Assessment of Systems Integrating Anaerobic Digestion and Algae Cultivation

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Abstract-This study assesses the integrated process system in order to evaluate its technical performance, which provides a solid basis for future economic analysis. In doing this, a study on integrated anaerobic digestion and algae cultivation was carried out. Two different scenarios were modeled: methane production, and combined methane and biodiesel production with each case generating electricity. These scenarios were analyzed and evaluated with respect to products output, energy performance, and nutrients and CO₂ recovery. The evaluation shows that, in a pond with a surface area of 1 acre, 101.18kg algae/day can be produced. The energy generated is in surplus of 1.65 % - 35.90% after supply for on-site use in algae cultivation, harvesting, lipid extraction, transesterification process and anaerobic digestion (AD) system. The nutrients in the AD effluent recovered are 64.8% Nitrogen, and 45% Phosphorus of the requirement for cultivation. The CO₂ generated within the system is 41.08% - 55.67% of the CO₂ needed in the pond. The waste paper used to raise the C/N ratio of substrates in AD is responsible for 37% of total energy input. The feasible technological path for the integrated system is in the simultaneous combined production of methane and biodiesel and electricity.

Keywords—Anaerobic Digestion, Microalgae biomass, integrated system, energy

1. Introduction

Microalgae biomass is characterised by unique advantages that makes it preferred feedstock to other energy crops. They can reproduce themselves very fast, doubling their biomass within 24 hours. There cultivation style does not make it compete with other conventional food crops in terms of land and nutrient use (Chisti, 2007). In addition, algae can grow well on waste water or salt water, not necessarily fresh water. Microalgae do not need application of pesticides or herbicides and, even though they are aquatic plant, they do not utilize as much water as the (Rodolfi 2009). terrestrial crops et al., Furthermore, on an integrated production of products and co-products within biorefinery microalgae is verv compatible with the CO_2 - rich flue gas from arrangement. combustion chamber can be recycled by microalgae for its metabolic activities.

Despite these tremendous advantages, setbacks exist in the areas of algae cultivation and conversion of the algae biomass to biofuels. A net analysis of production of biogas and biodiesel from algae conducted by Razon and Tan (2011) shows a low energy output of the products compared to high energy input requirement, mainly from algae cultivation (from fertilization of nutrient and CO₂), algae biomass drying and processing to biofuels. Based on the current available technology, commercial biofuels production from microalgae has not been economically feasible (Andersson et al., 2011 and DOE, 2007). On conservative estimations, the current technology would produce a large volume of biofuels from microalgae at the cost over \$8/gallon, in comparison to \$4/gallon from soybean oil currently. Bringing down this cost will necessitate a coordinated Research and Development (R&D) across the length and breadth of technical sectors over the following 5 to 10 years (DOE, 2007).

Since cultivation for the sole purpose of generating energy molecules is not quite economical from the life cycle point of view of the entire upstream and downstream processes, this study will evaluate the possibility of coupling algae cultivation with anaerobic digestion (AD) effluent for nutrient benefit. Providing a multiple technological options that are interdependent, an integrated techno-economic model and evaluation that covers the whole algae to biofuel supply chain may suggest the most economic pathway that can lead to a realistic, sustainable and viable algae-based biofuels and co-products biorefinery.

2. Methodology

Scenario Design

Two scenarios of integrated system are designed: algae cultivation with anaerobic digestion of algae biomass producing biogas, and algae cultivation with anaerobic digestion with some part of algae biomass cultivate used for biodiesel production while the oil extracted residue and glycerol and the remaining part of algae biomass are feedstocks to anaerobic digestion. In each case biogas is utilized in CHP system to generate heat and electricity, which will also be used to meet the on-site demand. The scenarios 1 and 2 are schematically described in figure 1 and figure 2 respectively.



Figure 1: Scenario (S1): Integrated Algae Cultivation with Production of Biogas



Figure 2: Scenario (S2): Integrated Algae Cultivation with Production of Biodiesel and Biogas

Modeling for the Integrated Process

In this section the fundamental concepts and assumptions are presented for the different processes: algae cultivation, harvesting, oil extractions, biodiesel production, biogas production, and electricity generation.

