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Biogas Production by Anaerobic Digestion of Date Palm Pulp Waste

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Abstract

The purpose of this preliminary study is to verify the possibility of using Iraqi Zahdi date palm biomass as a resource for biogas production, methane in particular using thermophilic anaerobic digestion with waste water treatment activated sludge. Moreover, is to investigate the influence of extra nutrients addition to the digestion mixture. Biogas was captured in sealed jars with remote sensing modules connected to computer with integrated program to record the gas pressure continuously. A total gas pressure with 67% Methane was produced from date pulp waste fermentation with a yield of 0.57 Lit for each gram volatile solid of substrate. Addition of 1% yeast extract solution as nutrient increased Methane yield in liters by 5.9%. This is the first time in literature to record biogas production data from Iraqi date palm biomass.

Keywords: Date palm, pulp, anaerobic digestion, biogas, phoenix dactylifera L.

1. Introduction

Date palm (*Phoenix dactylifera L.*) is one of the principal agricultural products in Middle East and North Africa region. Dates are available in huge amounts (100 million trees) yielding about 3,316,500 tons of palm secondary products per year including palm midribs, leaves, stems, fronds and coir (Taha, et al., 2006). In Iraq, nine million trees cover the middle and southern parts of the country, resulting in a surplus production of dates and other secondary biomass.

Date cultivars are fruits with high sugar content (55-70% wt) (Al-Niaimi & Jaafer, 1980). Traditionally they are used for food, or to produce sweets, sweet syrup (Dibs in Arabic), vinegar and alcoholic products. In Iraq, part of the biomass waste of all these industries, is used in the blend of animal food. However, a high percentage of this waste is currently disposed to the landfill without any further treatment. The disposed biomass is mainly cellulosic compounds with some sucrose sugar, fats and minerals. This fact makes it a high potential resource for biogas or biofuel production through fermentation process. This potential has been recently considered in the Middle East and Arabic region.

Very little research work has actually been done on the date palm biomass as a biofuel resource. However, there are many papers describing the dates physiochemical characteristics (Vandepopuliere, et al., 1995, Pillay, et al, 2005, Hamada, et al., 2002, Ismail, et al., 2008).

To the best knowledge of the author, research data on anaerobic digestion from date palm waste is not available in literature. The aim of present work is to investigate usage of date palm biomass as a resource of bio energy. A lab research is conducted to ascertain the applicability of biogas production from small, batch scale anaerobic digestion process of date pulp biomass. Cultivars of Zahdi date variety are selected as the resource of biomass due to their abundance in Iraq representing 60% of the country production (Al-Niaimi & Jaafer, 1980), utilizing waste activated sludge at a municipal wastewater treatment plant as the inoculums.

Cellulosic biomass can be converted into biofuel by catalysis with dilute acid, concentrated

acid, or enzymes known as cellulases. Anaerobic digestion of organic matter can be applied to both liquids and semi-solid wastes (Grover, et al., 2002).

In the absence of oxygen and certain other exogenous inorganic electron acceptors [e.g. nitrate, Mn(IV), Fe(lII), sulfate], cellulose is decomposed by the anaerobic community into CH_4, CO_2 , and H_2O through a complex microbial food chain (Leschine, 2008). The process can be divided into four stages, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis (Mackie & Bryant, 1995). Cellulose is hydrolyzed by cellulases enzymes produced by cellulolytic bacteria into monosaccharide sugars (e.g. cellobiose and cellodextrins, and some glucose). These sugars are fermented into CO_2, H_2 and fatty acids (acetate, butyrate and propionate) by other cellulolytic and other saccharolytic microorganisms. In third stage, homoacetogens use H_2 to reduce CO_2 to acetate. In addition to syntrophic bacteria activity that ferment fatty acids such as propionate and butyrate to CO_2, H_2 and acetate as well. Methanogens consume H_2 to reduce CO_2 to CH_4, and some methanogenic species convert part of the acetate produced to CH_4 and CO_2. Syntrophic bacteria play a key role in the decomposition of cellulose. These organisms grow very slowly, and only in the presence of H_2 consuming organisms. Thus the fermentation of fatty acids is usually the rate-limiting step in the anaerobic decomposition of cellulose (Leschine, 2008).

