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Technical Evaluation of Anaerobic Digestion of Microalgae Biomass For Methanation

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Abstract: *In certainty, algaehold great promise as a resource that, if properly developed, could become a sustainable biomass source for energy and fuels. This paper presents a process technical evaluation for methane (biogas) production using microalgae as feedstock in anaerobic digestion. In the light of carbon-nitrogen ratio (C/N) requirements of the substrates in the digester, the potential of bio-methanation, the energy performance, waste paper demand, and CO_2 and nutrient recovery were examined. Two scenarios were observed: digester carbon/nitrogen ratios C/N=15 and C/N=25, with each having 100kg alga biomass input. At C/N = 15, 41.71m^3 of methane was produced requiring 18.36kg waste paper input; total energy input and output was 948.58MJ and 1376.31MJ respectively; while nitrogen, phosphorus and CO_2 recovered was 68.4%, 45% and 48.39% respectively. At C/N = 25, 51.01m^3 of methane was produced requiring 44.68kg waste paper input; total energy input and output was 1476.60MJ and 1683.27MJ respectively.The nutrients in the AD effluent recovered are 4.59kgN and 0.69kgP. The CO_2 that can also be generated within the system is 55.67% and 68.08% of the $CO_2$for C/N = 15 and 25 respectively.The overall finding form this work is that waste paper used to raise the C/N ratio of substrates in AD comes with huge energy burden which is responsible for 44.19% of total energy input. Therefore it is suggested here that an alternative source of low carbon material be used for co-digestion instead of waste paper.*

Key Words: *Algae, Anaerobic Digestion, Methane, nutrient and CO_2, C/N ratio,waste paper*

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I. Introduction

Biogas is a naturally occurring byproduct of the breakdown of organic material, and isactively produced from a variety of sources, including animal waste, municipal solid waste, sewage and agricultural wastes using a process called anaerobic digestion. The main constituent of biogas is methane.Algae biomass can be used as feedstocks into anaerobic digestion system to produce biogas.In recent years microalgae has been discovered as a promising biomass with enormous natural chemical potential. One of these is its use as a source material to biofuels production which is a contribution to global efforts to finding an alternative to fossil fuels resources, which have great environmental consequences and inability to be renewed. Biogas can be used for different applications; most commonly and particularly for this study, it is used to generate heat and electricity. A biogas of mostly 69 -75% methane composition can be ideally produced from algae biomass of 80 -90% water content (Patel, 2012). After disruption of algae cells they are subjected to three-phase anaerobic microbial decomposition procedures, starting with hydrolysis of proteins, carbohydrates and lipids into their simple soluble components, then it is followed by the fermentation of these soluble components into volatile acids, alcohols, H_2 and CO_2. Methanogenesis is the last phase which converts the products of the previous step into methane and CO_2; as some amount of NH_3 and H_2S also produced from the entire process (Drapcho, 2008). The digester effluent which contains leftover of compounds of nitrogen and phosphorus may be recycled as fertilizer for algae cultivation.

However, to improve the digestion of algae and methane yield increase, Chen and Oweald (1998) assessed the thermochemical pre-treatment of algae biomass and found an increment of one third of methane yield when the algae biomass was pre-treated at 100^0C for 8hours at 3.7% volatile solids. The aim of physical or chemical pre-treatment is to break down the cell i.e cell disruption thereby making the organic material in the cell more reachable. Certain microalgae contain high level of nitrogen which results into greater production of ammonia, which is inhibitory in the digestion process as it alters the pH of the system. With this development, co-digestion with other organic wastes of a higher carbon and low nitrogen content is one option that can overcome this problem. Ehimen et al. (2011) investigated co-digestion with glycerol, where >50 % methane yield increment was shown. Similarly, co-digestion of micro algae with wastepaper was also experimented by Yen (2004) and Yen and Brune (2007) to adjust C/N ratio and a double of methane production rate resulted with hydraulic retention time of 10days. Sodium (in salt) can also exhibit a similar inhibitory effect at concentration above 0.5M, even though some reseachers observed that suitable microbes in digesters can adapt (Sialve et al., 2009; Demirbas and Demirbas, 2010).