1. Algae Cultivation

Culture:

A typical high rate pond for commercial algae production are operated at 0.2m to 0.4m depth, mixed with paddlewheels covering a pond size of about 0.5 hectares (Lundquist et al., 2010). Algae productivity (production rate) is a measure of the rate of algae biomass build-up in the pond. With open pond, depth is a factor of growth, as light exposure to the algae fluctuates which results in a fast reduction of growth with depth; and thus, the productivity is measured in g/m^2 .day (Ho et al. 2011; Frank et al., 2011).

Table 1: Assumptions for Algal Cultivation

| Parameter | range | Value used | Reference |
|---|---------|----------------------------------|--|
| Pond depth (m) | 0.2-0.4 | 0.2 | (Ron, 2007; Lundquist et al., 2010) |
| Temperature (⁰ C) | 20 - 30 | 25 | (Davis et al., 2011; Park et al., 2011) |
| Growth rate $(g/m^2/day)$ | 12 - 40 | 25 | (Davis et al., 2011; Park et al., 2011) |
| Electricity required: Paddlewheel(kWh/L) CO ₂ injection kWh/kgCO ₂) | | 2.4 x 10 ⁻⁵ 0.0222 | (Frank et al., 2011) (Frank et al., 2011; Kadam, 2001) |

From Table 1, the amount of algae produced from the pond can be computed assuming a basis of 1 acre $(4047m^2)$ pond, and algae production rate $(g/m^2/day)$. The cell density or concentration can be estimated from the depth of the pond and algae productivity, while the volume of algae produced can also be computed from the estimated algae concentration and the mass of algae produced. The CO_2 injection power estimated by Frank et al. was computed with pressure drop of 1.5m water equivalent and at efficiency of 67%. This power is considered without CO_2 uptake efficiency.

Nutrient consumption:

Although, based on Redfield ratio, the microalgae over a wide range of species is stoichiometrically assumed to composed of $C_{106}H_{181}O_{45}N_{15}P$ (Zhang et al., 2013). The ratio C : N : P (104 : 10 : 1) used here is lower than the Reyfield ratio with respect to carbon, nitrogen and phosphorus; the reason being that the resulting algae is expected to be cultivated under nitrogen depletion condition so as to increase lipid accumulation in the algae. Other studies by Chisti (2007) and Frank et al. (2011) used similar ratios of 100 : 11 : 1 and 103 : 10 : 1 respectively.

The breakdown of the composition is shown in Table 2.

| Table 2: Perc | entage M | lass Com | position | of Algae |
|---------------|----------|----------|----------|----------|
| Atomic Com | ponents | | | |

| | C104 | H ₁₈₁ | O ₄₅ | N ₁₀ | Р | Molecul |
|----------------------|-------|------------------|-----------------|-----------------|------|---------|
| | | | | | | ar mass |
| Atomic number | 104 | 181 | 45 | 10 | 1 | |
| Atomic mass (g/mol) | 12 | 1 | 16 | 14 | 31 | |
| Mass composition (g) | 1248 | 181 | 720 | 140 | 31 | 2320 |
| Percentage mass (%) | 53.79 | 7.80 | 31.03 | 6.03 | 1.34 | |

From this table, mass ratios of C : N : P in Algal biomass is 40:6:1.

 CO_2 utilization efficiency varies with different factors including pH of the cultivating medium, but estimations by Lundquiest et al. (2010) and Andersson et al. (2011) put it at 90% for clean CO_2 while 75% - 80% for flue gas.

Water Make-up for evaporation and leakages:

The net water loss as a result of evaporation depends on irregular climatic conditions such as relative humidity, ambient temperature, precipitation, and velocity of wind, in relation to location and season. The data have it that the U.S yearly average evaporative loss of water of an open pond is $0.88 \text{ m}^3/\text{m}^2$ over a mean cultivation of 222days (Murphy and Allen, 2011). This is equivalent to $0.004 \text{m}^3/\text{m}^2/\text{day}$

Pond leakage is another possible source of water loss to the ground. In Weissman et al. (1989), losses of 0.0011 to 0.0036m/day using a lined pond. In this assessment a good design and materials are assumed to be used to reduce the loss to $0.0011 \text{ m}^3/\text{m}^2/\text{day}$.

