Influence of Nutrients Addition for Enhanced Biogas Production from Energy Crops: A Review

Noxolo T Sibiya, Habtom B. Tesfagiorgis, and Edison Muzenda

***Abstract*—** Increased in energy demand due to the increase in population, global industrialization and urbanization has become a serious crisis in the world. Excessive utilization of fossil fuel as a primary source of energy brings about environment pollution, global climate change and health hazard. Therefore, an alternative source of energy, preferably renewable, is needed in order to reduce the dependency on fossil fuels. Biogas production via anaerobic digestion technology has been reported as the best solution for these energy issues and a promising prospect for future use. Its application and production optimization has been widely recommended due to that biogas is sustainable renewable source of energy, eco-friendly and cost effective. Preceding researchers have focused mainly on optimizing the process by studding the mechanical and physical aspects of the process while ignoring biological component of the system. Hence, any factor that affects the growth and metabolic activities of the bacteria responsible for the digestion of the organic matter can limit the biogas production and efficiency of the system. Growth factors such as micro-nutrients and macro-nutrients can have a direct effect on the growth of the microbial biomass and ultimately the biogas production.

***Keywords*—** Biogas, Methane, micro-nutrients, macro-nutrients, trace elements

I. INTRODUCTION

BIOGAS technology via anaerobic digestion is considered today as one of the most popular topics within the field of renewable energy [1]. In fact, biogas is estimated as fourth largest energy producer in the world covering about 10-15% of energy demand globally [2]. In addition, biogas technology provides energy, which is sustainable, renewable and cost effective. Biogas is produced when bacteria convert organic matter to methane gas in the absence of oxygen [3]. Although biogas can be produced easily, numerous researches have shown that the efficiency of methane production can be affected by several factors operating independently and in combination [4], [5]. According to Wilkie *et al.* [6] during AD, mineral nutrients are one of the significant factors for micro-organisms growth and activity. Nges *et al.* [13] reported that the characteristics of crops (grass or maize), including lack of essential nutrient, have resulted to problems such as low methane yields, acidification and process instability during mono- AD of energy crops. Therefore, adequate supplementation of nutrients in the digester is very important for the enhancement of biogas and methane production and process stability [7]. Nutrients are categorized as micro-nutrients and macro-nutrients. In this review, the influence of nutrients on biogas production is presented.

Noxolo T. Sibiya is with the Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Doornfontein, Johannesburg 2028.

H.B. Tesfagiorgis is with the Agricultural Research Council Institute for Industrial Crops (ARC-IIC), Private Bag: X82075. Rustenburg 0300.

E. Muzenda is with the Department of Chemical, Materials and Metallurgical Engineering, College of Engineering and Technology, Botswana International University of Science and Technology, Private Mail Bag 16, Palapye, Botswana, and as well as Visiting Professor at the University of Johannesburg, department of Chemical Engineering, Faculty of Engineering and the Built Environment, Johannesburg, P O Box 17011, 2028, South Africa.

II. MACRO-NUTRIENTS

Microbial metabolic activity during biologic process [8] is highly dependent on macronutrients such as (C, H, N, O and S) [9]- [10]. Microorganism use carbon for cell structure, nitrogen for protein biosynthesis, and sulphur during the methanogenesis phase [8]. According to Banks et al.[10], during AD, CH_4 and CO_2 are mainly the product from the conversion of C, H and O. On the other hand, N and S are normally converted to ammonia and H_2S. Ammonia can be used for process buffering [11]. While excessive amount of N in the feedstock may results in methanogens inhibition, too little may also results in a process destruction due to its insufficiency to meet the required level the growth of micro-organism [14], [15]. Ammonium nitrogen is normally available as ammonia ion HN_3^{+4} and free ammonia (NH_3]; however, the formation of free ammonia component is dependent on the pH level, temperature and total ammonia nitrogen (TAN) (demonstrated in Eq. 1)[16]. Free ammonia is more toxic in comparison to HN_3^{+4}as it can pass through the cell membrane, causing potassium deficiency and proton imbalance [15].

