Journal of Environment and Earth Science
ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online)
Vol 2, No.7, 2012

Methanol Production from Cow Dung

Olusegun A. Ajayi[1*] Sam. S. Adefila[2]
1. Department of Chemical Engineering, Ahmadu Bello University, Zaria. Kaduna State. Nigeria
2. Department of Chemical Engineering, Covenant University,Ota. Ogun State. Nigeria
E-mail and telephone of the corresponding author: +2348033175209 and segeaj@gmail.com

Abstract
The amount of agricultural biodegradable wastes generated in Nigeria is constantly on the increase. These wastes are mainly cellulosic materials from reared animal (feaces) and plants. The environmental awareness of most Nigerians is also far better than it used to be in about 30 years back. Accordingly, the paper considers economical use of one of this agricultural wastes-cow dung. The waste was anaerobically digested and acid treated in sequence to produce storable form of alternative energy, while the left over sludge could be used as a good quality farmland fertilizer. The quantities/qualities of methane gas and methanol produced were found to depend on slurry concentration, incubation period, pH value, operating temperature and carbon/nitrogen ratio of the dung. The gas chromatographic analysis conducted indicated that the unrefined biogas was determined to contain 57.23 mol% CH_4, 42.65mol% CO_2, 0.21mol% H_2S, 0.07mol% NH_3 and others. The refined biogas was analyzed and the composition was established to be: 59.45mol% CH_4, 14.65mol% CO_2, 0.11mol% H_2S, 0.04mol% NH_3 and others. This refinement was found to enhance the C/N ratio, making the organic component readily available for the acidic reaction. Spectroscopic analysis of the obtained liquid sample indicated formation of methanol. The purity of methanol produce was determined to be 92.5%, which compared slightly favorably with literature value of 98.9%. The boiling point and heat of combustion were found to compare favorably with literature values. The C/N ratio determined after the demethanization was found to be lower compared to the starting C/N ratio and the gang served as good source of manure.
Keywords- biomass, cow dung, fertilizer, methanol, renewable energy, methane, manure

1.0 Introduction

Biomass is a renewable energy resource derived from the carbonaceous waste of various human and natural activities. It is derived from numerous sources, including the by-products from the timber industry, agricultural crops, raw material from the forest, major parts of household waste and wood and even animal waste. Scientists are trying to explore the advantages of biomass energy as an alternative energy source as it is renewable and free from net CO_2 (carbon dioxide) emissions, and is abundantly available on earth in the form of agricultural residue, city garbage, cattle dung, firewood, etc. One fact which is evident in the literature is that the use of biomass, particularly livestock manure as fertilizer and feed has not grown with the continuously increasing rate of production of the manure itself. For instance, Wadman et al., (1987) pointed out that in the Netherlands, the total production of manure from housed cattle (during the winter period only) pigs, poultry, and fattening calves increased from 10 tonnes/ha in 1950 to 26 tonnes/ha in 1982. Neeteson and Wadman (1990) observed that within that same period however in the same country, the need to use animal manures as fertilizers decreased due to the widespread adoption of cheap inorganic fertilizers. Animal manure holds a tremendous energy potential. According to Kempel (2003), approximately 250million tons of dry feacal material are produced yearly, within U.S. animal agriculture, which is equivalent to 21 billion gallons of gasoline in energy terms.

A report issued by Nigerian National Petroleum Cooperation (NNPC) in 1987, indicated that the total oil reserve as at that year, could only serve the nation for about another 25years or thereabout. Additionally, the current galloping in prices of oil and gases worldwide is gradually eroding the comparative cost advantages of the petrochemicals to sourcing them from renewable sources. Renewable forms of energy under investigation today are solar, geothermal, wind and agricultural sources. It has been well established that animal manure holds a tremendous energy potential and that the level of civilization of a nation is measured by the ability of such nation to utilize all forms of energy in a safe and economical manner.