2. Algal Harvesting

The assumptions made as regards the dewatering mechanisms are presented in Table 3. A typical algae solid concentration is less than 0.5 kg/m³ (Andersson et al., 2011) after cultivation and when it has been flocculated and settled at the bottom of the settling tank, it would require mechanical means to dewater the algae slurry to about 20% solid before sending for further biofuels processing (Ron, 2007), especially for wet-extraction (Davis et al., 2011).

In this model, the volume of water drained from the bio-flocculation is assumed to be returned to the pond, while algae that are not retained in gravity thickener and centrifugation are taken to anaerobic digestion.

Table3:AssumptionsforBio-flocculation,GravityThickener, andCentrifugationDewateringMethodsValue usedReference

| <u>Bio-flocculation:</u> | | |
|---|----------------------|--------------------------|
| Retention efficiency (%) | 90 | Frank et al., 2011 |
| Output solid content $(0.5 - 2 \text{ wt\%})$ | 1 | Ron, 2007 |
| Electricity requirement (kWh/m ³) | 0.1 | (Wiley et al., 2011) |
| Gravity Thickener: | | |
| Retention efficiency (%) | 95 | (Lundquist et al., 2010; |
| Output solid content (2-3 wt%) | 2.5 | Andersson et al., 2011) |
| Electricity requirement (kWh/m ³) | 0.1 | |
| Centrifugation: | | |
| Retention efficiency (%) | 95 | Frank et al., 2011 |
| Output solid content (10 – 22wt%) | 20 | Ron, 2007 |
| Electricity requirement (kWh/galgae) | 3.3×10^{-3} | Frank et al., 2011 |
| | | |

3. Oil Extraction

Lipid content in a typical alga depends not only on its species but also its growth technique (Bai et al., 2011). This was supported by Williams and Laurens (2010) where it was reported that there is an opposite relationship between microalgae growth rate and its lipid content: as nitrogen or nutrient is limited in supply during cultivation, lipid and carbohydrate synthesis continues but protein synthesis stops.

Therefore this study seeks to consider 30% oil content on dry weight algae. And the feed flow of algae biomass to pre-treatment unit before lipid extraction is assumed to contain about 20 wt% solids. A schematic process diagram for lipid extraction procedures is shown in figure 3, starting with pretreatment of the algae biomass.





Pre-treatment:

Algae pre-treatment has been discovered to aid lipid extraction. This includes drying, cell disruption (Williams and Laurens, 2010), and heating (90°C) (Andersson, 2011) for added cell disruption. However to lessen cost of biodiesel production, drying option is stroke out (Chisti, 2008). Also supporting Chisti (2008) is Xu et al. (2011) in his study on energy assessment of dry and wet processing routes of algae biomass to biofuel, and then found out that dry processing route has higher fossil energy ratio than the wet route. Therefore, the alternative pre-treatment left cell disruption, which makes is use of mechanical, chemical, or enzymatic techniques (Williams and Laurens, 2010). Mechanical means has been reported in many literatures for algae cell rupture. Frank et al. (2011) in his analysis adopts mechanical method (pressure homogenization process) with electric power requirement of 0.183 kWh/ dry kg at 90% efficiency, and with inflow of 20 wt% algae solids content; while Xu et al. (2011) used bead milling process which demands electric power of 0.139 kWh/kg of algae biomass.

As input to the model, algae biomass with a solid content of 20 wt-% go into the cell disruption unit to be milled at 95% efficiency for 0.139 kWh/kg electrical power used. The slurry from the bead milling unit is heated up to about 95°C to disrupt the cell wall more. To estimate the energy required to heat-up the slurry from temperature of 25°C (within cultivation temperature range) to 95°C, the heat capacity of water (4.1813kJ/kg.°C) is assumed since the slurry contains only 20 wt% solid of algae. On the other hand, the undisrupted algae is assumed to appear in the algae cake after oil extraction and thus subsequently sent to anaerobic digestion.