A report by Fernandes *et al*. [18] showed that concentration of TAN in a range of 2.4-7.8 g NH_4-N/L (283-957 mg NH_4/NL did not inhibit the hydrolysis of tribytrrin or cellulose. Strik *et al.* [19] reported the possibility of reducing ammonia by controlling pH value, though biogas production was affected. Furthermore, Rajagopal *et al.*[20] pointed out that a stable and undisturbed anaerobic digestion of material with high ammonia can be achieved by operating the process under controlled pH, temperature, C/N ratio and utilization of acclimatized microflora to higher ammonia concentration set points. FAN of 1.1g/L which resulted in depletion of bacteria growth rate was observed at the pH level of 8 during anaerobic digestion of swine manure [21]. Free ammonia can be calculated using Eq. 6 and Eq.7 [22]

http://dx.doi.org/10.15242/IIE.E1115038

$$FAN = \frac{TAN}{1+10^{(PK_a - pH)}} \text{ ....Eq. 1}$$

$$pK_a = 0.09018 + \frac{2729.29}{T+273.15} \text{ ………………….Eq. 2}$$

Where FAN (NH3) is free ammonia, TAN is total ammonia nitrogen, T is the temperature (^{o}C) , pKa is dissociation constant ammonia ion. TAN in the digester can be predicted by using Bushwell equation (eq 1)[17]. Wang *et al.*, [23] investigated the effect of TAN concentration on solid-state AD of corn stover in a batch reactor at 37^{o}C. These authors observed that methane yield was reduced by 50% at a TAN concentration of 6.0g/Kg. Furthermore, at the concentration of 4.3g/Kg, reduction in the rate of reaction and microbial activities during hydrolysis of cellulose and methanogenesis were detected. Other suggestion on the ammonia concentration and other inhibitors are presented (Table1). Ammonia can be removed or reduced in the digester by using pre-treatment techniques including: Struvite precipitation, biological ammonia oxidation and air stripping etc. Air stripping is a common method used for slurries [24]. The optimal C/N ratio required by micro-organism for methane yield optimization is 20:1-30:1 [8]. High C/N ratio favors ammonia production, while low C/N ratio limits the growth of microorganism [8].

Previous researchers have reported that C/N can be optimized by mixing two or more substrate, one with high carbon content and another with high nitrogen content [11]. Though H_2S inhibition in methanogenesis is not clear, its removal or prevention is recommended for further usage of the product gas, especially if the gas will be used for vehicle fuel. According to Wang and Banks [12], H_2S production can be prohibited by addition of combined trace element with iron and acid (BDP, Kemina kemi AB, Sweden). Diaz et al. [27] divulge that H_2S present in biogas may reduce the lifespan of pipes used to transport biogas by corroding their internal and other installations such as pumps when biogas is utilized as a vehicle fuel. It has also been observed that the presence of 3.5% H_2S in biogas may make it inapplicable for energy recovery without specific treatment [28]. Watson and Watson *et al.* [29] investigated the effect of sulfide on α – glucosidases on starch anaerobic digestion. They reported that addition of sulphate and increasing its concentration decreased the activity of α- glucosidase .In contrast, Li et al. [30] reported that an addition of 500mg/l sulphate on the digester with an MBR and co-substrate (coffer grounds, milk, waste activated sludge) resulted in accumulation of propionic acid being completely degraded to methane, due to the bacteria. Several techniques including oxygen dosing [31], sodium molybate [33] and addition of Fe in the digester have been proven to be suitable for the removal of sulfide.

III. MICRO-NUTRIENTS

Micro-nutrients, also known as trace elements, may be used to improve the AD process performance. Commonly used trace elements include zinc, iron, cobalt, tungsten, and molybenum. According to Chan *et al.* [27], the capability of population to synthesise enzymes is dependent on the bio-availability of trace elements. Though addition of trace elements has been found to optimize the growth of methanogenic bacteria, an excess of their availability in a digester may lead to methane inhibition [34], [35].Therefore, the amount of trace element required for microorganism intake need to be calculated. Table 1 shows nutrients concentration needed by micro-organism for optimal process performance.