The intended contribution of this paper is to investigate the distribution of harvested algal biomass feed to AD unit and thereby assess the energy production output. The suggestions of the optimum ratios of C/N ratio in AD system by Yen and Brune and Ehimen et al., especially as it applies to algae bio-methanation, needs a further investigation with respect to energy burden that comes with the input materials to maintain the C/N ratio at the optimum in AD system. The requirements of this input material, waste paper in this study, will also be evaluated. The nutrients and CO_2 recoverable from the AD will be analysed.

The evaluation will be carried out using estimates from extrapolated data gotten from laboratory scale pilots systems and previous related work in the literature.

II. Methodology

In the light of carbon-nitrogen ratio (C/N) requirements of the substrates in the digester, the potential of bio-methanation, the energy performance, waste paper demand, and CO_2 and nutrient recovery were examined under two scenarios: C/N=15 and C/N=25. The integrated system of biogas production for this study is illustrated in Figure 1.

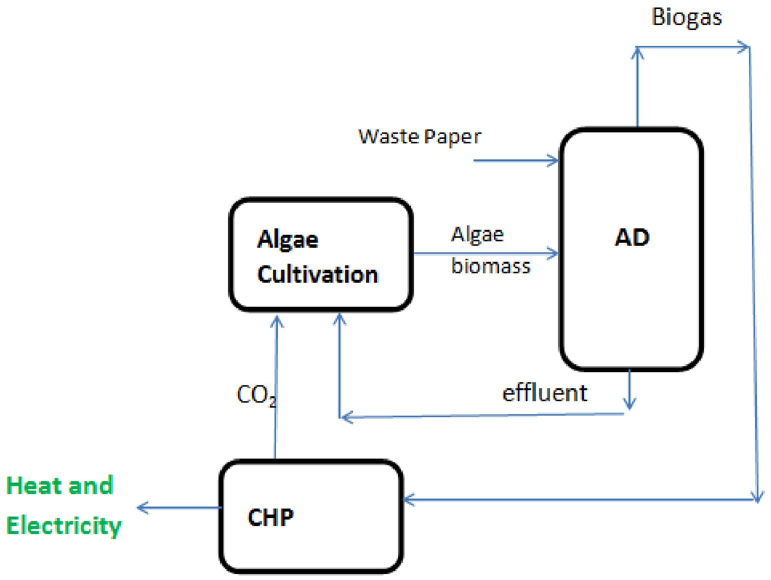

Figure 1: Integrated System of Biogas Production from Algal Biomass

2.1Modelling Assumptions

In this section the fundamental concepts and assumptions are presented for the different processes: alga biomass, biogas production, nutrient and CO_2 recovery, andheat and electricity generation.

2.1.1 Algae Biomass

The typical algae solid concentration is less than 0.5 kg/m^3 (Andersson et al., 2011) from cultivation. When flocculation and settlement mechanical means would be required to dewater the algae slurry to about 20% solid before further processing (Ron, 2007).In this work, the dewatered algae biomass is 100kg, which will be used for the productions of biodiesel and biogas. Although, based on Redfield ratio, the microalgae over a wide range of species is stoichiometrically assumed to composed of $C_{104}H_{181}O_{45}N_{10}P$ (Zhang et al., 2013; Chisti, 2007; Frank et al., 2011). The lower heating value (LHV) of alga biomass is assumed to be 30MJ/kg (Razon and Tan, 2011).

2.1.2 Biogas Production

The biogas production model in this section considers the inflows into the digester from fraction of harvested algae biomass, algae oil extracted residues, and crude glycerol produced from the biodiesel production unit. Other input, at small amount, to anaerobic digester includes the algae biomass not retained during dewatering stages, and unextracted-oil algae and undisrupted algae obtained during lipid extraction.