2. Experimental Work

2.1. Substrate Preparation

Biomass from Zahdi date cultivars was prepared to be in the same conditions as it is usually expelled from Syrup (Dibs) industry in Iraq. 200 g of Date fruits harvested in 2008 from the middle area of Iraq, were pitted and boiled with one liter distilled water in a beaker then cooled, filtered with fabric mesh, then rinsed with water and filtered again to get rid of as much as possible from its water soluble sugar content. The resulting biomass weight was 51% of the original pulp weight, and kept in 4 ^oC refrigeration for further testing.

2.2. Methodology & Procedure

The Waste Management Lab/ Cornell University (USA) methodology for anaerobic digestion, was used to perform this research work. Biomass from Zahdi dates was treated with anaerobic digestion in thermophilic conditions at 55 ^oC. 300 ml glass jars fitted with wireless computer controlled modules from Ankom, were used as the small batch reactors. The remote sensing modules measures the total gas pressure produced during the period of fermentation experiment.

In order to keep the fermentation medium close to neutral pH (7.0-7.5), which is necessary for hydrolysis of fatty acids, 50 mM BES buffer solution (N,N-bis-2-hydroxyethyl-2-amino-ethane sulphonic acid) was used to prepare incubation medium. One ml of 5 g/L yeast extract solution was added as the only external nutrient for the inoculums. No trace elements were added to the fermentation solution as the date biomass is normally rich with many minerals such as Potassium, Calcium, Boron, Iron, Manganese, Magnesium and Cobalt (Al-Niaimi & Jaafer, 1980). Blank samples of deionized water (DIW) were placed under experiment conditions to observe pressure drop/increase due to temperature variation during sampling and adding substrate. Methane yield will be normalized to the volatile solids of biomass and original carbon added to the solution.

2.3. Initial Substrate Testing

Samples of substrate and inoculums were tested for Total Solid (TS) and Volatile Solid (VS) content to verify the best food/biomass ratio of mixing. Proportion of C:N was also measured with metal analyzer from CE Instruments, NC 2500 to calculate initial carbon and nitrogen added to the fermentation batch. Three grams of substrate were weighed in dried and cooled crucibles, then placed in 105 ^oC Fisher Isotemp oven (0-200^o C) for 24 hrs, then cooled in the desiccators for 1 hr. After weighing, crucibles were placed in 550 ^oC Lindberg SB Muffle furnace (0-600^o C) to maintain TS, VS and ash content of the substrate.

2.4. Anaerobic Digestion Procedure

BES solution (50 mM) was used to prepare two groups of triplicate samples for digestion. The first group included 100 ml BES plus 5 ml of activated sludge with addition of 1% yeast extract solution as the nutrient. While the second group, was only BES solution with 5 ml of activated sludge. A third group of jars containing DIW only

were incubated as well and treated exactly as the samples. Jars were flushed with nitrogen to remove traces of oxygen from fermentation medium.

After incubation for 48 hrs, to exclude any biogas produced from the activated sludge, incubation jars were opened to add 0.5 g of substrate and flushed again with nitrogen.

Gas samples for GC analysis were taken every 48 hrs through the experiment period. Liquid gas chromatograph from Gow-Mac Series 580, dual detector for Methane/CO_2/N_2 measurement with Supleco 80/100 Porapak Q, 6' x ¼" column was used. Helium was used as the carrier gas with 35 ml/min flow rate. While Hydrogen percentage in the total gas produced was measured with another Gow-Mac Series 580, dual detector with Hydrogen Analysis Column: Supelco 60/80 Carboxen 1000, 5' x 1/8".

Samples from liquid phase were filtered with 0.2 µm paper filter then treated 1:1 with 2% Hydrofluoric acid and tested for VFA with Hewlett-Packard 5890 Series II (With autosampler) and VFA Column: Supelco Nukol, 15m x 0.53mm x 0.5um film thickness. The experiment took place until the total gas pressure was constant for three consecutive days, then jars were opened for final measurements of pH, VFA, and SCOD.

