sugars by hydrolytic enzyme such as lipase, protease, amylase and cellulase [84] excreted by microbes present in the stage. Hydrolysis can be the rate determining step if the substrate is large molecule. However, the rate limiting law is acetogenesis and methanogenesis if the substrate is readily degradable[85]. Hydrolytic bacteria which hydrolyse the organic materials are facultative anaerobic in nature. The first group of bacteria includes facultative as well as strict anaerobes are Cellulomonas, Bacillus, Eubacteria.

Acidogenesis

Hydrolysed products are further broken into variety of obligate and facultative fermentative micro-organisms during acidogenesis to produce organic acids such as acetic acid, propionic acid, butyric acid, lactic acid, alcohols, hydrogen and carbon dioxide. Acidogenic (acid forming) bacteria e.g., Clostridium, converts sugars, amino acids and fatty acids to the above organic acids, some alcohols, ketones, H_2 and CO_2, The products from acidogenesis step consist of 51% acetate, 19% H2/CO2 and 30% reduced products such as higher VFA, alcohols and lactates[86]. Acetate is the main product of carbohydrate fermentation. The pH of the product is decreased due to production of organic acids. Acidogenesis is the fastest step in the anaerobic digestion of complex organic material.

Acetogenesis

It is the biochemical reaction where simple monomers are converted in the volatile fatty acids (VFA). This is the anacrobic digestion process in which hydrogen gas is generated as a bye-product along with VFA and alcohols. Ethanol, propionic acid and butyric acid are converted to acetic acid by acetogenic bacteria by the following three reaction:

CH3CH2OH + H2O CH3COOH+2H2 (1)

CH3CH2COOH + 2H2O CH3COOH + CO_2 + 3H2-(ii)

CH3CH2CH2COOH + $2H_2O$ 2CH3COOH + $2H_2$- (iii)

The activity of microorganisms during acidogenic anaerobic reactors is studied at mesophilic and thermophilic temperature ranges[87]. Hydrogen producing acetogenic groups of bacteria metabolizes higher organic acids (propionate, butyrate, H_2 etc.), ethanol and certain aromatic compounds (i.e., benzoate) into acetate, Hydrogen, and CO_2[88]. Hydrogen producing acetogenic bacteria are capable of producing acetate and H_2 from higher fatty acids..

Methanogenesis

Methane is produce by the methanogens in the methanogenesis step. Methanogens are divide into two categories: A certain group of acidophilic micro-organisms are called as the acidotrophic bacteria which generate about 70% methane from VFA while the rest 30% methane is produced by the hydrotropic micro-organisms from carbon dioxide and hydrogen[89].

Acetotrophic methanogens are called as the acetoclastic or acetate splitting methanogens which convert acetate into methane and carbon dioxide . Hydrogenotrophic methanogens (i.e., Hydrogen using chemilithotrops convert H_2 and CO_2) to methane.

Liquid hot water pre-treatment

It is one of the hydrothermal pre-treatment methods applied for the pre-treatment of lignocellulose materials since several decades ago. Water under high pressure can penetrate in to the biomass, hydrated cellulose and remove hemicellulose and part of lignin. No addition of chemical is required here.

Microwave-chemical pre-treatment

The microwave-chemical pre-treatment is resulted in a more effective pre-treatment than the conventional heating chemical pre-treatment by accelerating reactions during the pre-treatment process [90]

Thermo chemical treatment

Thermal pre-treatment is a process of heating lignocellulosic materials at certain temperature and pressure to destroy the structure of materials in several thermal pre-treatment techniques by using steam, hot water etc[91]. The main limitation of this technology is the formation of inhibitors such as furfural and soluble phenolic compounds which inhibits the methane formation. In order to minimize the formation of inhibitors external alkali may be added to keep the pH (4-7) [92]. During thermal treatment, lignocellulose is heated at above 150-180°C, parts of lignicellulose will start to solubilize. First the hemicellulose followed by lignin [93]. Thermal pre-treatment is effective for the enhancement of methane production due to thermal hydrolysis. Thermal pre-treatment at 100°C temperature 28% increase of biogas and 25% methane[94].