Khanal *et al.* [36] reported that the needed trace elements may be estimated using the empirical formula of intact microorganism cell, as shown in eq 3 [36].

$$C_nH_aO_bN_c + \left[n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4}\right]H_2O \rightarrow \left[\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right]CH_4 + \left[\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8}\right]CO_2 + {}_cNH_3 \text{...eq3}$$

TABLE I
MICRO-NUTRIENTS AND MICRO-NUTRIENTS CONCENTRATION SUITABLE FOR MICRO-ORGANISM

Parameter	Concentration of inhibition (g/L)
Volatile fatty acid	>2 (as acetic acid)
	> 6.8 (as overall volatile acids)
Total ammonia nitrogen	1.5-3 (at pH> 7.6)
Free ammonia	0.6
Sulfide	0.25 (as H_2S at pH 6.4-7.2)
	0.09 (as H_2S at pH 7.8 -8.0)
Sulfide	>0.1 (as soluble sulfide)
Calcium	2.5-4.5
	8 (strong inhibitory)
Magnesium	1-1.5
	3 (strongly inhibitory)
Potasium	2.5-4.5
	12 (strongly inhibitory
Sodium	3.5-5.5
	8 (strongly inhibitory)
Heavy metals	
Copper(Cu)	0.0005 (soluble metal)
	0.15*
Cadmium(Cd)	0.15
Iron(Fe)	1.71*
Chromium (Cr^{3+})	0.003
Chromium (Cr^{6+})	0.5
Nickel	0.002

Amongst trace elements, cobalt and nickel has shown positive influence in anaerobic digestion of energy crops including grass silage. Cobalt contains vitamin B_{12}, which is involved in the transferring of methyl during methogenesis [36]. The effect of adding trace element to mono-digestion of grass silage at high organic loading rates was investigated by Wall *et al.* [37]. This was done by comparing two reactors, one operated in mono-digestion and other in co-digestion at the VS of (80% grass silage and 20% dairy slurry) for 65 weeks and trace elements were added for 5weeks. The authors reported higher methane yield in co-digestion reactor compared to mono-digestion reactor. However, they further noted an increase by 12% specific methane yield (SMY) with biomethane efficiency of (1.01) was observed when cobalt, iron and nickel were added into a mono-digestion reactor. Co was further reported to stimulate the acetogenesis and

http://dx.doi.org/10.15242/IIE.E1115038

methanogenes [38]. Pobeheim *et al.* [39] analyzed the impact of Ni and Co on AD of maize silage in semi-continuous reactor. These authors reported that the limitation of Co and Ni results to process instability and biogas production inhibition. Nevertheless, increasing the level of Co upto 0.05mg/kg FM and Ni up to 0.6mg/kg Fm increased the OLR to 4.3 g ODML/d with process being stable and high metabolism of acetic and propionic acid. Although addition of trace elements has been identified as co-factor in AD, overdosing of some trace elements may results in methane inhibition, as some nutrients are stimulatory at low concentration but toxic at high one [40]. Javis *et al.* [40] optimized biogas production from grass clover silage by adding cobalt on the digester. However, they were encountered with a problem of process stability and efficiency when a concentration of cobalt was increased to 0.02mg/l. Furthermore, reduction of these trace elements has been reported to form excessive production of volatile fatty acids (VFAs) such as propionic, acetic acid, butyric and veric acid. These VFAs are regarded as major intermediate product in anaerobic digestion [42]. They are mainly produced during hydrolysis and acedogenises phase [43]. VFA are normally converted to acetate, hydrogen and carbon dioxide, which may be used for methane production, however at high concentration they are capable of causing inhibition in methanogens metabolism [44]. Schmidt *et al.* [40] reported an increase in VFAs production during anaerobic digestion of wheat during Fe, and Ni deficiency. Espinosa *et al*. [41] also observed a reduction of propionic acid (5291mg/l to 251 mg/l) and increased COD removal from 44% to 58 when the digester was supplemented with Fe (100 mg/l), Ni(15 mg/L), Co(10 mg/L) and Mo (0.2 mg/l) during anaerobic degradation of VFA in molasses silage . For this methane was increased from 10.7 to 14.8 l/d (NTP). The excessive accumulation of VFA may cause pH declination [47], [48], which may results in toxicity, reactor failure and consequently a reduction in methane production [48]. Sieger and Banks [50] observe the inhibition of the cellulolytic activity at VFAs concentration of 2g/l and ultimately cellulose hydrolysis decrement.

