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Bio-Alcohol from Anaerobic Co-Digestion of Agriculture and Animal Wastes

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Abstract

Background/Objectives: Efficient management of organic waste is necessary to avoid negative impacts on the environment and highly potential to be converted into biofuel. The objective of this study was to conduct preliminary analysis of organic wastes that used for biofuel production and characterization of bio-liquids produced. **Methods/Statistical Analysis:** Cow dung, pineapple peel, vegetable waste, fish waste and leftover chicken were used in production of methanol from methane system using anaerobic co-digestion method conducted at room temperature, pH 6.4-7.0 for 19 and 30 days in 500 mL of bio-reactor. Gas Chromatography Thermal Conductively Detector (GC-TCD) was used in determination of methane while bio-alcohol formed was detected by High Performance Liquid Chromatography (HPLC). **Findings:** Co-digestion of R2 (cow dung mixed pineapple skin) produced highest methane (23.07% wt), bio-methanol (19.08 g/L), bio-ethanol (51.30g/L) and glucose (35g/L). This study proved that co-digestion of organic wastes able to produce biogas and bio-alcohol better than digestion of only one substrate. **Application/Improvements:** The upgrading stage of bio-liquid produced is required to optimize the yield of the bio-liquid and increasing the productivity in large scale study so that it will be qualified for biofuel application.

Keywords: Bedak sejuk, Cosmetic Powder, Natural Cosmetic, Rice Starch, Safety Evaluation

1. Introduction

Currently high demand of fuel as source energy, greenhouse gases issues and increasing of organic wastes are critical problem that need to be solved[1–3]. Literature review state that 80% of world energy still comes from fossil fuel[4]. The organic wastes or biomass such as cow dung was produced in range 200-300 tonne/day[5] and able to produced 250-500 L CH_4/day[6]. About 70249 tonnes of pineapples wastes produced in year 2008 able to generate 1.8 x 10^{15} MWj of electricity energy[7]. This phenomenon suggested for usage of solid organic wastes from agricultural and farm to generate energy such as bio oil for human need. Besides, the issues of solid wastes management can be solved while reducing the cost of operation. Anaerobic digestion is chosen by the most previous study because the ability to improve stability of the process so that maximum biogas and bio oil will achieve[8,9]. The focus of this paper is to carry out the physical analysis of bio wastes for bio oil production via anaerobic digestion followed by characterization of biogas and bio liquid obtained.

2. Experimental

2.1 Sample Preparation and Physical Analysis

The cow dung was supplied from the Ladang Ternakan Bangi and the organic wastes (vegetables, pineapples, poultry and fish) were supplied by Seksyen 16 Market Bandar Baru Bangi. All samples were dried at temperature 40°C for 2-3 days and grinded until 1-2 mm of the size. Physical analysis of each sample (Moisture (M), Total Solid (TS), Volatile Solid (VS) ash and fix carbon) were

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conducted according to American Society for Testing and Material (ASTM) E949-88 and E897-88 (2004) and National Renewable Energy Laboratory (NREL).

The ultimate analysis of component carbon, hydrogen, nitrogen, sulphur and oxygen were conducted by instrument CHNSO analyzer from Faculty of Forestry Universiti Putra Malaysia. The samples are mixed and label as R1 (cow manure mixed vegetables waste), R2 (Cow manure mixed pineapple skin), R3 (wet leftover, fish and chicken leftover) and R4 (cow manure).

2.2 Anaerobic Co-Digestion

The anaerobic digestion was conducted in 500 mL of conical flask with ratio of organic wastes 1:1 which 2/3 of the flask is filled with samples. This conical flask was closed with rubber stopper that contain two flexible tubes where the first tube for biogas collection while second tube for bio liquid collection. First and second digesters prepared contain of pineapple and vegetable substrate while third digester contain of fishery and poultry wastes where the digestion process was carried out for 18 day before the cow dung was added and left until reached days-30 at room temperature. The pH of wastes mixture was maintained until 6.8-7 by using Natrium Hydroxide (NaOH) solution. The N_2 was purged into the flask before the digestion was started. The biogas sample was collected through water displacement method.