Feedstock pretreatement such as heating or cell disruption may improve biogas yield (Chen and Oweald, 1998), but such processes is not considered in the model of this study as the biogas yield also depends on certain factors such as algae species and cultivation condition, and as such, the energy requirement for pretreatment may be avoided in the analysis.

Organic Dry Matter (ODM) also sometimes referred to volatile solids defines the quantity of convertible material into biogas. When ash content is deducted from the total solids gives the quantity of ODM. The amount of ODM of microalgae vary from species, as reported in Zhu and Lee (1997) study on dry weigh and ash free dry weight determination of selected marine microalgae. In their work, ash content of 9 – 22 wt% of various selected species of algae was reported, and this translates to 78 – 91 wt% ODM. Also reported are the corresponding lipid, carbohydrate and protein composition of the algae. In this assessment study, 91 wt% ODM is adopted for algae species with 31% oil content, which is in line with 30% assumption made earlier for oil content. The ODM for crude glycerol, and methanol, as used in a study by Andersson et al. (2011) are 85.03 wt% and 99 wt% respectively, which will also be adopted in this study.

The specific theoretical biogas yield is widely known to be the reflection and pointer to the maximum biogas projected to be produced from a specific waste (Angelidaki et al., 2011). Angelidaki et al came up with fundamental stoichiometric of waste consisting of carbon, hydrogen and oxygen from whichthe specific methane yield equation was formulated. It is shown below that

$$C_xH_mO_n + \left(x - \frac{m}{4} - \frac{n}{2}\right)H_2O \rightarrow \left(\frac{x}{2} + \frac{m}{8} - \frac{n}{4}\right)CH_4 + \left(\frac{x}{2} - \frac{m}{8} + \frac{n}{4}\right)CO_2 \qquad 1$$

$$y = \frac{\left(\frac{x}{2} + \frac{m}{8} - \frac{n}{4}\right)22.4}{12x + 8 + 16n} \qquad 2$$

Where y is the specific yield (m^3/kgODM); x is carbon content; m is hydrogen content; and n is oxygen content.

In practical sense, the theoretical yield of biogas from microalgae biomass has been reported by authors in previous study, however, the techno-economic assessment of anaerobic digestion of microalgae conducted by Zamalloa et al. (2010) for three different scenarios reported the assumed value of $0.5m^3$/kgODM as the biogas yield. A much lower values of $0.3m^3$/kgODM were adopted by Frank et al. (2011) who extrapolated experimental data gotten by Ehimen et al. (2011) for different peak yield. Methane yield may vary depending on the composition of the feed (Drapcho et al., 2008). However, Zamalloa and associates were not too conservative about their choice of the yield and assumed all condition for a higher yield is fulfilled. This model therefore, assumes $0.5m^3$/kgODM specific methane yield from a biogas composition of 70% methane and 30% CO_2.
The specific theoretical methane yield for glycerol and methanol are estimated from Equation 2.

The specific methane yield from algae residue is reduced by approximately $1/3^{rd}$ of the algae biomass methane yield (Brune et al., 2009)

In the process of biogas production through AD system, some gaseous substances such as ammonia and hydrogen sulphide are released in small quantity from the amine and sulphide groups of amino acids (Drapcho et al., 2008). Previous research have shown that nitrogen content of the algae biomass has a significant effect on the yield of methane, even though nitrogen is an essential nutrient element for the anaerobic flora cells. However, this can be overcome by either extraction of protein to reduce the nitrogen or co-digestion with low nitrogen substrates such as glycerol, manures, waste paper and sawdust (Brune et al., 2009).
Thermophilic (50^oC to 55^oC) regime of bioconversion is assumed in the digester for biogas production (Vindis et al., 2009),