IV. Conclusion

The impact of nutrients addition in anaerobic digestion of energy crops have been reviewed in this paper. All reviewed papers showed that addition of nutrients enhance biogas production and leads to process stability. The optimal C/N ratio required by micro-organism for methane yield optimization is 20:1-30:1. High C/N ratio favours ammonia production, while low C/N ratio limits the growth of microorganism. Commonly used trace elements include Zinc, Iron, Cobalt, tungsten, and Molybenum, however Cobalt and Molybenum has been reported as the most preferable. Although trace elements are essential for bacterial growth, an overdose of these nutrients may result in methane inhibition. This is attributed to the fact that some trace elements are effective at low concentrations but toxic at higher ones. Therefore, the required trace elements may be calculated by using Bushwell equation (eq 3).

Acknowledgment

This work was supported by a research grant from South African Energy National Development Institute (SANEDI). The University of Johannesburg Global Excellence Strategy is acknowledged for providing Noxolo Sibiya with a bursary.

References

[1] D. Deublein, & A. Steinhauser, "Biogas from waste and renewable resources: an introduction," John Wiley & Sons, 2001.

[2] F. Cherubini, N.D. Bird, A. Cowie, G. Jungmeier, B. Schlamadinger, & S. Woess-Gallasch," Energy-and greenhouse gas-based LCA of biofuel and bioenergy systems: Key issues, ranges and recommendations," *Resources, Conservation and Recycling*. Vol. 53, pp. 434-447, 2009. http://dx.doi.org/10.1016/j.resconrec.2009.03.013

[3] A. Demirbaş, " Biomass resource facilities and biomass conversion processing for fuels and chemicals,"*Energy conversion and management*. Vol. 42, pp.1357-1378, 2001. http://dx.doi.org/10.1016/S0196-8904(00)00137-0

[4] M. Lebuhn, F.Liu, H. Heuwinkel, & A. Gronauer, "Biogas production from mono-digestion of maize silage-long-term process stability and requirements," *Water science and technology*, Vol. 58, pp. 1645, 2008. http://dx.doi.org/10.2166/wst.2008.495

[5] L. Molnar, & I. Bartha, "Factors influencing solid-state anaerobic digestion," *Biological wastes*, Vol.*28*, pp.15-24, 1989. http://dx.doi.org/10.1016/0269-7483(89)90045-1

[6] A. Wilkie, M. Goto, F.M. Bordeaux, & P.H. Smith, (1986). Enhancement of anaerobic methanogenesis from napiergrass by addition of micronutrients.*Biomass*, Vol. 11, pp.135-146, 1986. http://dx.doi.org/10.1016/0144-4565(86)90043-0

[7] J. Clark and F. Deswarte, Introduction to chenicals from biomass, John Wiley & Sons, 2014.

[8] C. Mao, Y. Feng, X. Wang, & G. Ren, "Review on research achievements of biogas from anaerobic digestion,"*Renewable and Sustainable Energy Reviews*, Vol.*45*, pp.540-555, 2015. http://dx.doi.org/10.1016/j.rser.2015.02.032

[9] H. Lindorfer , B. Lenz , D. Banemann & J. Clemens , " Biogas production from agro-industrial waste – Possibilities to improve efficiency"

[10] C.J.B. SONIA HEAVEN, "Optimisation of biogas yields from anaerobic digestion by feedstock type," *The biogas handbook: Science, production and applications*, pp.131, 2013.