2.2 Factors Influencing Bio-hydrogen Production

The characteristics of substrates and the factors affecting the process have an important role in the performance of the anaerobic digestion process and can be checked. Changes in the process parameters can lead to termination of the microbial activity and affecting the productivity. The factors affecting the bio-hydrogen production are discussed below:

PH

The pH plays an important role in the generation of bio-hydrogen as it affects the microbial growth, ion concentration, membrane potential and protein synthesis [95]. Controlling the pH to an optimal level helps in suppressing the methanogenic activity which increases the bio-hydrogen production as pH acts as a rate determining factor. A pH between5.5 to 6 is an ideal for production of bio-hydrogen by repressing the bio-hydrogen consumers and promoting bio-hydrogen producers as at higher or lower pH inhibits the hydrogenase activity during fermentation. The optimal pH for bio-hydrogen generation from food residue is between 4 to 5.5, whereas the pH was between 6 to 7 for straw, rice bran and bark [96]. However, the control of pH throughout the fermentation is not economically feasible due to huge necessity of reagents. Generally, the acid production rate is monitored by the pH controlling systems before addition of alkali. When the rate of acid production is slow, it indicates microbial lowering of feed strength due to sporulation and irregular feeding.

Inoculum

The biocatalyst type and the pre-treatment play an important part in efficient fermentation of bio-hydrogen. The main basis in inoculum preparation for starting the acidogenic process is the difference between the hydrogen-consuming and hydrogen-producing bacterial activities. Hydrogen-producing bacteria form spores to protect themselves against extreme acidity, temperature and alkalinity while methanogens lack such capabilities. Pure cultures is used for bio-hydrogen production, they are susceptible to contamination which required aseptic conditions. Mixed cultures are well accepted in industries as they require minimum processing and are cost-efficient [97].

Retention time

Retention time greatly effects the production of bio-hydrogen and other by-products during fermentation. The most commonly used retention time is 72 h whereas the production of bio-hydrogen increases with a decrease in the hydraulic retention time [98]. Bio-hydrogen production is improved after the reduction of the retention time from 20 h to 12 h. Batch digestion studies using chemical, dairy and distillery wastewater showed maximum production with retention time between 0 to 14 h [99].The continuous production of bio-hydrogen was a long retention time of 3 days without any issues related to methanogenesis [100]. The major factors contributing to hydraulic retention time are the substrate type, inocula activity, pH and organic loading rate. Generally, an optimum retention time between 8 to14 h is an efficient bio-hydrogen production [101].

Conclusion

Methane can be decomposed to grapheme (C) and hydrogen. The success of methanogenesis and hydrogen production generate organic manure. The manure can be further treated for vermy compost as well as soil management. Being agricultural based economy; India can fulfil the crisis of energy for future.

Bio hydrogen production technology is a renewable form of energy production with huge benefits such as low energy consumption, mild conditions, no pollution and adaptability to a wide range of raw materials. In addition, hydrogen can significantly replace the current fuel demand due to its applications in power generation, heating and transportation. Although bio-hydrogen has numerous advantages, technological barriers such as storage of hydrogen, up gradation and advancement in fuel cell technology with some drawbacks.

Reference

[1] Armaroli, N., & Balzani, V. (2007). The future of energy supply: challenges and opportunities. Angewandte Chemie International Edition, 46(1-2), 52-66.

[2] Birol, F. (2015). Indian ener outlook. InternationalEnergy Agency, 1.

[3] Balachandar, G., Khanna, N., & Das, D. (2013). Biohydrogen: Chapter 6. Biohydrogen Production from Organic Wastes by Dark Fermentation. Elsevier Inc. Chapters.

[4] Han, S.K. and H.S. Shin (2004). Biohydrogen production by anaerobic fermentation of food waste. International Journal of Hydrogen Energy. 29: 569-577

[5] Holm-Nielsen, J.B., Al Seadi, T.and Oleskowicz-Popiel,P. (2009). The future of anaerobic digestion and biogas utilization, Bioresource Technology, 100(22): 5478-5484

[6] Courtney, B. and Dorman, D. (2003). World Wide Fossil Fuels. Chemistry Department of Louisiana State University, July 11.

[7] Dow, K. and Downing, T. (2006) The Atlas of Climate Change: Mapping The World's Greatest Challenge. Los Angeles: University of California Press.

[8] Mills, D.M.MA. (2009). Climate Change, Extreme Weather Events, and US Health Impacts: What Can We Say? Journal of Occupational and Environmental Medicine 51(1): 26-32.