2.3 Analysis of Biofuel

The liquid sample was centrifuged at 8000 rpm for 10 minutes where the supernatant was filtered into vial bottle by using 0.45 µm syringe filter. The instrument of HPLC was used to examine the liquid component presence; 1) Alcohol and glucose under mobile phase 0.005 N sulphuric acid, fix mobile Rezex ROA, RI index detector at temperature 60°C and phase speed 0.6 mL/min 2) Organic acid under 0.0013 N sulphuric acid (mobile phase), fix mobile Rezex ROA, Ultraviolet detector at temperature 40°C and phase speed 0.6 mL/min. The carbohydrate analysis was conducted by using 1 mL supernatant mixed with 1 mL of 5% phenol solution added into 5 mL of sulphuric acid. The biogas component was determined by using Gas Chromatography Thermal Conductivity Detector (GC-TCD) model Hewlett Packard 5890, USA with Carboxen type of column, 30 m x 0.25 mm x 0.10 µm operate at 50°C until 190°C for 10°C/minute.

2.4 Organic Acid

Mobile phase used was 0.0013 N sulphuric acid (H_2SO_4) while fix phase was Rezex ROA. Detector Ultraviolet (UV) used at 40°C and mobile phase velocity 0.6 mL/min.

2.5 Analysis of Biogas

Biogas collected by water displacement method was analyzed by instrument Gas Chromatography Thermal Conductively Detector (GC-TCD) model Hewlett Packard 5890, USA with column carboxen, 30 m x 0.25 mm x 0.10 µm. The instrument was operate at 50°C to 190°C over 10°C/minit and helium was used as the gas carrier.

3. Results and Discussion

3.1 Physical and Ultimate Analysis

Physical data of biomass is shown in Table 1 where the high moisture content of all sample (29.10-46.35%) explained the potential of alcohol product formed while highest VS found in cow dung (4.87%) and chicken waste (4.60%). Value of carbon, hydrogen and nitrogen for each sample are illustrated in Table 2. Vegetables wastes contain high value of element carbon and hydrogen than other wastes, so it highly potential to become bio-oil.

Table 1. Physical analysis data

Sample	M (%)	VS (%)	Ash (%)	FC (%)	Author
Cow dung	35.11	4.87	12.03	47.99	Present
Pineapple skin	46.35	0.43	3.65	49.57	Present
Vegetable waste	29.10	0.87	2.80	67.23	Present
Chicken waste	36.58	4.60	0.71	58.11	Present
Fishery	40.03	0.18	4.11	55.68	Present

The result in Table 3 shows both TS and VS decreased because of usage in digestion by methanogenic bacteria[10]. Value of VS was used to estimate the substrate quantity that potential to form methane[11] while ratio TS/VS indicate the performance of anaerobic digestion and productivity of biogas. The sample R2 give highest value of

TS/VS ratio (5.29) and R1 give lowest TS/VS ratio (2.53) due to high content of lignin presence in the sample affect in slow digestion occur.

Table 2. Ultimate analysis data

Sample	C (%)	H (%)	N (%)	Author
Cow dung	18.67	4.84	2.44	Present
Pineapple skin	16.67	4.96	1.88	Present
Vegetable waste	32.41	8.95	4.91	Present
Chicken waste	15.72	5.06	9.73	Present
Fishery	20.85	6.01	9.03	Present

3.2 Biogas and Methane Production

The production of methane depends on reaction of H_2 and CO_2 where these gases together with acetic acid were consumed by methanogen to form CH_4 and CO_2[12,13]. Microorganism that is responsible to produce CH_4 is obligate anaerobic and very sensitive in changing of surrounding[14]. Note that methanogenic from acetate act as limited rate for wastes that easily hydrolyzed[15]. Biogas product was detected highest in sample R2 (13.17 mL/g substrate), followed by R1 (10.08 mL/g substrate) and R4 (3.88 mL/g substrate). About 23.07% of CH_4 produced by R2 considered highest than samples R4, R3 and R1 while about 5.71% to 14.01% CO_2 was detected in each sample. These CO_2 formed because of dominant hydrolysis, acidogenic and acitogenic phase compare to methanation phase.