3. Results & Data Analysis

Initial values of total solids (TS), volatile solids (VS), Carbon C and Nitrogen N of the substrate and inoculums are listed in Table 1. The volatile solids of substrate and inoculums was 39.82%, 2.37% respectively with a ratio of 16.8:1. A ratio of 10:1 inoculums to substrate by weight was selected in order to maintain approximate ratio of volatile solids substrate to volatile solids Inoculums 2:1. Also the nitrogen content of the substrate was found 2.35%, which indicates the demand for extra amount of nutrients to provide nitrogen for bacteria growth in the fermentation batch. Al-Niaimi & Jaafar (1980) have measured the protein content in Zahdi date fresh fruit. Their results showed 2.16% as nitrogen. That elucidates our results if we consider the pretreatment process of the substrate.

The average of total biogas produced from nutrient added group was 9.953 psi (0.0045 gmol), while the group without nutrient addition produced 7.276 psi (0.0032 gmol). The accumulation of total gas pressures produced from the two groups of jars are illustrated in Fig. 1

Table 1,
Initial Data of Substrate and Inoculums.

Item	TS%	VS%	Carbon C, wt%	Nitrogen N, wt%
Substrate	40.74	39.82	21.49	2.35
Inoculum	3.71	2.37	1.23	0.19

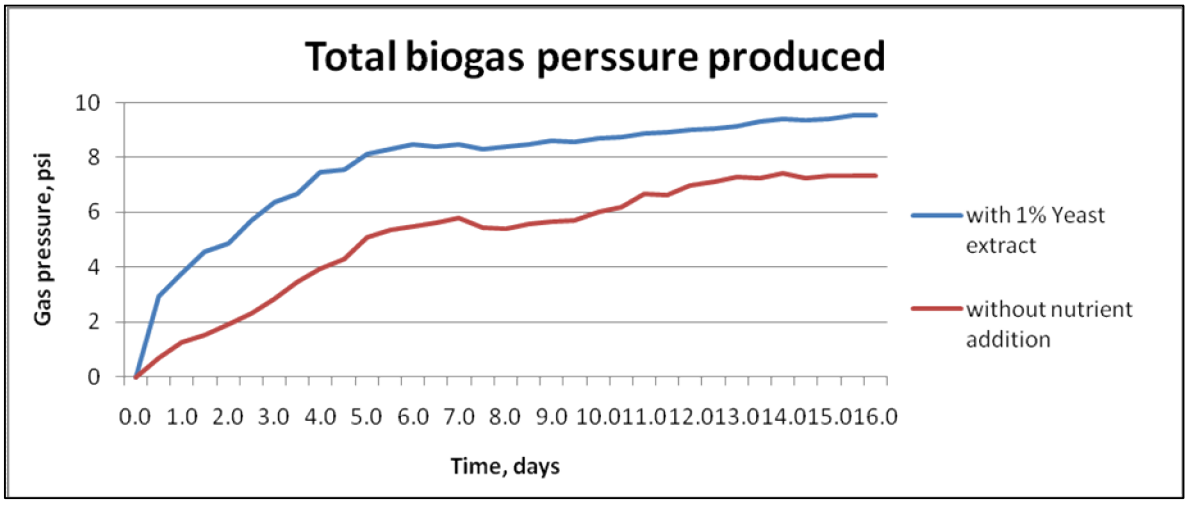

Fig.1. Total Biogas Pressure Produced During Period of Experiment.

The influence of adding nutrient solution can be clearly observed with a 36% increase in total gas pressure. The reason for this result is that in thermophilic degradation of cellulose, propionate accumulates in higher magnitudes at temperatures higher than 53° C; this was explained by the increase of H_2 concentration that results into decrease of propionate metabolism (Speece et al. 2006). Addition of a complex nutrition solution, including organic nutrients such as yeast extract will increase the growth of Syntrophic bacteria which is responsible of propionate metabolism (Leschine, 2008).

