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## Bio Synthesis of Methanol from Goat Manure Via Anaerobic Fermentation

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### ABSTRACT

Bio-methanol production from goat manure fermentation is one of alternative way in order to supply clean fuel and renewable energy that reduces environment problems. The focuses of this study are proximate and ultimate analysis of the sample together with profile of bio-methanol production from goat manure under anaerobic fermentation at 29 °C for 44 days operate in batch bioreactor. Besides, the kinetics parameters show the amount of feedstock used and bio-methanol produced by biomass samples by differences conversion process. The C/N ratio of current study is 21.5:1 while 86.18% of total solid, 12.90% volatile solid, 13.82% moisture and 7.47% ash present by preliminary test of sample. Nutrient content in goat manure can be arranged in sequence of value 2.70 Na>0.37 Ca> 0.19 Cu >0.03 Mg ≥ 0.03 K > 0.02 P > 0.01 Fe (ppm). For maximum methane 65.8%, about 0.909% bio-methanol produced compare than 45.72% methane produced 0.095% of bio-methanol. In addition, this study showed that bio-methanol decreased (0.26% to 0.1%) as methane percentages decreased from 57.31% to 45.72%.

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## INTRODUCTION

There are about 5000 trillion ft<sup>3</sup> of methane escape in the atmosphere which encourage for methane recycling into valuable chemical as methanol (Tamang and Kasipathy, 2010). In addition, high demand for this chemical encourage production in bio synthesis rather than thermochemical which required more energy and high operating cost (Shafie, S.M., 2011). Animal waste show the highest methane escape in Malaysia atmosphere from 1994 to 2004 and goat manure is chosen as raw material as this waste is consist high carbon and total solid value. The focuses of this paper are proximate and ultimate analysis, profile study of methane and methanol and also kinetic parameter study for methanol production.

### Experimental Procedure:

Proximate analysis is performed to determine total solid and moisture content according to ASTM E949-88, while volatile matter and ash content referring to ASTM E897-88 and ASTM E830-87. Instruments EA1112 branded *ThermoFinnigan* located in Faculty of Science and Technology UKM is used to analyze the percentage of elements carbon, hydrogen, nitrogen and oxygen in the sample for ultimate analysis while nutrient content such as phosphorus, magnesium and calcium were analyzed by using Inductive Coupled Plasma (ICP). Anaerobic condition are designed and set up by using invented batch glass bio-reactor (2 Liter) with temperature probe 29°C. About 200g to 400g solid sample used in each test with addition of distillate water then sample remain in the reactor for 44 days where each 4 days of operating time the biogas were collected by using gas bag and liquid product were analyzed. Biogas produced was analyzed by gas chromatographic thermal conductivity detector (GC-TCD) Hewlett Packard 5890 instrument from United State, Carboxen column 30 x 0.25 mm x 0.10 µm film thickness, operating from 50 °C to 190 °C at 10 °C /min with helium as carries gas at initial oven temperature 60 °C. The formation of liquid bio-methanol products are detected by using gas High Performance Liquid Chromatography brand Agilent Technology, 1200 series under condition mobile phase 0.02 M sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), SaX type of column, RI detector with flow rate 0.6 ml/min at temperature 30 °C.

## RESULT AND DISCUSSION

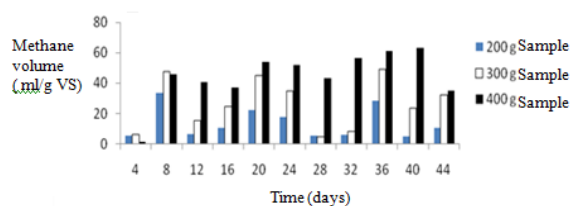
Table 1 below is a result of component for proximate and ultimate analysis that content C (36.16%) and H (6.7%) that should be considered for bio energy production (Tamang and Kasipathy, 2010). The C content of goat manure in this study is considered higher (36.16%) and closed with references by ASAE (2005), 40% who studied in mixed of agricultural and animals waste while about 2% of N consists inside the goat manure (ASAE 2005). The C/N ratio of current study is 21.5:1 which is in the range of suitable 16:1 - 25:1 as mention by other authors (ASAE 2005). About 86.18% of total solid, 12.90% volatile solid, 13.82% moisture and 7.47% ash content inside the goat manure, which are closed with references data. Nutrients are necessary component of microbial cell growth and for synthesis of new cells as well as physicochemical conditions for optimum growth of microorganisms (Khanal, S., 2008). Nutrient content in goat manure can be arranged in sequence of value  $2.703 \text{ Na} > 0.366 \text{ Ca} > 0.193 \text{ Cu} > 0.032 \text{ Mg} \geq 0.032 \text{ K} > 0.024 \text{ P} > 0.009 \text{ Fe}$  (ppm).