Hexane Lipid Extraction:

Solvent extraction of lipid from algae has been demonstrated with solvents such as butanol, ethanol, 2-Propanol. Frank et al. (2011) reported experiments conducted by the Aquatic Species Program researcher that made use of these solvents as effective though at the solvent wet biomass ratio of 3:1, and with 15% solid content. However, previous studies have come up with assumptions various that results from mathematical modelling and simulation of range of data to arrive at optimum solvent ratio, extraction time, and energy demand. In this analytic work, the parameters presented by Frank et al. (2011) for wet hexane extraction at 95% extraction efficiency are adopted. The electric power required to separate lipid-rich-hexane and algae residue via disk stack centrifuge is 0.1 kWh/kg oil, while the heat energy required for vaporization of hexane is 1800kJ/kg oil.

4. Biodiesel Production

The lipid extracted are converted to biodiesel through a chemical conversion process called trasesterification. The representation of this process is given by: Triglycerides + Monohydric alcohol = Glycerol + Monoalkyl esters (Biodiesel). This reaction occurs using a base or acid catalyst. For maximum conversion of triglyceride excess of alcohol is required after which the excess is recovered for reused (Drapcho et al., 2008; Demirbas and Demirbas, 2010). Thus, David and Adamu (2009) in their biodiesel production study reported the optimal alcohol : oil ratio of 6:1 used in order to achieve an approximately 98 wt% conversion to biodiesel, using a base catalyst, which yielded a product containing 10 wt% glycerol. In other words it means that every 1kg of biodiesel produced contains 0.1kg of glycerol as the by-product.

In this study, the free fatty acid in the oil is assumed to be 0.05% (Andersson et al., 2011), and thus pretreatment part of the oil is not modelled. Direct based catalysed transesterification route is also adopted since the free fatty acid in the algal oil is less than 5% (Drapcho et al., 2008).

Drapcho et al. (2008) also recorded that biodiesel yield from low free fatty acid oil usually exceed 98%, with base catalyst (NaOH) 1% wt concentration to avoid saponification side reaction. Therefore, 99.8% conversion rate is assumed.

The mixture of biodiesel and glycerol are separated and glycerol sent to anaerobic digester while biodiesel is taken to purification unit, where 97% purity is assumed to be achieved. The biodiesel and alcohol content in glycerol is assumed to be negligible. It is also assumed in this study that biodiesel produced contains 76 wt% carbon (Schlagermann et al., 2012). To determine the specific yield of biodiesel from the algal oil, the fatty acid composition in the oil has been reported in the literature from previous studies. Dapcho et al. (2008) reported fatty acid content in algal oil of different species. Oil from specie of algae is used for analysis in this study. Table 4 shows composition of fatty acid in the algal oil extracted from *Chlorella vulgaris* biomass.

Table 4: Fatty Acids and Compositions in Algal Oil from *Chlorella vulgaris* Dapcho et al. (2008)

| Fatty Acid | Molecular. Formula | Molar mass | Compo sition | Mass (g/mol) |
|------------------------|-----------------------|---------------|-----------------|-----------------|
| | | (g/mol) | (%) | (0) |
| C16:0 (Palmitic acid) | $C_{16}H_{32}O_2$ | 256 | 34 | 87.04 |
| C16:1(Palmitoleic acid | $C_{16}H_{30}O_2$ | 254 | 3 | 7.63 |
| C18:0 (Stearic acid) | $C_{18}H_{36}O_2$ | 284 | 1 | 2.84 |
| C18:1(Oleic acid) | $C_{18}H_{34}O_2$ | 282 | 7 | 19.74 |
| C18:2(Linoleic acid) | $C_{18}H_{32}O_2$ | 280 | 28 | 78.40 |
| C18:3(Linolenic acid) | $C_{18}H_{30}O_2$ | 278 | 26 | 72.28 |
| | | | Total = | 267.93 |

From Table 4, the molecular formula of the algal oil is computed to be 267.93 g/mol.