[9] Sen, Z. (2009). Global warming threat on water resources and environment: a review. Environmental Geology. 57: 321-329.

[10] Jaynes, D. (2010) Global Warming: Myths & Realities. Social Sciences. SOC 461-11.

[11] Wuebbles, D.J. and K. Hayhoe (2002), Atmospheric methane and global change, Earth-Science Reviews, 57: 177-210.

[12] Khanal S.K.(2008). Anaerobic Biotechnology for Bioenergy Production, published by John Wiley & Sons

[13] Rao, P.V., Baral, S.S., Dey, R. and Mutnuri, S. (2010) Biogas generation potential by anaerobic digestion for sustainable energy development in India. Renewable and Sustainable Energy Reviews. 14: 2086-2094.

[14] Rao, P.V., Baral, S.S., Dey, R. and Mutnuri, S. (2010) Biogas generation potential by anaerobic digestion for sustainable energy development in India. Renewable and Sustainable Energy Reviews. 14: 2086-2094.

[15] Weiland, P. (2010). Biogas production: current state and perspectives. Applied Microbiology and Biotechnology, 85(4): 849-860.

[16] Tong, X., Smith, L.H., McCarthy, P.L., (1990).Methane fermentation of selected lignocellulosicmaterials. Biomass 21: 239-255.

[17] Li, Y., Park, S.Y., and Zhu, J. (2011). Solid-state anaerobic digestion for methane production from organic waste. Renewable and Sustainable Energy Reviews, 15(1): 821-826

[18] Rafique R., Poulsen T.G., Nizami A.S., Asam Z.Z., Murphy J.D. and Kiely G., (2010), Effect of thermal, chemical and thermo-chemical pre-treatments to enhance methane production. Energy, 35(12): 4556-4561.

[19] Braun, R. and Wellinger, A. (2002).Potential of co-digestion. Institute of Agrobiotechnology. Dept of Environmental Biotechnology, Lorenz Strasse.

[20] Angelidaki, I. and B.K. Ahring. (1993). Thermophilic anaerobic digestion of livestock waste: The effect ofammonia. Applied Microbiology Biotechnology, 38: 560-564.

[21] Abe, JO, Popoola, API, Ajenifuja, E & Popoola, OM 2019, ‘Hydrogen energy, economy and storage: review and recommendation’, International Journal of Hydrogen Energy, Vol. 44, pp. 15072-086.

[22] Saidi, M, Gohari, MH & Ramezani, AT 2020, ‘Hydrogen production from waste gasification followed by membrane filtration: a review’, Environmental Chemistry Letters, vol. 18, pp. 1529-1556.

[23] Cheng, MH, Dien, BS, Lee, DK & Singh, V 2019, ‘Sugar production from bioenergy sorghum by using pilot scale continuous hydrothermal pretreatment combined with disk refining’, Bioresource Technology, vol. 289, pp. 121663.

[24] Kothari, R., Singh, D. P., Tyagi, V. V., & Tyagi, S. K. (2012). Fermentative hydrogen production–An alternative clean energy source. Renewable and Sustainable Energy Reviews, 16(4), 2337-2346.

[25] Hawkes F.R., Dinsdale R., Hawkes D.L. and Hussy I. (2002), ‘Sustainable fermentative bio hydrogen: Challenges for process optimization’, Int. J. Hydrogen Energy, Vol. 27, pp. 1339-1347.

[26] Cohen A., Van Gemert J.M., Zoetemeyer R.J. and Breure A.M. (1984),‘Main characteristics and stoichiometric aspects of acidogenesis of soluble carbohydrate containing wastewater’, Process Biochemistry, Vol. 19, pp. 228-237

[27] Ren N., Wang B. and Huang J. (1997), ‘Ethanol type fermentation of carbohydrate wastewater in a high rate acidogenic reactor’, Biotechnol. Bioeng., Vol. 54, pp. 428-433

[28] Shin H.S., Youn J.H. and Kim S.H. (2004), ‘Hydrogen production from food waste in anaerobic mesophilic and thermophilic acidogenesis’, Int. J. Hydrogen Energy, Vol. 29, pp. 1355-1363.