[11] R. Rajagopal, D.L. Massé, & G. Singh, "A critical review on inhibition of anaerobic digestion process by excess ammonia," *Bioresource technology*, Vol.143, pp.632-641, 2013. http://dx.doi.org/10.1016/j.biortech.2013.06.030

[12] Z. J. Wang, C.J. Banks, " Report: anaerobic digestion of a sulphate-rich highstrengthlandfill leachate: the effect of differential dosing with FeCl3," *WasteManage*. Res. 24, pp.289–293, 2006. http://dx.doi.org/10.1177/0734242x06065232

[13] I.A. Nges, A. Björn, & L. Björnsson, "Stable operation during pilot-scale anaerobic digestion of nutrient-supplemented maize/sugar beet silage," *Bioresource technology*, Vol.118, pp. 445-454, 2012. http://dx.doi.org/10.1016/j.biortech.2012.05.096

[14] J.L. Chen, R. Ortiz, T.W. Steele, & D.C. Stuckey, "Toxicants inhibiting anaerobic digestion: A review," *Biotechnology advances*, Vol.*32*(8), pp.1523-1534, 2014. http://dx.doi.org/10.1016/j.biotechadv.2014.10.005

[15] O. Yenigün, & B. Demirel, "Ammonia inhibition in anaerobic digestion: a review," *Process Biochemistry*, Vol. *48*(5), pp.901-911, 2013. http://dx.doi.org/10.1016/j.procbio.2013.04.012

[16] K. Koch, M. Lübken, T. Gehring, M. Wichern, & H. Horn, " Biogas from grass silage–measurements and modeling with ADM1," *Bioresource technology*, Vol.101(21),pp. 8158-8165, 2010. http://dx.doi.org/10.1016/j.biortech.2010.06.009

[17] J. Pan, X. Chen, K. Sheng, Y. Yu, C. Zhang, & Y. Ying, "Effect of ammonia on biohydrogen production from food waste via anaerobic fermentation," *International Journal of Hydrogen Energy*, Vol.*38*(29), pp. 12747-12754, 2013. http://dx.doi.org/10.1016/j.ijhydene.2013.06.093

[18] T.V. Fernandes, K.J. Keesman, G. Zeeman, & J.B. van Lier, " Effect of ammonia on the anaerobic hydrolysis of cellulose and tributyrin," *biomass and bioenergy*, Vol.*47*, pp.316-323, 2012.

[19] D. P. B. T. B. Strik, A. M. Domnanovich, & P. Holubar, " A pH-based control of ammonia in biogas during anaerobic digestion of artificial pig manure and maize silage," *Process Biochemistry*, Vol.41 (6), pp.1235-1238, 2006. http://dx.doi.org/10.1016/j.procbio.2005.12.008

[20] R. Rajagopal, D.I. Massé, & G. Singh, " A critical review on inhibition of anaerobic digestion process by excess ammonia," *Bioresource technology*, Vol.143, pp.632-641, 2013. http://dx.doi.org/10.1016/j.biortech.2013.06.030

[21] K.H. Hansen, I. Angelidaki, & B. K. Ahring, "Anaerobic digestion of swine manure: inhibition by ammonia," *Water research*, Vol.*32*(1), pp.5-12, 1998. http://dx.doi.org/10.1016/S0043-1354(97)00201-7

[22] B. Calli, B. Mertoglu, B. Inanc, & O. Yenigun, "Effects of high free ammonia concentrations on the performances of anaerobic bioreactors," *Process Biochemistry*, Vol.40 (3), pp.1285-1292, 2005. http://dx.doi.org/10.1016/j.procbio.2004.05.008

[23] Z. Wang, F. Xu, & Y. Li, "Effects of total ammonia nitrogen concentration on solid-state anaerobic digestion of corn stover," *Bioresource technology*,Vol. 144,pp. 281-287, 2013. http://dx.doi.org/10.1016/j.biortech.2013.06.106

[24] M. Walker, K. Iyer, S. Heaven, & C.J. Banks, " Ammonia removal in anaerobic digestion by biogas stripping: An evaluation of process alternatives using a first order rate model based on experimental findings," *Chemical Engineering Journal*, Vol.178, pp.138-145, 2011. http://dx.doi.org/10.1016/j.cej.2011.10.027

[25] F. Omil, R. Méndez, & J. M. Lema, "Anaerobic treatment of saline wastewaters under high sulphide and ammonia content," *Bioresource Technology*, Vol.54 (3), pp. 269-278, 1995. http://dx.doi.org/10.1016/0960-8524(95)00143-3