2.1.3 Carbon-Nitrogen Ratio

The measure of carbon and nitrogen in organic substrates is characterized bycarbon: nitrogen ratio (C/N ratio). The suggested optimum C/N ratio in AD system is between 15 – 30 (Ehimen et al. 2009), 20 – 32 (Jayaweera et al., 2007), 20 – 25 (Yen and Brune, 2007) and, 20 -30(Verma, 2002). Higher than 30 indicates that there will be rapid utilization of nitrogen by methanogens in the digester and consequently results in low biogas production; while lower than 15 means NH_3 build-up and thus leads to high pH value beyond 8.5, which is toxic to methanogens (Ehimen et al. 2009). The optimal C/N ratio can be achieved by co-digesting a mixture of the substrates with high and low C/N ratios; high C/N ratio material some of which are waste paper, woody materials and glycerol (Verma, 2002;Ehimen et al. 2011).

Ehimen et al. (2011) further conducted another study on digestion of *Chlorella* oil extracted residues conducted,although their investigation was constrained to hydraulic retention time (HRT) of 15 days at varying temperatures between 25 - 40^{o}C, with C/N ratios of 5.4–24.17 and loading density of 5–50 kg ODM/m^3 digester volume, and therefore, the optimum C/N ratio was found to be 12.44 when co-digested with glycerol.

In this study, waste paper is used. C/N ratio of 15 will be investigatedin a thermophilic digester operation. Waste paper is used to boost the C/N ratio in the digester. The carbon content of waste paper varies with paper type and source, however, 38% carbon is adopted from a study by Jeon et al. (2007), and specific methane yield of paper of 0.452m^3/kg ODM, and assumed 92% ODM for paper.

The electricity requirement for mixing in the substrates in the digester is 0.108 kWh/kg TS, and the thermal energy demand for operating temperature is 0.68 kwh/kg TS (Collet et al. 2011). Nonetheless, Frank et al. (2011) considered the need to further increase solid concentration from the digestate to 30%, and hence an added electric power of 0.028 kWh/kg TS, in comparison to a disk stack centrifuge, was taken into account.

2.1.4 Biogas Clean Up

Crude biogas from anaerobic digestion contains components or impurities, such as CO_2, H_2S, NH_3, H_2, moisture, etc. These impurities have to be removed in the cleaning up to avoid possible corrosion and deposits in the engine/turbine during combustion. Technological methods employed for the clean-up includes membrane separation, adsorption (with activated carbon), absorption (scrubbing), and cryogenic distillation (Frank et al., 2011).

This assessment considers scrubbing by water since CO_2 is quite soluble in water while CH_4 is barely soluble. The level of clean up depends on the requirement for combustion in CHP turbines and engines, and specifications for upgrade to bio-methane fuel quality. About 96 vol% of CH_4 rich upgraded gas, requires energy consumption of 0.301 kWh/m^3 of clean CH_4 (Collet et al., 2011). The CO_2 dissorbed from the CO_2 rich water is therefore recycled to supplement the CO_2 required in the algae cultivation.For the sake of this study, and data availability, 0.10 kWh/m^3 of energy will be assumed since such purity may not be needed for CHP.

2.1.5 Nutrients and CO_2Recovery from Anaerobic Digestion

The effluent from the anaerobic digestion after biogas production is categorised into liquid and solid digestates which is made up of organic and mineral substances (Frost and Gilkinson, 2010; Zhang et al., 2013), as shown in Figure 2. The liquid part of the post-digestion is returned back to algae cultivation pond to supplement the required algae nutrient, while the solid digestates can be sold for soil conditioning to increase soil fertility.

In the modelling of nutrient recycling, carbon balance is carried out around the entire system. CO_2 is assumed to be the sufficient source of carbon needed by the microalgae.

The C wt% is estimated from the stoichiometric composition of microalgae considered in the study, that is C : N : P (104 : 10 : 1). The total C in digester is accounted for through the harvested algae biomass, and waste paper; while the C exits the digester in the biogas and digestates produced. C is returned to cultivation pond through recovered CO_2.