[29] Hansel A. and Lindblad P. (1998), ‘Mini-review: Toward optimization of cyanobacteria as biotechnologically relevant producers of molecular hydrogen - A clean energy source’, Appl. Environ. Microbiol., Vol. 50, pp. 153-160.

[30] Cecchi F., Marcomini A., Pavan P., Fazzini G. and Mata Alvarez J. (1989), ‘Mesophilic digestion of the refuse organic fraction sorted by plant performance and kinetic’, Waste Management and Research, Vol. 22, pp. 33-41

[31] Benemann J. (1998), ‘Hydrogen biotechnology: progress and prospects’, Nat. Biotechnol., Vol. 14, No. 9, pp. 1101-1103.

[32] Keasling J.D., Benemann J.R., Pramanik J., Carrier T.A., Jones K.L. and VanDien S.J. (1998), ‘A tool kit for metabolic engineering of bacteria: Applications to hydrogen production’, In. Bio hydrogen, Plenum Press, New York, pp. 87-98.

[33] Das D. and Veziroglu N.T. (2001), ‘Hydrogen production by biological processes: a survey of literature’, Int. J. Hydrogen Energy, Vol. 26, pp. 13-28

[34] Collet C., Adler N., Schwitzguebel J.P. and Peringer P. (2004), 'Hydrogen production by Clostridium thermolacticum during continuous fermentation of lactose', Int. J. Hydrogen Energy, Vol. 29, pp. 1479-1485.

[35] Kawagoshi Y., Hino N., Fujimoto A., Nakao M., Fujita Y., Sugimura S. and Furukawa K. (2005), 'Effect of inoculum conditioning on hydrogen fermentation and pH effect on bacterial community relevant to hydrogen production', J. Biosci. Bioeng., Vol. 100, No. 5, pp. 524-530.

[36] Bisaillon A., Turcot J. and Hallenbeck P.C. (2006), 'The effect of nutrient limitation on hydrogen production by batch cultures of Escherichia coli', Int. J. Hydrogen Energy, Vol. 31, No. 11, pp. 1504-1508.

[37] Veziroglu T.N. and Brbir F. (1992), 'Hydrogen: the wonder fuel', Int. J. Hydrogen Energy, Vol. 17, pp. 391-397.

[38] Sung S., Raskin L., Duangmanee T. and Padmasiri Simmons J.J. (2002), 'Hydrogen production by anaerobic microbial communities exposed to repeated heat treatments', Procs. of the 2002 US DOE Hydrogen Program Review, NREL, pp. 35-44.

[39] Khanal S.K.(2008). Anaerobic Biotechnology for Bioenergy Production, published by John Wiley & Sons

[40] vanLier, J.B., Tilche, A., Ahring, B.K., acarie, H., Moletta, R., Dohanyos, M., Hulshoff Pol, L.W., Lens P. and Verstraete, W. (2001) New perspectives in anaerobic digestion. Water Science and Technology. 43(1): 1-18,

[41] Leitao, R.C., van Haandel, A.C., Zeeman, G., Lettinga, G. (2006).The effects of operational and environmental variations on anaerobic wastewater treatment systems: A review. Bioresource Technology, Vol. 97, pp 1105–1118.

[42] Vindis, P., Muresec, B., Janzekovic, M. and Cus, F. (2009). The impact of mesophilic and thermophilic anaerobic digestion on biogas production. Journal of Achievements in Materials and Manufacturing Engineering, 36(2): 192-198.

[43] Gerardi, M.H. (2003). The microbiology of anaerobic digesters.John Wiley & Sons.

[44] Mata-Alvarez, J., 2003. Fundamentals of the anaerobic digestion process, in: Mata-Alvarez, J., Biomethanization of the organic fraction of municipal solid waste. IWA Publishing, pp. 1-20.

[45] Marchaim, U (1992). Biogas Processes for Sustainable Development. Publications Division, Food and Agriculture Organization of the United Nations, VialedelleTerme di Caracalla, Rome, Italy.http://www.fao.org/docrep/t0541e/t0541e06.htmRetrieved on 25/3/2011

[46]] Mata-Alvarez, J., 2003. Fundamentals of the anaerobic digestion process, in: Mata-Alvarez, J., Biomethanization of the organic fraction of municipal solid waste. IWA Publishing, pp. 1-20.