**Table 1:** Component of goat manure for anaerobic fermentation.

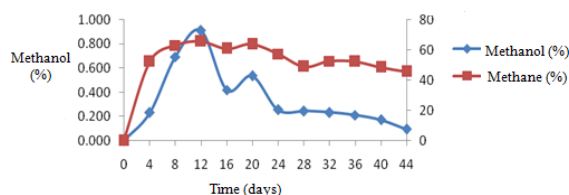
Component	Value	Component	Value
C (% wt)	36.16	Ash (%)	7.47
N (% wt)	2.0	P (ppm)	0.024
H (% wt)	6.7	Mg (ppm)	0.032
O (% wt)	48.4	Cu (ppm)	0.193
C/N	18.08	K (ppm)	0.032
Total solid (%)	86.18	Na (ppm)	2.703
Volatile solid (%)	12.90	Fe (ppm)	0.009
Moisture (%)	13.82	Ca (ppm)	0.366

The maximum volume of methane produced for 200g samples along 44 days is 33.23ml/g VS followed by 49.31ml/ g VS for 300g, and the highest is 63.18 ml/ g VS methane for 400 g samples. The increasing of methane volume is directly proportional to the initial mass of samples used for anaerobic fermentation as shown in Figure 1. The Figure 2 is a profile of methane and bio-methanol produced during 44 days of fermentation at 29°C, show that bio-methanol accumulate for each 4 days are depends on methane amount produced during anaerobic fermentation. For maximum methane 65.8%, about 0.909% bio-methanol produced compare than 45.72% methane produced 0.095 % of bio-methanol. The percentages of bio-methanol decreased (0.256% to 0.095%) for decreasing of methane percentages from 57.31% to 45.72%. Enzyme called methane monooxygenase (MMO) involved in oxidation of methane that content inside of methanotrophs microorganism that able to form bonded membrane (pMMO) and this mechanism required atmosphere oxygen in order to form methanol from methane (Andréa, D.S.R., 2009).

Kinetic parameter studied in Table 2 below show that the authors Gullu & Demirbas (2001) produced 185 kg of bio-methanol/ 1 metric ton solid waste and 1-2% volume or 6 gallon bio-methanol/ ton wood by pyrolysis process. Conversion of biomass to bio-fuel through gasification are the commercial process studied by Hasegawa et al. (2010), Xu et al (2011), Amigun et al. (2010) and Van Ren et al. (2011)]. Bio synthesis methana (30 %) and *Methylosinus trichosporium* IMV 3011 produced  $20 \mu \text{ mol L}^{-1}$  methanol (Xin, J.Y., 2004).



**Fig. 1:** Volume of methane produced for 44 days fermentation.



**Fig. 2:** Methane and bio-methanol produced for 44 days fermentation.

**Table 2:** Kinetic parameter methanol production.

Authors	Process	Source	Kinetic parameter	Percentage (%)
Gullu & Demirbas 2001	Pyrolysis	Solid waste	185 kg bio-methanol / 1 metric ton waste	18.5
		Wood	6 gallon bio-methanol / 1 ton wood	1-2
Hasegawa et al. 2010	Gasification	Wood	510 L methanol / 1 metric ton wood	-
Xu et al. 2011	Gasification	Bio-syngas+ rice husk	1.32 kg/(kg catalyst h) bio-methanol / 120kg/h rice husk oil	1.1
Amigun et al. (2010)	Gasification	Corn waste	6 million ton/yr of bio-methanol / 1.33 ton/ha waste	-
Van Ren et al. 2011	Gasification	Wood	18.237 t h <sup>-1</sup> methanol / 81.540 t h <sup>-1</sup> kayu	22.4
Weimer et al. 1996	Gasification+ electrolysis	CO <sub>2</sub>	200 ton methanol/h from 3.125 x 10 <sup>6</sup> mol CO <sub>2</sub> /h	6.4
Xin et al. 2004	Bio synthesis	Methane : 30 %, CO <sub>2</sub> : 40% O <sub>2</sub> : 30% + <i>Methylosinus trichosporium</i> IMV 3011	20 µ mol L <sup>-1</sup> methanol	-
Present	Fermentation	Methane + oxygen		0.91

**Conclusion:**

The proximate and ultimate analysis had been conducted to show the characteristics of goat manure to become bio-fuel via data of C, H, N, O, total solid, volatile matter, moisture and ash content. It is thought that the amount of bio-methanol increase as amount methane gas produced by goat manure sample increased because of the formation of membrane by methane monooxygenase (MMO) in oxidation of methane to methanol by methanotrophs microorganism.

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