In similar manner, Nitrogen (N) and Phosphorus (P) balance is carried out. In the recycling of nutrients from AD effluents (digestates), Zhang et al. (2013) and Frank et al. (2011) respectively made estimation of 60% and 50% of P making its way to solid digestate. The N split, as estimated by Frank et al. was 20% N remains in the solid digestate while 80% N fraction in the liquid, out of which 5% N is lost through volatilization of NH_3 when liquid digestate is returned into the cultivation pond. And thus, only 75% N is recovered to algae culture.

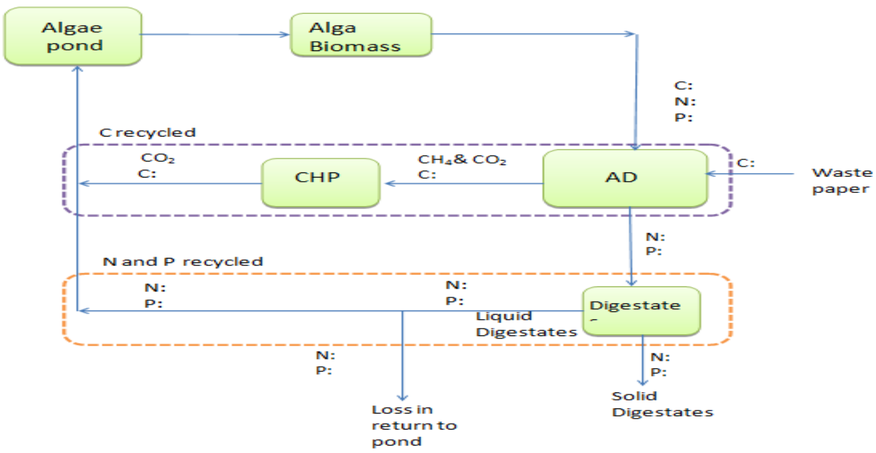

Figure 2: Nutrients Mass Flow through the Process System

In this analysis, 70% N will be considered as recovered to algae culture as 20% N makes its way to solid digestate, and 10% N is assumed lost through volatilization of NH_3. Similarly, 50% P is assumed makes its way to solid digested.

III. Result

At the higher ratio of C/N in the digester, more input of waste paper is required to boost the carbon content in AD; its implications on the total process energy, nutrient and CO_2 recovery are shown in Table 1. Figure 3 represents the energy input into the system from electricity, heat, alga biomass and waste paper.

Table 1: Material flow and Energy Performance of the System Comparing C/N: 15 and C/N: 25

	AD C/N Ratio	
	C/N = 15	C/N = 25
Methane Produced (m^3)	41.71	51.01
Total Energy Input (MJ)	948.58	1476.60
Total Energy Output (MJ)	1376.31	1683.27
Electricity Demand (MJ)	471.44	512.02
Heat Demand (MJ)	267.86	332.28
Alga Biomass LHV (MJ)	300.00	300.00
Waste paper Material LHV (MJ)	312.14	759.50
Waste paper required (kg)	18.36	44.68
Nitrogen recovered (kg)	4.59	4.59
Phosphorus recovered (kg)	0.69	0.69
CO_2 recovered (%)	55.67	68.08