3.3 Volatile Fatty Acid (VFA) and Biofuels

Production of VFA such as acetic acid, propanoic acid and butyric acid are high as illustrated in Figure 1 until Figure 4 caused in decreasing of pH value drastically (7 to 4.5). High values of acetic acid compare to butyric and propanoic acid explained the dominant phase of acidogenic that interrupt the methanogenic phase in digester. The highest methanol and ethanol recorded are 19.08 g/L and 51.30g/L in sample R2. Methanol become intermediate for the next biochemical reaction caused this alcohol decreased as the time digestion increased. Note that glucose and ethanol are substance that converted into acetate in third stage of anaerobic phase[16]. Through anaerobic digestion, methanol highly potential to become methane by methanogens under certain circumstance and also required to form acetate and butyric[17].

3.4 Carbohydrate and Glucose

The value of glucose presence indicated the substrate decomposition as the decreasing of glucose value in the samples caused in increasing of acetic acid value and decreasing of pH. Microorganism presence in the digester consumed glucose to form ethanol, propanoic and acetic acid[16,18]. The result of HPLC shows that the fish and chicken wastes through more rapid hydrolysis phase compare to other samples supported by highest production of VFA that sample. The R2 give highest amount of glucose (35 g/L) followed by R4 (7 g/L), R1 (8 g/L) and R3 (2 g/L). The amount of glucose obtained considered higher for maximum product of bio-methanol and bio-ethanol compare to previous study[19–21]. The presence of lignin in dry wastes slow down the process of hydrolysis as lignin decomposition occurs slowly. The data of methanol production by present study are compared with previous study in Table 4 where the difference in the data caused by several factors such as pre-treatment (substrate size), type of digestion and pH controlled.

4. Conclusion

Co-digestion of substrate were form more methane and bio-fuel as proven by this study. The vegetable waste is suitable substrate for co-digest with cow manure because

Table 3. Value of TS/VS and methane production

Sample	TSi (%)	TSf (%)	Reduction (%)	VSi (%)	VSf (%)	Reduction (%)	TS/VS	Methane (%)
R1	12.32	9.20	25.32	4.87	1.02	79.06	2.53	0.69
R2	19.99	7.37	63.13	3.78	0.99	73.81	5.29	23.07
R3	12.05	7.65	36.51	2.94	1.57	46.71	4.10	1.52
R4	11.18	7.21	41.14	2.82	0.78	72.34	3.96	1.64

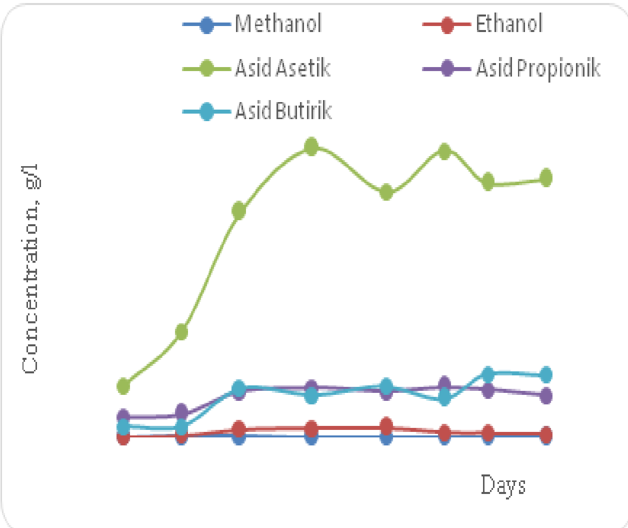

Figure 1. Bio-liquid composition in sample R1.