According to Akinbami et al., (2001), Nigeria produced about 227,500 tons of fresh animal waste daily. The paper noted that since 1kg of fresh animal waste produces about 0.03 m^3 of biogas, then Nigeria can produce about 6.9 million m3 of biogas every day. In addition to all this, 20kg per capita of municipal solid waste (MSW) has been estimated to be generated in the country annually. Going by the census figures 140 million inhabitants, the total generated MSW would be at least 2.8 million tonnes every year. With increasing urbanization and industrialization, the annual MSW generated will continue to increase. Biogas production can therefore be a profitable means of reducing or even eliminating the menace and nuisance of urban waste in many cities by recycling them; while at the same time contributing towards providing adequate solution to the seemingly intractable problem of energy security. In addition, some recent surveys viz-a-viz findings by Methanol Holdings

(Trinidad) Limited (2005) and Methanol Institute (2003) showed that about 186 gallons of methanol can be produced from one ton of biomass feedstock.

In many parts of the developing world, cow dung is used as a fertilizer, fuel, insect repellent, thermal insulator and as sealant for smokeboxes on steam locomotives. Cow dung is also an optional ingredient in the manufacture of adobe mud brick housing depending on the availability of materials at hand (Gobar gas, 2000 and www.answers.com/topic/cow-dung, 2007). In recent times, the dung is collected and used to produce biogas to generate electricity and heat. The gas is a rich source of methane and is used in rural areas of India and elsewhere to provide a renewable and stable source of electricity. Cow dung gas is 55-65% methane, 30-35% carbon dioxide, with some hydrogen, nitrogen and other traces. Its heat value is about 600 B.T.U.'s per cubic foot. Cow dung slurry is composed of 1.8-2.4% nitrogen (N), 1.0-1.2/a phosphorus (P_2O_5), 0.6-0.8%, potassium (K_2O) and from 50-75% organic humus. About one cubic foot of gas may be generated from one pound of cow manure at 75 F. This is enough gas to cook a day's meals for 4-6 people. About 225 cubic feet of gas equals one gallon of gasoline. The manure produced by one cow in one year can be converted to methane which is the equivalent of over 50 gallons of gasoline (www.iscowp.org, 2007).

Methane, a major constituent of biogas has found numerous applications in virtually all the facet of life. Despite this, methane is definitely more deleterious to the environment than the widely feared CO_2. The Environmental Protection Agency uses a statistic called Global Warming Potential (GWP) to measures how much heat one molecule of a gas will trap relative to a molecule of carbon dioxide. Methane has a GWP of 21, which means it's 21 times more effective at preventing infrared radiation from escaping the planet. So, although methane emissions may be relatively piddling, they're definitely a cause for concern. Their one saving grace is an atmospheric lifetime of just 12 years, versus between 50 and 200 years for carbon dioxide (Koerner, 2007). Aside its environmental challenges, methane is difficult to store. In the past, it was typically used as energy sources by immediately combusting it in a generator for the production of electricity. The difficulties in marketing, storing and its negative impact on the environment made its application to be considered as being enviro-economically unfriendly and unfeasible.

Among the different candidate products of methane conversion, methanol (CH_3OH) is probably the one which is recently attracting more interest. Methanol was first produced from pyrolysis of wood, resulting in its common English name of wood alcohol. Presently, methanol is usually produced using methane (the chief constituent of natural gas) as a raw material. It may also be produced by pyrolysis of many organic materials or by Fischer Tropsch from synthetic gas, so be called biomethanol. Production of methanol from synthesis gas using biomass-to-liquid can offer methanol production from biomass at efficiencies up to 75%. Widespread production by this route has a postulated potential, to offer methanol fuel at a low cost and with benefits to the environment. Besides, methanol is recommended as a component of motor fuel and also in the production of high-octane additives to fuels (Smith et al, 1992). Leading nations in this technology are China, who has advanced from the use of covered lagoons to high capacity modern biodigesters (Koerner, 2007 and Kempel, 2003) and United State of America with current production capacity in excess of 1.2 billion gallons of methanol per year (Fry, 2006). Recently, design of an economical bioreactor for biomass was reported by Ačai and Polakovič (2007) and Wilkie et al, (2004) proving the importance and advancement in this process.