[47] Khanal S.K.(2008). Anaerobic Biotechnology for Bioenergy Production, published by John Wiley & Sons

[48] Scherer, P.A., Vollmer, G.R., Fakhouri, T. and Martensen, S., (2001).Development of a methanogenic process to degrade exhaustively the organic fraction of municipal

[49] Sternenfels, U.M.C. (2012).Compost Physicochemical Characteristics Influencing Methane Biofiltration.PhD Thesis, Department of Civil Engineering, University of Calgary.

[50] Marchaim, U (1992). Biogas Processes for Sustainable Development. Publications Division, Food and Agriculture Organization of the United Nations, VialedelleTerme di Caracalla, Rome, Italy.http://www.fao.org/docrep/t0541e/t0541e06.htmRetrieved on 25/3/2011

[51] Kayhanian, M. (1994) Performance of a high-solids anaerobic digestion process under various ammonia concentrations. Journal of Chemical Technology and Biotechnology, 59: 349-352.

[52] Hartmann, H. and Ahring, B. K. (2006). Strategies for the anaerobic digestion of the organic fraction of municipal solid waste: an overview. Water Science and Technology, 53: 7-22.

[53] Marchaim, U (1992). Biogas Processes for Sustainable Development. Publications Division, Food and Agriculture Organization of the United Nations, VialedelleTerme di Caracalla, Rome, Italy.http://www.fao.org/docrep/t0541e/t0541e06.htmRetrieved on 25/3/2011

[54] Igoni, H., Ayotamuno, M.J., Eze, C.L., Ogaji., S.O.T. and Probert, S.D. (2007). Designs of anaerobic digesters for producing biogas from municipal solid waste. Applied Energy, 85: 430-438.

[55] Dana, R. (2010). Micro-scale Biogas Production: A beginner's guide National Sustainable Agriculture information service.www.attra.ncat.org.

[56] Angelidaki., I and Ahring, B.K. (1992). Effects of free long-chain fatty acids on thermophilic anaerobic digestion.Applied Microbiology and Biotechnology. 37: 808–812.

[57] Broughton, M.J., Thiele J.H., Birch, E.J. and Cohen, A.(1998). Anaerobic batch digestion.Biotechnology Letters. 3:159–164.

[58] Angelidaki, SP Petersen, BK Ahring (1990) Effects of lipids on thermophilic anaerobic digestion and reduction of lipid inhibition upon addition of bentonite

Applied microbiology and biotechnology 33 (4), 469-472

[59] Ostrem, K. and Themelis, Nickolas J. (2004). "Greening Waste: Anaerobic Digestion for Treating the Organic Fraction of Municipal Solid Wastes" Earth Engineering Center Columbia University

[60] Campos, E., Jordi, P. and Xavier, F. (1999). Co-digestion of pig slurry and organic wastes from food industry. Proceedings of the II International Symposium on Anaerobic Digestion of Solid Waste. Barcelona. Junio pp. 192-195.

[61] Fioresea, G, Guarisoa, G. and Polimeni, A. (2008). International Congress on Environmental Modelling and Software Integrating Sciences and Information Technology for Environmental Assessment and Decision Making. 4th Biennial Meeting of iEMSs. http://www.iemss.org/iemss2008/index.php?n=Main.Proceedings.

[62] Neves, L., Oliveira, R. and Alves, M.M. (2009). Co-digestion of cow manure, food waste and intermittent input of fat. Bioresource Technology. 100:1957–1962.

[63] Vindis, P., Muresec, B., Janzekovic, M. and Cus, F. (2009). The impact of mesophilic and thermophilic anaerobic digestion on biogas production. Journal of Achievements in Materials and Manufacturing Engineering, 36(2): 192-198.

[64] Verstraete, W., Morgan-Sagastume, F., Aiyuk, S., Waweru, M., Rabaey, K., Lissens, G. (2005).Anaerobic digestion as a core technology in sustainable management oforganic matter. Water Science and Technology, 52 (1-2), 59-66

[65] Parker, D.B., Williams, D.L. Cole, N.A. Auvermann, B.W. andRogers, W.J. (2002). Dry Nonheated Anaerobic Biogas Fermentation Using Aged Beef Cattle Manure, ASABE Meeting Paper No. 024142.