[26] V. O'Flaherty, T. Mahony, R. O'Kennedy, & E. Colleran, " Effect of pH on growth kinetics and sulphide toxicity thresholds of a range of methanogenic, syntrophic and sulphate-reducing bacteria," *Process Biochemistry*, Vol.33(5), pp.555-569. 1998. http://dx.doi.org/10.1016/S0032-9592(98)00018-1

[27] J. L. Chen, R. Ortiz, T.W. Steele, & D.C. Stuckey, "Toxicants inhibiting anaerobic digestion: A review," *Biotechnology advances*, Vol.32 (8), pp.1523-1534, 2014. http://dx.doi.org/10.1016/j.biotechadv.2014.10.005

[28] Anonymous, "oxygen, air and nitrate for the microaerobic removal of hydrogen sulphide in biogas from sludge digestion," *Bioresource technology*, Vol.101 (20), pp. 7724-7730. http://dx.doi.org/10.1016/j.biortech.2010.04.062

[29] P. Peu, J.F. Sassi, R. Girault, S. Picard, P. Saint-Cast, F. Béline, & P. Dabert,(2011). Sulphur fate and anaerobic biodegradation potential during co-digestion of seaweed biomass (Ulva sp.) with pig slurry. *Bioresource technology*, Vol.102 (23), pp.10794-10802, 2011. http://dx.doi.org/10.1016/j.biortech.2011.08.096

[30] S. D. Watson, & B. I. Pletschke, "The effect of sulfide on α-glucosidases: Implications for starch degradation in anaerobic bioreactors," *Chemosphere*, Vol.65 (1), 159-164, 2006. http://dx.doi.org/10.1016/j.chemosphere.2006.03.011

[31] Q. Y.Y. Li, W. Qiao, X. Wang, & K. Takayanagi, "Sulfate addition as an effective method to improve methane fermentation performance and propionate degradation in thermophilic anaerobic co-digestion of coffee grounds, milk and waste activated sludge with AnMBR," *Bioresource technology*,Vol. 185, pp.308-315, 2015. http://dx.doi.org/10.1016/j.biortech.2015.03.019

[32] I. Díaz, S.I. Pérez, E.M. Ferrero, & M. Fdz-Polanco, "Effect of oxygen dosing point and mixing on the microaerobic removal of hydrogen sulphide in sludge digesters," *Bioresource technology*, Vol.102 (4), pp.3768-3775, 2011. http://dx.doi.org/10.1016/j.biortech.2010.12.016

[33] D.R. Ranade, A.S. Dighe, S.S. Bhirangi, V.S. Panhalkar, & T.Y. Yeole, "Evaluation of the use of sodium molybdate to inhibit sulphate reduction during anaerobic digestion of distillery waste," *Bioresource technology*, Vol.68(3), pp.287-291, 1999. http://dx.doi.org/10.1016/S0960-8524(98)00149-7

[34] I.A. Nges, F. Escobar, X. Fu, & L. Björnsson, "Benefits of supplementing an industrial waste anaerobic digester with energy crops for increased biogas production.," *Waste management*, *32*(1), 53-59, 2012.

[35] B. Demirel, & P. Scherer, "Trace element requirements of agricultural biogas digesters during biological conversion of renewable biomass to methane," *Biomass and Bioenergy*, Vol. 35(3),pp. 992-998, 2011. http://dx.doi.org/10.1016/j.biombioe.2010.12.022

[36] S.K. Khanal, "Anaerobic biotechnology for bioenergy production," *Iowa: Wiley-Blackwell*. pp.179, 2008. http://dx.doi.org/10.1002/9780813804545

[37] D.M. Wall, E. Allen, B. Straccialini, P. O'Kiely, & J.D. Murphy, "The effect of trace element addition to mono-digestion of grass silage at high organic loading rates," *Bioresource technology*, Vol.172,pp. 349-355, 2014. http://dx.doi.org/10.1016/j.biortech.2014.09.066