Methanol has a high octane rating (RON of 107 and MON of 92), which makes it a suitable gasoline substitute. It has a higher flame speed than gasoline, leading to higher efficiency as well as a higher latent heat of vaporization (3.7 times higher than gasoline), meaning that the heat generated by the engine can be removed more effectively, making it possible to use air cooled engines. Besides this, methanol burns cleaner than gasoline and is safer in the case of a fire. However, methanol has only half the volumetric energy content of gasoline i.e.8,600 BTU/lb (Wilkie et al, 2004).

The direct oxidation of methane to an easily transportable liquid such as methanol has attracted great experimental and theoretical interest due to its importance as an industrial process and as the simplest model for alkane oxidation. Although no direct, efficient methane-methanol conversion scheme has yet been developed, significant advances have been made using iron-containing catalysts. Wang and Otsuka (1994) have studied the direct oxidation of methane to methanol using an $FePO_4$ catalyst and N_2O and H_2/O_2 as the oxidizing agents. Despite the high catalytic selectivity obtained for methanol production, the reaction yield is low. Other approaches that have achieved modest success include direct oxidation by nitrous oxide in plasma, oxidation of methane to a methyl ester with a platinum catalyst, and direct methane-methanol conversion using an iron-doped zeolite (Metz, 2009). However, there is no information in the open literature on non-catalytic conversion of methane (sourced from cow dung) into methanol.

Accordingly, this paper presents preliminary findings from direct production of methanol from cow dung with the goals of developing the technology locally, mitigating its environmental effects and probable use of the spent slurry (here termed gang) obtained from the dung as fertilizer.

2.0 Methodology

The following procedures were employed in the production of methanol from cow dung.

2.1 Sample Collection and Treatment

The cow dung was collected from the Faculty of Veterinary Medicine, Ahmadu Bello University, Main Campus, Zaria, Nigeria. It was sun dried, pulverized and sieved to a desired particle size less than 1mm. The carbon-nitrogen ratio of the dung was experimentally determined, using the Kjeldahl test method. The moisture content, total solid, pH, loss of ignition and volatile contents were also determined. The treated sample was stored in a vacuumed dry place to preserve the pre-determined parameters.

2.2 Slurry Preparation and Gas Collection

Slurry concentrations of 60g/l and 80g/l, using potable water, were prepared from the already treated cow dung. The pH of the slurry was adjusted to 7.1. The slurries prepared were later transferred separately into a four-liter size batch digester, where it was subjected to anaerobic digestion and agitated on daily basis, as suggested by Metz (2009), Kalia and Singh (2001), Baere (1999) and An and Preston (1999). The cow dung slurry became swollen by the formation of internal biogas bubbles during the fermentation process. Evolution of gases was monitored within six days of microbial action on the cow dung by means of a locally fabricated and calibrated gas collecting devise. Thus, establishing the total amount of gas produced from any given batch, over the period.

2.3 Gas Purification

Biogas is a mixture of gases like CH_4 and CO_2 with other trace gases such as H_2S, N_2, and NH_4 etc, depending on feed stock (Stewart, 1980), hence the need for its purification. Gas chromatographic analysis was carried out on the produced and purified biogas. Substantial amount of the biogas produced was transferred into a tubular reactor containing reagents through capillary connected to an inverted calibrated gas collector. The biogas was passed over NaOH, to remove CO_2 and was later allowed to flow over alkaline pyrogallol solution, in order to remove any free oxygen present in the formed gas. The hydrogen sulphide component was removed from the biogas by passing it over iron filling contained in a third reactor in series. The next reactor containing calcium chloride was used to absorb water vapour resulting in formation of dehydrated methanol.

2.4 Methane Conversion

The purified methane gas produced was reacted with weak sulphuric acid, in place of SO_3 or Marshall's acid radical, to form methane-sulfonic acid (MSA) as detailed by other authors, namely: Norddahl (2000), Richards (2004) and Mukhopadhyay and Bell (2004 a & b). The produced MSA was subjected to heat, to obtain methanol and sulphur IV oxide. The SO_2 was later passed over water to form H_2SO_3 acid, which was reintroduced insitu into the system. The other expected competing products formed along with MSA namely methyl-methane sulfonate (MMS) and dimethyl ether (DME), as shown in the reaction scheme, are also known to boost the yield of methanol via hydrolysis. This hydrolysis stage was achieved by introducing water and sulphuric acid in excess, which also facilitated the production of sulphonic acid. The reactions taking place are presented as:

$$H_2SO_4 + CH_4 \rightarrow CH_3SO_3H + H_2O$$

$$CH_3SO_3H \rightarrow CH_3OH + SO_2 \qquad (Selective)$$

Additionally,

$$2CH_3SO_3H \rightarrow CH_3SO_3CH_3 + H_2O + SO_2$$
$$(Non-Selective)$$

$$2CH_3SO_3H \rightarrow 2CH_3OCH_3 + 2SO_2 + H_2O$$
$$(Non-Selective)$$

$$CH_3OCH_3 + H_2O \rightarrow 2CH_3OH$$

The presence of methanol in the sample was done using infrared spectrophotometer, before further treatments and investigation, as represented in Figures 1. The expected peaks were compared with a control, i.e. commercial methanol, to show the characteristic bands used in identifying the presence of methanol.

2.5 Determination of Methanol Properties

The boiling point of the sample and the heat of combustion of methanol produced were experimentally determined using the method detailed by Chaco (1993). The weight percent of alcohol (assumed to be mainly methanol) contained in a unit volume of sample was determined using the open flame combustion method. This method employed the principle that only the alcoholic content in the sample would be combusted while the left over is mainly water content. The analysis assisted in ascertaining the purity of methanol produced.

2.6 Determination of Fertilizing Properties of the slurry

It is imperative to establishment the usefulness of the slurry left after the digestion process and also to ascertain the environmental friendliness of the slurry. The carbon/nitrogen ratio and pH for the gang were determined and the result obtained is shown in Table 2. The gang was used to fertilize tomato plant, in order to confirm its application as fertilizer for plants. Undigested cow dung was also used for fertilization of tomato plant, while another plant was allowed to grow with and without the addition of commercial organic fertilizer.

3.0 Discussion of Results

The composition of cow dung shown in Table 1 tends to compare favorably with those in the open literature.

The spectroscopic analysis of the liquid product shown in Figure 1 gives a strong band around 3000cm^{-1}, which is attributed to C-H stretch of alcohol. The group frequency between 1231cm^{-1} and 1453cm^{-1} noticed in the spectra correspond to strong O-H bond of alcohol. The band noticeable between 1046cm^{-1} and 1190cm^{-1} was attributed to strong C-O stretch in alcohols. The irregularity noticed around the bands aforementioned, was assumed to be as a result of the presence of competitive products like MMS and DME, mentioned in section 2.4. This irregularity in band was not noticed in the spectra of known methanol analyzed along with the sample, as represented in Figure 1. The characteristic band for OH group in alcohol at 3300cm^{-1} was not noticed at all in both samples but band at 1050cm^{-1} attributed to CH_3 group was noticed. In conclusion, the produced methanol had all the required bands to confirm its successful production from cow dung.

The gas chromatographic analysis conducted indicated that the unrefined biogas was determined to contain 57.23 mol% CH_4, 42.65mol% CO_2, 0.21mol% H_2S, 0.07mol% NH_3 and others. The refined biogas was analyzed and the composition was established to be: 59.45mol% CH_4, 14.65mol% CO_2, 0.11mol% H_2S, 0.04mol% NH_3 and others. This refinement was found to enhance the C/N ratio, making the organic component readily available for the acidic reaction.

The boiling point of the product was found to be 79.3^{0}C, which differs significantly from literature value of 64.7^{0}C for pure methanol. The difference in the values was attributed to the presence of impurities, resulting from the colligative property effect. The heat of combustion was obtained to be 701kJmol^{-1}, which was a little lower than the literature value of 726.3kJmol^{-1}. The discrepancy between the results and literature values, could be attributed to either or combinations of these factors: modification made on the equipment, property and quality of fuel used in the burner and more importantly on law of liquid mixture (methanol and impurities composite). From the open flame combustion test, it was observed that 92.5 vol. % of the sample was completely combusted, while 7.5 vol. % was left. This inferred that the produced methanol is about 92.5% pure, if we assume that all other impurities are non-combustible.