[66] Deublein D. and Steinhauser, A. (2008). Biogas from Waste and Renewable Resources. Weinheim, Germany, Wiley-VCH.

[67] Shuler, M.L. and Kargi. F. (2002). Bioprocess Engineering: Basic Concepts. Second Edition. Upper Saddle River, New Jersey. Prentice Hall Inc.

[68] Angelidaki, I. and Ellegaard, L. (2003). Codigestion of manure and organic wastes in centratlized biogas plants; status and future trends. Applied Biochemistry and Biotechnology, 109(1-3): 95-106.

[69] Sreenivas, R.R; Phil, H., Jon, W and Andy R. (2009) Optimizing biogas fermentation using the Taguchi methodology, Institute for Grassland and Environmental Research, North Wyke, Okehampton,

[70] Chae, K.J., Yim, S. K., Choi, K. H., Park, W. K. and Lim, D. K.(2002). Anaerobic digestion of swinemanure:Sung-Hwan farm-scale biogas plant in Korea. Division of AgricultureEnvironment and Ecology, National Institute of Agricultural Science and Technology, Kyungki, Korea.

[71] Buendía, I.M., Francisco, J.F., José, V. and Lourdes, R. (2009). Feasibility of anaerobic codigestion as a treatment option of meat industry wastes. Bioresource Technology 100:1903–1909.

[72] Verstraete, W., Morgan-Sagastume, F., Aiyuk, S., Waweru, M., Rabaey, K., Lissens, G. (2005).Anaerobic digestion as a core technology in sustainable management oforganic matter. Water Science and Technology, 52 (1-2), 59-66

[73] Salminen, E. and Rintala, J. (2002). Anaerobic digestion of organics solid poultry slaughterhouse waste – a review. Bioresource Technology. 83(1):13–26

[74] Verstraete, W., Morgan-Sagastume, F., Aiyuk, S., Waweru, M., Rabaey, K., Lissens, G. (2005).Anaerobic digestion as a core technology in sustainable management oforganic matter. Water Science and Technology, 52 (1-2), 59-66

[75] Molinuevo, B., Ma Cruz G., Ma Cristina, L., Milagros, A.citores. (2009). Anaerobic co-digestion of animal wastes (poultry litter and pig manure) with vegetable processing wastes Agricultural Technological Institute of Castilla and Leon, FincaZamaduenas, Valladolid, Castillaand Leon, Spain.

[76] Buendía, I.M., Francisco, J.F., José, V. and Lourdes, R. (2009). Feasibility of anaerobic codigestion as a treatment option of meat industry wastes. Bioresource Technology 100:1903–1909

[77] Vindis, P., Muresec, B., Janzekovic, M. and Cus, F. (2009). The impact of mesophilic and thermophilic anaerobic digestion on biogas production. Journal of Achievements in Materials and Manufacturing Engineering, 36(2): 192-198

[78] Molinuevo, B., Ma Cruz G., Ma Cristina, L., Milagros, A.citores. (2009). Anaerobic co-digestion of animal wastes (poultry litter and pig manure) with vegetable processing wastes Agricultural Technological Institute of Castilla and Leon, FincaZamaduenas, Valladolid, Castillaand Leon, Spain.

[79] Shih, J.C.H. (1993). Recent development in poultry waste digestion and feather utilization – a review. Poultry Scince, 72: 1617–1620.

[80] ElMahgary, Y. (2009). Modern Technology from Nordic Countries for AD of Industrial Biowaste &WastewaterTreatment. Regional and Industrial Pollution and CO_2Emission.

[81] Speece, R.E. (1996). Anaerobic Biotechnology for Industrial Wastewaters. Nashville, TN, Archae Press.

[82] Shuler, M.L. and Kargi. F. (2002). Bioprocess Engineering: Basic Concepts. Second Edition. Upper Saddle River, New Jersey. Prentice Hall Inc.

[83] Speece, R.E. (1996). Anaerobic Biotechnology for Industrial Wastewaters. Nashville, TN, Archae Press.

[84] Parawira, W., Murto, M., Read, J.S., Mattiasson, B. (2005). Profile of hydrolases and biogas production during two-stage mesophilic anaerobic digestion of solid potato waste. Process Biochemistry, 40 (9): 2945-2952.