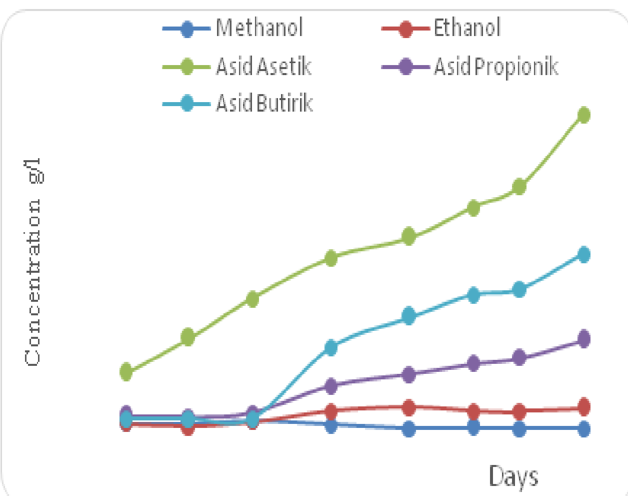

Figure 2. Bio-liquid composition in sample R2.

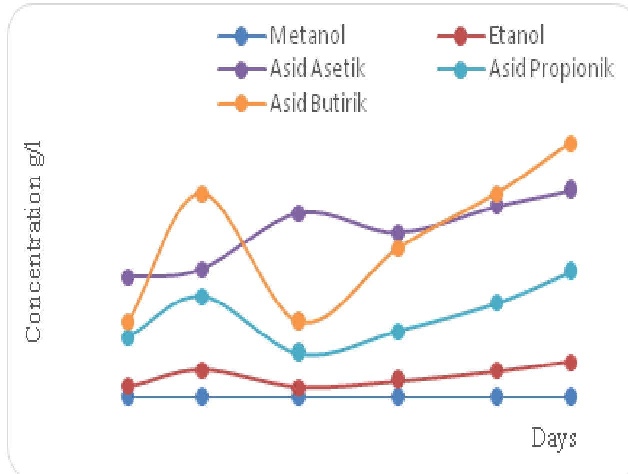

Figure 3. Bio-liquid composition in sample R3.

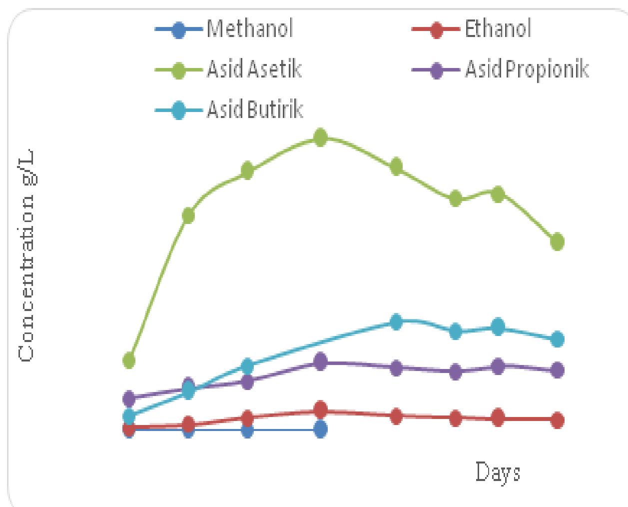

Figure 4. Bio-liquid composition in sample R4.

Table 4. Production of methanol by anaerobic digestion

Reference	Sample	Methanol (%)
Present	Cow manure	0.150
	Cow manure and vegetable waste	0.682
	Cow manure and pineapple waste	0.189
	Cow manure and wet waste	-
[19]	Goat dung	0.940
[20]	Cow manure and Bagasse	1.620
	Cow manure and banana skin	0.040
	Cow manure and leftover rice	1.040
	Cow manure, bagasse, raw glycerine	0.00013
	Cow manure, banana skin, raw glycerine	-
	Cow manure, leftover rice, raw glycerine	0.00010

of its ability to decompose rapidly compare to other substrate. This co-digestion successfully obtained biogas and bio-liquid that highly potential to become biofuel. The upgrading stage of bio-liquid produced is purposed for the future study to optimize the yield of the bio-liquid and increasing the productivity in large scale study.