Figure 2 presents the amount of gas and methanol produced from 60g/l solution of cow dung. The gas and consequently, the methanol production increase as a result of continuous effect of microbial action on the dung, as shown in figure 2. The drop in methanol production that peaked at 146hrs of incubation may be as a result of reduction in reagent's level needed to facilitate the methane conversion. This is assumed because the pretreatment reagents (NaOH, $CaCl_2$ and pyragoll and iron filling) were not changed at the course of this experiment. Additionally, the available (digestible) carbon on which the microbial is acting might have almost been used up for methanol production. The increase in side-product formation leads to increase in the rate and quantity of biogas formed and subsequently, methanol.

Figure 3 shows the volume of gas and methanol obtained from 80g/l solution of cow dung. The amount of gas produced increased simultaneously with the amount of methanol derived. The gas production peaked at 149hrs showing reduction in activity of microbial action. Here the amount of methanol produced remained almost constant between 147hrs and 150hrs. The pretreatment reagents were refreshed and the conversion continued to be higher than gas produced, though the total volume of methanol drop as a result of sharp drop in gas production. This is an indication of the efficiency of the purification processes and hence conversion.

Figure 4 compares the rate of methanol production as a function of slurry concentration and retention time. It can be seen from the figure that the rate increased with higher concentration. Similar observation was made by Andrew (1982). The rate of methanol production was observed to increase faster at the beginning of the reaction, i.e. 144 to 146 hrs, for slurry concentration of 60g/l. This was noticed to later increase with respect to the higher concentration 80g/l.

Though not part of this work, but the spent slurry (here termed gang), was found to serve as a better replacement for synthetic fertilizer. The tomato grown using undigested cow dung and that with digested one, indicated little or no difference in appearance, taste, growth and texture. This shows that despite the pretreatment of this waste, the gang was still found useable. The C/N ratio for the already used and de-methanized cow dung was found to be low, indicating it being rich in nitrogen content and lean in carbon (Koerner, 2007 and Andrew, 1982), as depicted in Table 2. This test proves that part of the carbon content in the starting material had been consumed and employed in the methanol production.

4.0 Conclusion

This work shows that direct production of methanol from cow dung without the use of catalyst is possible. The rate of methanol production increases with increase in slurry concentration and retention time. The effect of microbial action on the dung reduces continuously throughout the reaction period, indicating reduced activity of the organism and hence reduction in yield. The findings in this work also that spent cow dung could be reuse for the purpose of fertilizing plants.

5.0 References

Ačai, P. and M. Polakovič (2007). Design of a large-scale surface-aerated bioreactor for biomass production using a VOC substrate. Journal of Biotechnology, Volume 132, Issue 2, pp 149–155

Akinbami, J.F.K; Ilori, M.O; Oyebisi, T.O; Akinwumi, I.O. & Adeoti, O. (2001). Biogas Energy Use in Nigeria. Renewable and Sustainable Energy Review. Vol. 5, pp. 97-112.

An, B. X. and Preston, T R. (1999). Gas production from pig manure fed at different loading rates to polyethylene tubular biodigesters. Livestock Research for Rural Development, Volume 11, Number 1

Andrew G. H. (1982). Methane from cattle waste-Effect of temperature and influent substrate concentration on kinetic parameter (k). Biotechnology and Bioengineering, vol.XXIV, pg. 2039-2052

Baere L de. (1999). Anaerobic digestion of solid waste-State of the art. Second Symposium on Anaerobic Digestion of Solid Waste. Barcelona, 15-17 June.

Chaco A.E.(1993). *Laboratory Course in Organic Chemistry,* Basic University Chemistry Series, Benin City, Nigeria.

Cow dung obtained from http://www.answers.com/topic/cow-dung-1 assessed on 4/14/2009

Fry, L.T. (2006). Methane digesters for fuel gas and fertilizer, adapted on 24th June, from www.journeytoforever.org/biofuel_library

Gobar gas -methane experiments in India, assessed via www. green-trust.org/2000/biofuel/methane.html

Kalia,A.K. and Singh, S.P. (2001). Effect of mixing digested slurry on the rate of biogas production from dairy manure in batch fermenter. Energy Sources, 23, 711-715

Kempel, T. (2003). The Utah manure-to-energy project. Published by Swine News-North Carolina Cooperative Extension Service, vol.26 No:7

Koerner, B.I. (2007). The other greenhouse gases. Is methane really worse for the environment than carbon dioxide". The Green Lantern, adapted from www.slate.com

Marchaim, U. (1992). Biogas Processes for Sustainable Development. FAO Agricultural Services Bulletin 95. Food and Agricultural Organization of the United Nations.