GC analysis was conducted frequently to measure CH_4, CO_2 and H_2 production. Results were adjusted to the zero point of adding substrate and the pressure variation due to temperature change and sampling. Results of total gas composition are listed in Table 2. CH_4% was found in nutrient added group and substrate only group 67.43%, 67.56% respectively. It can be seen from Table 2 that the nutrient addition has given significant improvement to the total gas production but did not alter the gas composition and CH_4% although it did increase the g-mol of CH_4 produced. In addition, H_2% was nil in both groups. The absence of H_2 in the produced gas leads to the conclusion of effective methanogenation of CO_2 into CH_4. However, this also might indicate the demand of higher substrate/inoculums ratio in order to meet Methanogens growth.

Figure 2 illustrates the mol% of methane produced in each of the two groups of jars. The highest rate of Methane production was in the first three days of fermentation and reached to the end in 14 days. The exponential curve of Methane vol.% produced explains the metabolism sequence of fermenting bacteria starting with high rates of cellulose degradation into fatty acids then metabolism by methanogens into Methane.

Table 2,
Total Gas Pressure and Gas Composition Produced from Date Palm Pulp Waste.

Measurement	1% Nutrient Modules	Substrate only Modules
Total biogas pressure, psi	9.593	7.276
CH_4%	67.43	67.56
CO_2%	32.56	32.44
H_2%	0.00	0.00

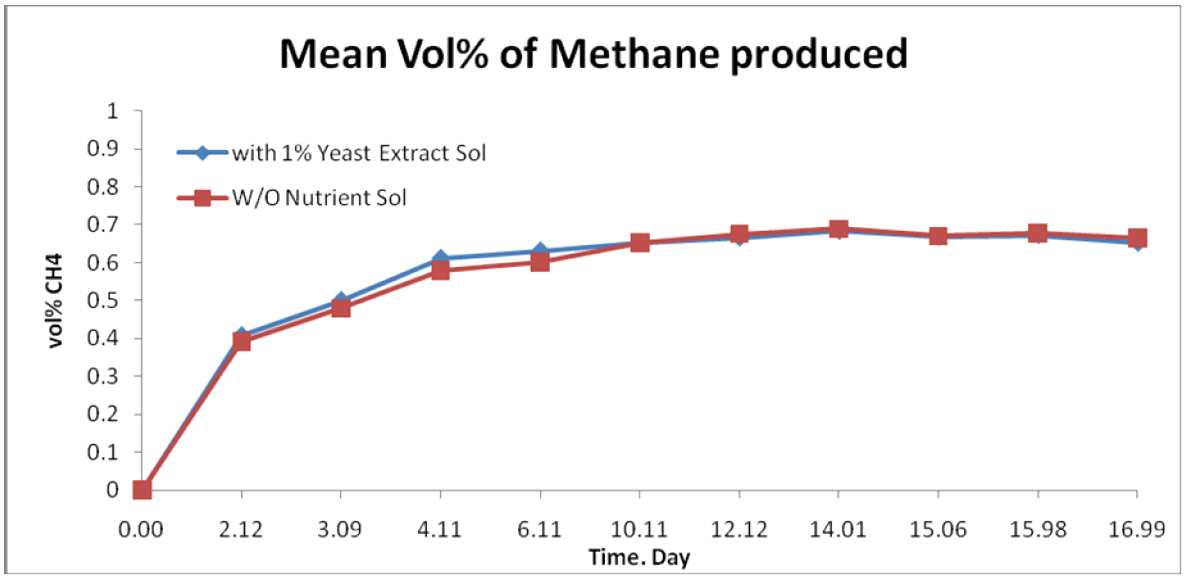

Fig.2. Mean Values of Methane Vol. % Produced From Two Groups of Mixtures, with and without Addition of Nutrients.

Methane yield calculations were referred to the VS weight of initial substrate. Results are listed in Table 3. Addition of nutrients has increased the yield of methane by approximately 39% as L/g VS substrate which is close to the increase in total gas pressure, and 5.9% as g/g VS substrate respectively.

Standard deviations STDEV of total gas pressure and methane percentage readings are shown in Table 4.

Table 3,
Methane Yield in Two Groups of Samples, One with Addition of 1% Yeast Extract and the Second without Addition of Nutrients.