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6. References

1. Schamphelaire L, Verstraete W. Revival of the biological sunlight to biogas energy conversion system. Biotechnology Bioenergy. 2009 Jun; 103(2):296–304.
2. Shamsul NS, Kamarudin SK, Rahman NA, Kofli NT. An overview on the production of bio-methanol as potential renewable energy. Renewable and Sustainable Energy Reviews. 2014 Apr; 33:578–88.
3. Mekhilef S, Saidur R, Safari A, Mustaffa WESB. Biomass energy in Malaysia, current state and prospects. Renewable and Sustainable Energy Review. 2011; 15(7):3360–70.
4. Goldemberg J, Coelho ST, Nastari PM, Lucon O. Ethanol learning curve - The Brazilian experience. Biomass and Bioenergy. 2003; 26(3):301–4.
5. Omar R, Harun RM, Mohd Ghazi TI, Wan Azlina WAKG, Idris A, Yunus R. Anaerobic treatment of cattle manure for biogas production. Department of Chemical and Environmental Engineering. Universiti Putra Malaysia; 2010.
6. Johnson KA, Johnson DE. Methane emissions from cattle. Journal of Animal Science. 1995 Aug; 73(8):2483–92.
7. Shafie SM, Mahlia TMI, Masjuki HH, Yazid AA. A review on electricity based on biomass residue in Malaysia. Renewable and Sustainable Energy Reviews. 2012 Aug; 16(8):5879–89.
8. Kangle KM, Kore SV, Kulkarno GS. Recent trends in anaerobic co-digestion: A review. Universal Journal of Environmental Research and Technology. 2012 Aug; 2(4):210–9.
9. Tchobanoglous GH, Theisen SA. Integrated solid waste management: Engineering principles and management issues. McGraw Hill International Editions, Civil Engineering Series 6. Singapore: Mcgraw Hill Inc; 1993 Jan.
10. Aragaw T, Andargie M, Gessesse A. Co-digestion of cattle manure with organic kitchen waste to increase biogas production using rumen fluids as inoculum. International Journal of Physical Sciences. 2013 Mar; 8(11):443–50.
11. Wilkie AC. Anaerobic digestion of dairy manure: Design and process considerations. Daily Manure Management Conference. NRAES. 2005 Mar; 176:301–12.
12. Hashimoto A, Chen Y, Varel V. Ultimate methane yield from beef cattle manure: Effect of temperature, ration constituents, antibiotic and manure age. Agriculture Wastes. 1981 Oct; 3(4):241–56.
13. Bitton G. Overview of co-digestion study. Wastewater microbiology. New Jersey, Hoboken: John Wiley and Sons; 2005.
14. Rozzi A, DiPinto AC. Start up and automation of anaerobic digesters with automatic bicarbonate control. Bioresource Technology. 1994; 48:215–9.
15. Mosey FE, Fernandes XA. Patterns of hydrogen in biogas from the anaerobic digestion of milk sugars. Water Science Technology. 1989 Apr; 21(4-5):187–96.
16. Ostrem K. Greening waste: Anaerobic digestion for treating the organic fraction of municipal solid wastes. Earth Engineering Center. Columbia University; 2014.
17. Florencio L, Field JA, Lettinga G. High rate anaerobic treatment of alcoholic wastewaters. Brazilian Journal of Chemical Engineering. 1997 Dec; 14(4).
18. Bilitewski B, Hardtle G, Marek K. Waste Management. New York: Springer; 1994.
19. Shamsul NS, Kamarudin SK. Biosynthesis of methanol from goat manure via anaerobic fermentation. Australian Journal of Basic and Applied Science. 2014 Oct; 8(19):81–3.
20. Anitha M, Kamarudin SK, Shamsul NS, Kofli NT. Determination of bio-methanol as intermediate product of anaerobic co-digestion in animal and agriculture wastes. International Journal of Hydrogen Energy. 2015 Sep; 40(35):11791–9.
21. Shamim RS, Islam SMK, Rafiqul IM, Khaled H, Kamrun N, Roy CK, MdEkhlas U, Choudhury N. Isolation of yeasts from raisins and palm-juice and ethanol production in molasses medium. Indian Journal of Science and Technology. 2016 Mar; 9(12):1–8.