Methanol Holding (Trinidad) Limited accessed on www.ttmethanol.com, 2005

Methanol Institute accessed on www.methanol.org, 2004

Metz, R.B. (2009). Methane-to-methanol conversion by gas-phase transition metal oxide cations: experiment and theory, assessed on 24th January via www.chem.umass.edu

Mukhopadhyay, S. and Bell, A.T. (2004a). Catalyzed sulfonation of methane to methanesulfonic acid" . Journal of Molecular Catalysis A: Chemical 211 59–65

Mukhopadhyay, S. and Bell, A.T. (2004b). Direct Sulfonation of Methane to Methanesulfonic Acid by Sulfur Trioxide Catalyzed by Cerium(IV) Sulfate in the Presence of Molecular Oxygen. Adv. Synth. Catal., 346, 913-916

Neeteson, J. J. and Wadman, W.P. (1990). Ammonia Volatilization and Nitrate Leaching after Animal Manure Application to Agricultural Crops. Proceed. Of the 6th International Symp. On Agricultural and Food Processing Wastes. ASAE, St. Joseph, MI, USA, pp 148–157.

Nigerian National Petroleum Cooperation (NNPC) News Bulletin, April 1987

Norddahl B. R. (2000). The BIOREK concept for the conversion of organic effluent to energy, concentrated fertilizer and potable water. First World Conference: Biomass for Energy and Industry, Seville, 5-9 June.

Richards, A. K (2004). Anhydrous conversion of methane and other light alkanes into methanol and other derivatives, using radical pathways and chain reactions with minimal waste products. WIPO Patent Application WO/2004/041399 (Application Number: PCT/US2003/035396)

Scott, C.D (1984). Generation of methane from cattle waste. Fourth on Biotechnology and Bioengineering in energy production and conversion, Biotechnology and Bioengineering symposium, No 12, Interscience publication, John Wiley and Sons, N.Y

Smith, W.H., Wilkie, A.C and Smith, P.H. (1992). Methane from biomass and waste- a program review TIDE 2(1) 1-20

Uses for cow dung adopted from www.iscowp.org assessed on 20th Oct, 2007

Wadman, W.P; Sluijsmans, C.M.J. & De la Cremer, L.C.N. (1987). Value of Animal Manure: Changes in Perception. In: Animal Manure on Grassland and Fodder Crops. Fertilizer or Waste? H.G. Van der Meer, R.J. Unwin, Martinus Nijhoff Public,Dordrecht. pp 1-6.

Wang, Y and K. Otsuka, (1994). J. Chem. Soc. Chem. Commun. **1994**, 2209

Wlikie, A.C., Smith, P.H and Bordeaux, F.M. (2004). An economical bioreactor for evaluating biogas potential of particulate biomass. Bioresource Technology 92,103-109.

TABLE 1: COMPOSITION OF COW DUNG

Parameter	Moisture (%)	Ash (%)	C/N	Total volatile solid (%)	pH
Cow dung	27.9	33.25	30.3	81.5	6.9

TABLE 2: COMPOSITION OF SPENT COW DUNG SLURRY

Parameter	Moisture (%)	Ash (%)	C/N	Total volatile solid (%)	pH
Gang	Not determined	Not determined	21.8	Not determined	7.5