Result	Yeast Extract Nutrient	W/O nutrient	Increase % due to Nutrient addition
Total biogas produced, g-mol	0.0045187	0.0032189	40.38
CH_4 yield, g/ g VS substrate	0.2381	0.1716	38.78
CH_4 yield, L/ g VS substrate	0.613	0.579	5.9
CH_4 yield, g/ g Carbon in substrate	0.513	0.318	61.32

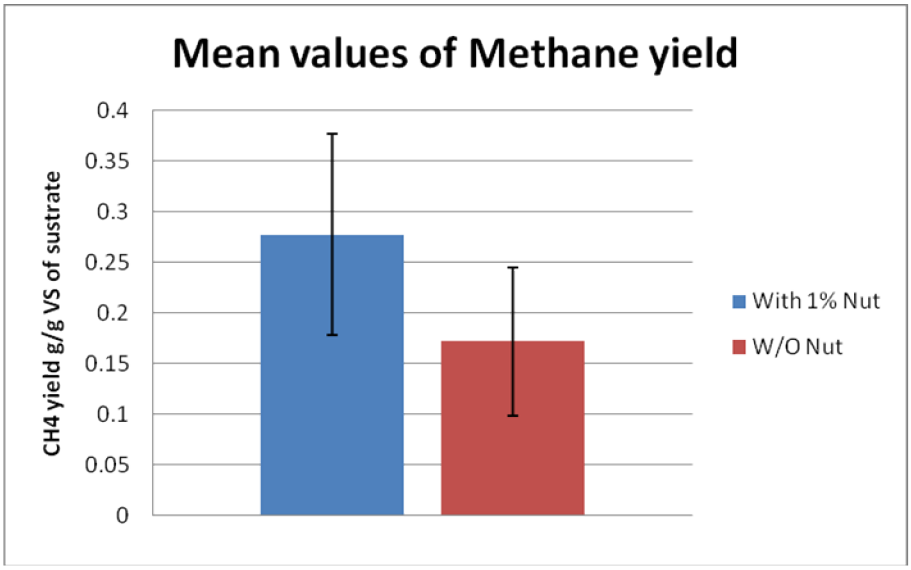

Fig.3. Mean Values of Methane Yield in Two Groups of Modules with and without Nutrient Addition, in g/g Volatile Solids in Substrate.

Table 4,
Standard Deviations (STDEV) of Total Gas Pressure, Methane Percentage and Methane Yield.

Measurement	1% Nutrient Modules	STDEV	Substrate only Modules	STDEV
Total biogas P, psi	9.593	1.249	7.276	2.713
CH_4%	67.43	0.013	67.56	0.010
CH_4 yield, g/ g VS substrate	0.2381	0.0378	0.1716	0.0731
CH_4 yield, L/ g VS substrate	0.613	0.036	0.579	0.0246

4. Conclusions

The high volatile solids content in date palm biomass compared to the inoculums indicates a high potential of biogas production from a small amount of biomass, and this is a positive factor in commercial calculations for future economic Bioenergy projects. In respect to biogas production, a ratio of 67% methane of the total gas produced and a yield of 0.6 lit/g VS substrate, in addition to the short time cycle of biogas production can be considered very promising results for date palm fruits biomass to be of a great potential. Abundance of the date palm trees in Iraq, sustainable production of the dates, and the physiochemical characteristics of the biomass in this fruit, provide the viability of producing biofuels in a commercial scale.

5. References

[1] Agler, M.T., Garcia, M.L., Lee, E.S., Schlicher, M. and Angenent, L.T. (2008). Thermophilic Anaerobic Digestion to increase the Net Energy Balance of Corn Grain Ethanol. DOI: 10.1021/es800671a. Environ. Sci. Technol, 42, 6723-6729.

[2] Al-Niaimi, J.H. and Jaafer, A.A. (1980). (Arabic). Physiology, Anatomy and Morphology of Date Palm Tree. Basarh University Press, p: 185-192.

[3] Bruce, a.M., Kouzeli-Katsiri, A. and Newman, P.J. (1984). Anaerobic Digestion of Sewage Sludge and Organic Agricultural Wastes. Elsevier Applied Science Publishers. UK. 1st edit., P: 65.