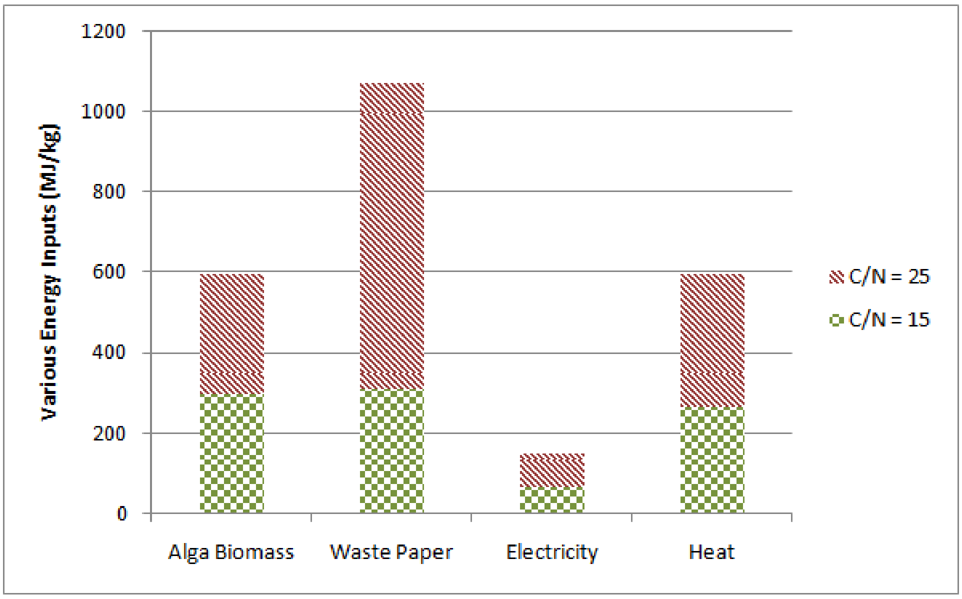

Figure 3: Energy Input from Electricity, Heat and Materials

IV. Discussion of Result

In the AD system, biogas is produced, $CO_2$and nutrients are recovered which can be recycled back to the algal pond, and methane is taken to the CHP system for heat and electricity generation. Substrates to AD are sourced from the harvested algal biomass and waste paper. The analysis follows the basic assumptions outlined in sections 2.1.1 to 2.1.5.

From Table 1, nutrients recoverable: 4.59kgN and 0.69kgP remain unchanged irrespective of algal biomass fed to AD in all the scenarios. It is observed that more CO_2 is recovered when more CH_4 is produced, since CO_2 is produced along with CH_4 as biogas from AD and from combustion of CH_4 in CHP system. The higher the waste paper input, the more the biogas produced, but the higher the energy input into the system, majorly from the waste paper material. The total energy input when C/N=25 increases to 1476.60MJ, which is 55.66% increment; while its corresponding energy output increases to 1683.27MJ, which is 22.30% increment. Waste paper requirement also increases to 44.68kg which is 143.32% increment. The input energy comes hugely from the waste paper input (see Figure 3) whose quantity is quite significant and yet with low carbon content which yields little amount of methane.

Waste paper input comes with huge energy burden which is responsible for 44.19% of total energy input (see Figure 3).The reason could be that the estimated energy content of dry wood was assumed for the waste paper which takes into account the energy for drying. Energy input of wood is much lower with moisture content (Kofman, 2010), and as AD operates in moist medium, some carbon-rich substrates (wet wood, papermill residues) could be used in place of dry waste paper.

V. Conclusion

A study of an assessment of biogas production from using alga biomass as feedstock in anaerobic digestion (AD), and nutrient recovery from the AD effluents has been carried out. The possible technological paths were examined, and descriptive model developed to enable the estimation of material and energy flow in the system. With the aid of Microsoft Excel tool, analysis was carried out to observe the mass and energy performance of the system of designed scenarios.

Using AD C/N ratio of 25 places great energy burden on the system, and low energy output. However, it is observed here that waste paper with high carbon content may not necessarily suggest a better methane output that will enhance CO_2 production, but a low carbon content paper in large quantity, even if the specific methane yield is as low as it is used in this study. The reason is that there is a limit to waste paper input with respect to C/N ratio to AD.

VI. Recommendation

With the challenge of energy input from waste paper, it is suggested here that a study be conducted on systems integrating anaerobic digestion and biomass production or investigate a suitable material of low energy input for co-digestion while optimum C/N ratio is sustained. The biomass includes algae cultivation for feed to biogas and biodiesel production, and wood cultivation for use as co-digestion in AD.

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