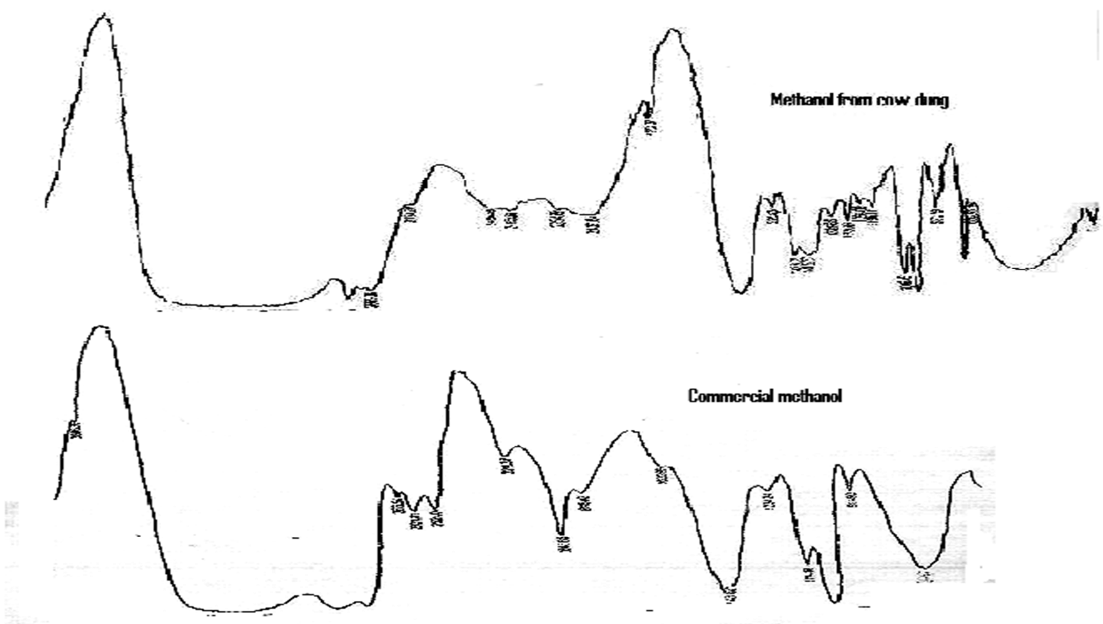

Figure 1: IR Spectra of methanol from cow dung and commercial methanol

Journal of Environment and Earth Science
ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online)
Vol 2, No.7, 2012

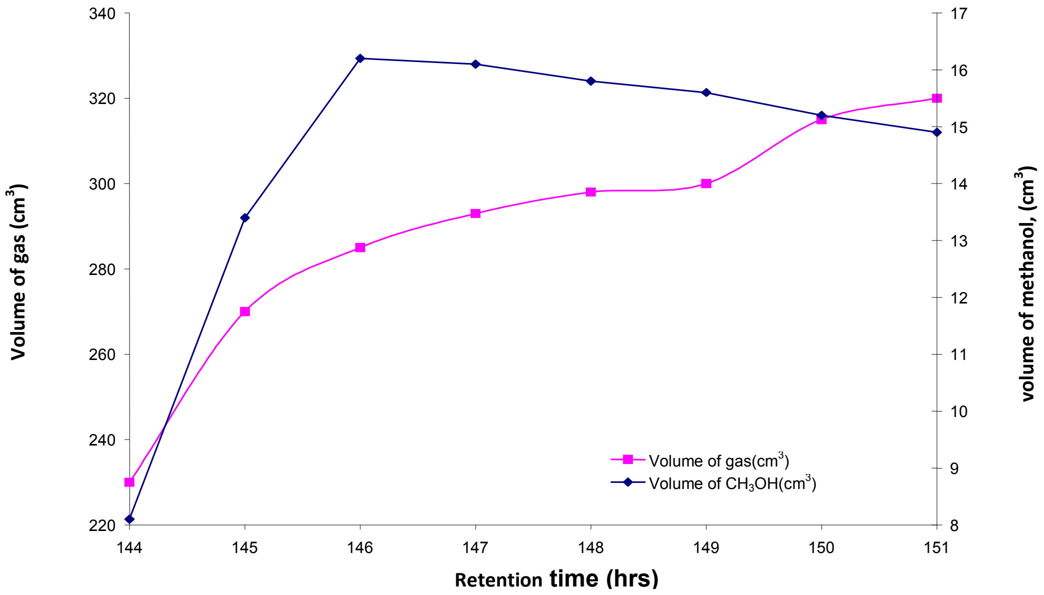

Figure 2: Volume of gas and methanol produced from 60g/l slurry as a function of retention time