[38] L. Florencio, P. Jeniček, J.A. Field, & G. Lettinga, "Effect of cobalt on the anaerobic degradation of methanol," *Journal of fermentation and bioengineering*, Vol.75(5),pp. 368-374, 1993. http://dx.doi.org/10.1016/0922-338X(93)90136-V

[39] H. Pobeheim, B. Munk, H. Lindorfer, & G.M. Guebitz, " Impact of nickel and cobalt on biogas production and process stability during semi-continuous anaerobic fermentation of a model substrate for maize silage," *Water research*, Vol.45(2), pp.781-787, 2011. http://dx.doi.org/10.1016/j.watres.2010.09.001

[40] A. Jarvis, A. Nordberg, T. Jarlsvik, B. Mathisen, & B.H. Svensson, "Improvement of a grass-clover silage-fed biogas process by the addition of cobalt," *Biomass and Bioenergy*, *12*(6), 453-460, 1997. http://dx.doi.org/10.1016/S0961-9534(97)00015-9

[41] T. Schmidt, M. Nelles, F. Scholwin, & J. Pröter, "Trace element supplementation in the biogas production from wheat stillage–Optimization of metal dosing," *Bioresource technology*, Vol.168, pp.80-85, 2014. http://dx.doi.org/10.1016/j.biortech.2014.02.124

[42] A. Espinosa, L. Rosas, K. Ilangovan, & A. Noyola, " Effect of trace metals on the anaerobic degradation of volatile fatty acids in molasses stillage," *Water Science and technology*, Vol.32(12), pp. 121-129, 1995. http://dx.doi.org/10.1016/0273-1223(96)00146-1

[43] Q. Wang, M. Kuninobu, H.I. Ogawa, & Y. Kato, " Degradation of volatile fatty acids in highly efficient anaerobic digestion," *Biomass and Bioenergy*, Vol.16(6), pp.407-416, 1999. http://dx.doi.org/10.1016/S0961-9534(99)00016-1

[44] W.S. Lee, A.S.M. Chua, H.K. Yeoh, & G.C. Ngoh, " A review of the production and applications of waste-derived volatile fatty acids," *Chemical Engineering Journal*, Vol.235,pp. 83-99, 2014. http://dx.doi.org/10.1016/j.cej.2013.09.002

[45] Z. Xu, M. Zhao, H. Miao, Z. Huang, S. Gao, & W. Ruan, " In situ volatile fatty acids influence biogas generation from kitchen wastes by anaerobic digestion," *Bioresource technology*, *163*, 186-19, 2014. ttp://dx.doi.org/10.1016/j.biortech.2014.04.037

[46] L. Yang, & Y. Li, "Anaerobic digestion of giant reed for methane production," *Bioresource technology*, Vol.171,pp. 233-239,2014. http://dx.doi.org/10.1016/j.biortech.2014.08.051

[47] L.Yu, M. Bule, J. Ma, Q. Zhao, C. Frear, & S. Chen, "Enhancing volatile fatty acid (VFA) and bio-methane production from lawn grass with pretreatment," *Bioresource technology*, Vol.162,pp. 243-249, 2014. http://dx.doi.org/10.1016/j.biortech.2014.03.089

[48] W. Zhang, L. Zhang, & A. Li, "Anaerobic co-digestion of food waste with MSW incineration plant fresh leachate: process performance and synergistic effects," *Chemical Engineering Journal*, Vol.259, pp.795-805, 2015. http://dx.doi.org/10.1016/j.cej.2014.08.039

[49] O. Pakarinen, P. Kaparaju, & J. Rintala, " The effect of organic loading rate and retention time on hydrogen production from a methanogenic CSTR," *Bioresource technology*, Vol.102(19), pp.8952-8957, 2011. http://dx.doi.org/10.1016/j.biortech.2011.07.020

[50] I. Siegert, & C. Banks, "The effect of volatile fatty acid additions on the anaerobic digestion of cellulose and glucose in batch reactors," *Process Biochemistry*, Vol.40 (11), pp. 3412-3418, 2005. http://dx.doi.org/10.1016/j.procbio.2005.01.025