[85] Björnsson, L., Murto, M., Jantsch, T.G. and Mattiasson, B. (2001). Evaluation of new methods for the monitoring of alkalinity, dissolved hydrogen and the microbial community in anaerobic digestion. Water Research, 35(12): 2833-2840.

[86] Angelidaki, I., Ellegaard, L., Sorensen, A.H., Schmidt, J.E. (2002). Anaerobic processes. In: Angelidaki I, editor. Environmental biotechnology.Institute of Environment and Resources.Technical University of Denmark (DTU). pp. 1-114.

[87] Liu, W.T., Chan, O.C. and Fang,H.H.P.(2002). Microbial community dynamics during start-up of acidogenic anaerobic reactors, Water Research., 36(13): 3203- 3210.

[88] Zinder E.R. (1998). Conversion of acetic acid to methane by thermophiles. In Anaerobic Digestion, edited by E.R. Hall and P.N. Hobson, pp. 1-12.Procceding of the 5th International Symposium on Anaerobic Digestion, Bologna, Italy

[89] Sowers, K.R. (2010). Methanogenesis, in Encyclopedia of Microbiology – Ecological & Environmental Microbiology, edited by M. Schaechter et al., pp. 265-286, Elsevier, New York, N. Y.

[90] Zhu, H., Stadnyk, A. Béland M.,and Seto P.(2008) Co-production of hydrogen and methane from potato waste using a two-stage anaerobic digestion process, Bioresource Technology, 99(11),5078-5084.

[91] Triantafyllidis K., Lappas A. and Stöcker M. (2013). The role of catalysis for the sustainable production of bio-fuels and bio-chemicals. 608 p. -Elsevier, Amsterdam, The Netherlands

[92] Hendriks, A.T.W.M. and Zeeman, G. (2009). Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresource Technology 100: 10–18.

[93] Bobleter, O. (1994). Hydrothermal degradation of polymers derived from plants. Progress in Polymer Science. 19: 797–841.

[94] Rafique R., Poulsen T.G., Nizami A.S., Asam Z.Z., Murphy J.D. and Kiely G., (2010), Effect of thermal, chemical and thermo-chemical pre-treatments to enhance methane production. Energy, 35(12): 4556-4561.

[95] Chang, H, Zou, Y, Hu, R, Feng, H, Wu, H, Zhong, N & Hu, J 2020, 'Membrane applications for microbial energy conversion: a review', Environmental Chemistry Letters, vol. 18, pp. 1581-1592.

[96] Venkata, MS, Bhaskar, YV, Krishna, TM, ChandrasekharaRao, N, LalitBabu, V & Sarma, PN 2007, 'Biohydrogen production from chemical wastewater as substrate by selectively enriched anaerobic mixed consortia: Influence of fermentation pH and substrate composition', International Journal of Hydrogen Energy, vol. 32, pp. 2286-95.

[97] Kumar, G, Cho, SK, Sivagurunathan, P, Anburajan, P, Mahapatra, DM & Park, JH 2018, 'Insights into evolutionary trends in molecular biology tools in microbial screening for biohydrogen production through dark fermentation', International Journal of Hydrogen Energy, vol. 43, pp. 19885-901.

[98] Abe, JO, Popoola, API, Ajenifuja, E & Popoola, OM 2019, 'Hydrogen energy, economy and storage: review and recommendation', International Journal of Hydrogen Energy, Vol. 44, pp. 15072-086.

[99] Bharathiraja, B, Sudharsana, T, Jayamuthunagai, J, Praveenkumar, R, Chozhavendhan, S & Iyyappana, J 2018, 'Biogas production - A review on composition, fuel properties, feed stock and principles of anaerobic digestion', Renewable vol. 90, pp. 570-582. and Sustainable Energy Reviews,

[100] Rabelo, CABS, Soares, LA, Sakamoto, IK, Silva, EL & Varesche, MBA 2018, 'Optimization of hydrogen and organic acids productions with autochthonous and allochthonous bacteria from sugarcane bagasse in batch reactors', Journal of Environmental Management, vol. 223, pp. 952-63.

[101] Gonzales, RR & Kim, SH 2017, 'Dark fermentative hydrogen production following the sequential dilute acid pretreatment and enzymatic saccharification of rice husk', International Journal of Hydrogen Energy, vol. 42, pp. 27577-83.