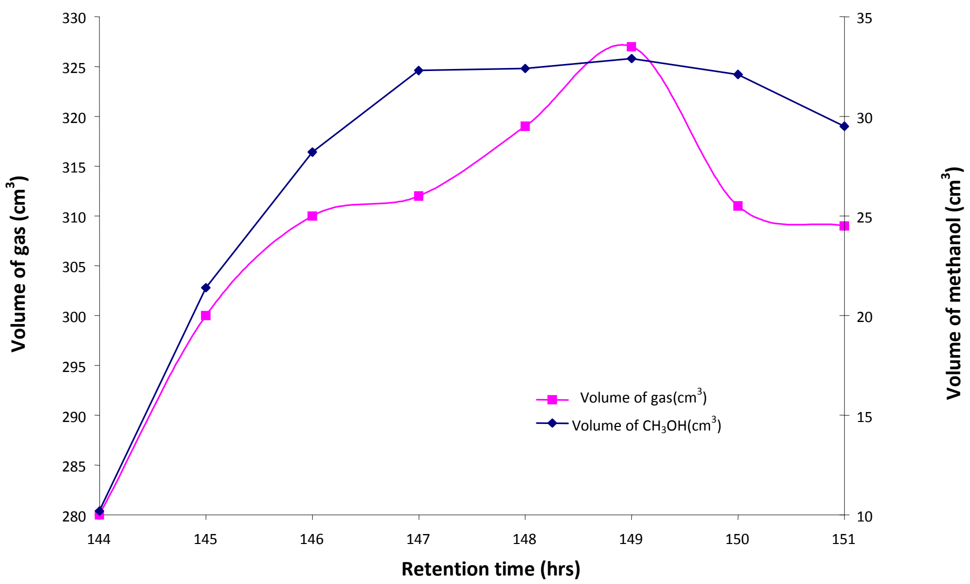

Figure 3: Volume of gas and methanol recovered from 80g/l slurry as a function of retention time

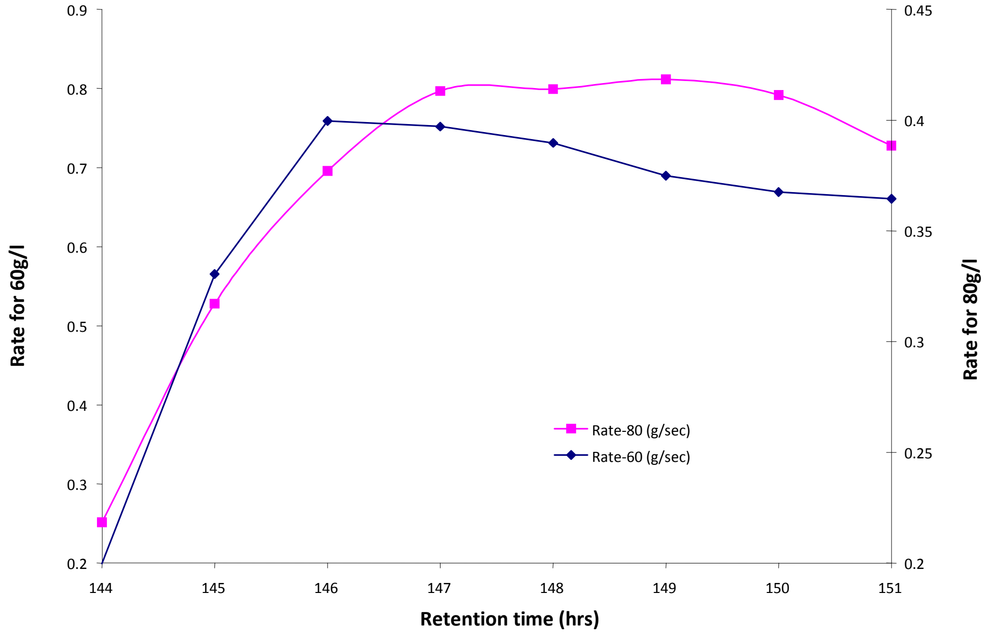

Figure 4: Rate of methanol production as a function of retention time and slurry concentration.