[4] Grover, V.I., Grover, V.K. and Hogland, W. (2002). Recovering energy from waste Various Aspects. Science Publishers, Inc. Enfield (NH), USA, 1st edit. p:44-45.

[5] Hamada, J.S., Hashim, I.B. and Sharif, F.A. (2002). Preliminary analysis and potential uses of date pits in foods. Food Chemistry, 76, (2), 135-137.

[6] Ismail, B., Haffar I., Baalbaki, R. and Henry, J. (2008). Physico-chemical characteristics and sensory quality of two date varieties under commercial and industrial storage conditions. LWT, 41, 896-904.

[7] Kaylen, M., Van Dyne, D.L., Choi, Y-S. and Blasé, M. (2000). Economic feasibility of producing ethanol from lignocellulosic feestocks. Bioresource Tech., 72, 19-20.

[8] Leschine, S.B. (1995). Cellulose Degradation in anaerobic environments. Annu. Rev. Microbiology, 49, 399-426.

[9] Lucia, L.A., Argyropoulos, D.S., Adamopoulos, L. and Gasper, A.R. Chemicals and Energy from Biomass. Can. J. Chem., 84, 960-970.

[10] Mackie, R.I. and Bryant, M.P. (1995). Anaerobic digestion of cattle waste at mesophilic and thermophilic temperatures. *Appl Microbiol Biotechnol,* 43, 346-350.

[11] Malherbe, S. and Cloete, T.E. (2002). Lignocellulose biodegradation: Fundamentals and applications. Reviews in Environmental Science & Bio/Technology, 1, 105-114.

[12] Pillay, A.E., Williams, J.R., El-Mardi, M.O., Hassan, S.M. and Al-Hamdi, A. (2005). Boron and the alternate-bearing phenomenon in the date palm. J of Arid Environment, 62, (2), 199-207.

[13] Poh, P.E. and Chong, M.F. (2009). Development of anaerobic digestion methods for palm oil mill effluent (POME) treatment. 100, (1), 1-9.

[14] Speece, R. E., Boonyakitsombut, S., Kim, M., Azbar, N. and Ursillo, P. (2006). DOI: 10.2175/106143006X95492. Overview of Anaerobic Treatment: Thermophilic and Propionate Implications. Water Environ. Res., 78, 460-473.

[15] Taha, I., Steuernagel, L. and Ziemann, G. (2006). Chemical modification of Date Palm Mesh Fibers for Reinforcement of Polymeric Materials. Part I: examination of Different Cleaning Methods. 14, (8), 767-778.

[16] Vandepopuliere, J.M., Al-yousif, Y. and Lyons,J.M. (1995). Dates and date pits as ingredients in broiler starting and Coturnix quail breeder diets. *Poultry Science*, 74, (7), 1134-1142.

انتاج الغاز الحيوي من الهضم اللاهوائي لمخلفات لب التمر

خالدة عبد الخالق جعفر
مركز الادريسي للاستشارات الهندسية والبيئية
ص ب ١٦٨ السليمانية العراق

الخلاصة

الهدف من هذه الدراسة الاولية هو تبيان احتمالية استخدام مخلفات لب تمر الزهدي العراقي كمصدر لانتاج الغاز الحيوي، الميثان خصوصا باستخدام الهضم اللاهوائي الحراري مع الفضلات المحفزة لوحدة معالجة مياه المجاري بالاضافة الى ذلك دراسة تأثير اضافة مغذيات خارجية الى مزيج الهضم. تم جمع الغاز الحيوي بواسطة علب زجاجية محكمة الغلق بواسطة حساسات الكترونية يتم التحكم بها عن بعد من خلال برنامج الحاسوب لتسجيل ضغط الغاز الناتج باستمرار. الغاز الحيوي الناتج احتوى على نسبة ٦٧% غاز الميثان بناتج مقداره ٠.٥٧ لتر غاز لكل غم مواد صلبة طيارة من المادة الاولية. ان اضافة محلول خلاصة الخميرة بنسبة ١% قد حسن من ناتج الميثان بنسبة ٢٠% في المرحلة الاولى في الابحاث العلمية حيث تنشر نتائج انتاج الغاز الحيوي من فضلات لب التمر العراقي.