Energy involvement in biodiesel production is majorly in the purification unit and process flows. In concern of this, a study conducted by Janulis (2004) on energy consumption reduction in biodiesel fuel life cycle reported a total energy input for biodiesel process to be 540 MJ/tonne biodiesel, excluding the energy requirement for alcohol production. In this study energy input of 540kJ/kg biodiesel is assumed.

In this assessment, water balance in the rinsing of biodiesel and the catalyst neutralization are not considered.

5. 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.

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 - 22wt% 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 which the specific methane yield equation was formulated. It is shown below that

$$C_{x}H_{m}O_{n} + \left(x - \frac{m}{4} - \frac{n}{2}\right)H_{2}O \rightarrow \left(\frac{x}{2} + \frac{m}{8} - \frac{n}{4}\right)CH_{4} + \left(\frac{x}{2} - \frac{m}{8} + \frac{n}{4}\right)CO_{2}$$
 3.1

$$y = \frac{\left(\frac{x}{2} + \frac{m}{8} - \frac{n}{4}\right)22.4}{12x + 8 + 16n}$$
 3.2

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 technoeconomic assessment of anaerobic digestion of microalgae conducted by Zamalloa et al. (2010) for three different scenarios reported the assumed value of 0.5m³/kgODM as the biogas yield. A much lower values of 0.3m³/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% CO₂.

The specific theoretical methane yield for glycerol and methanol are estimated from Equation 3.2

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).

The measure of carbon and nitrogen in organic substrates is characterized by carbon: 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 NH₃ 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°C, with C/N ratios of 5.4–24.17 and loading density of 5–50 kg ODM/m³ digester volume, and therefore, the optimum C/N ratio was found to be 12.44 when co-digested with glycerol.

Since the feedstocks to AD will include both algae biomass and waste paper in this study, C/N ratio of 15 will be investigated in 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 0.452m³/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.

6. Biogas Clean Up

Crude biogas from anaerobic digestion contains components or impurities, such as CO_2 , H_2S , NH₃, H₂, 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/m³ 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/m³ of energy will be assumed since such purity may not be needed for CHP.

7. Nutrient Recovery and Recycling 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). The liquid part of the postdigestion 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 integrated system as shown in figure 4. 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). Not all these C from cultivation pond go into digester as certain amount of lipid is extracted from the algae biomass from which biodiesel is produced. The total C in digester is accounted for through the algae residues after lipid extraction, glycerol, fraction of 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 as shown in figure 5. In this case, N and P are assumed to be absent in the extracted oil, and negligible loss of N and P is also assumed during the integrated biofuels production. 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 NH₃ when liquid digestate is returned into the cultivation pond. And thus, only 75% N is recovered to algae culture.



Figure 5: Nitrogen and Phosphorus 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 NH₃. Similarly, 50% P is assumed makes its way to solid digested.

8. Combine Heat and Power (CHP) System

The heat and electricity production on-site through CHP system is utilized by various process units in the integrated algae-biofuel production system. With the CHP system the importation of power and fossil energy demand will be reduced as heat will be generated from the methane produced. Conversion efficiency is factor on the amount of energy derived.

$$\eta = \frac{Q_E + Q_{Th}}{Q_{Fuel}}$$

Where η is the efficiency, Q_E is the useful electrical power output, Q_{Th} is the useful heat energy, and Q_{Fuel} is the total fuel energy input. 85% of CHP efficiency is assumed with 50% heat and 35% electricity. The lower heating value of methane is 50 MJ/kg (Staffell, 2011).

Energy Balance

To carry out evaluation of energy balance of the integrated system, it is important to examine the energy input throughout the process, as illustrated in Figure 6. For energy balance evaluation in this study, algae cultivation phase and algae biomass transformation to biofuel production will be considered, as indicated by dotted lines in Figure 6. In addition, the energy contents (lower heating values, LHV) of the input materials will be considered as an approach to energy balance analysis, only to analyse the integrated system alone. The study does not intend to consider the life cycle energy consumed for producing each of the input materials. In other words, chemical inputs with no LHV are not considered.



Figure 6: Flow Diagram Showing Various Inputs into the System for Energy Balance Evaluation

In cultivation stage, nutrients and electricity are the main energy input, and for each of these the amount used and the energy coefficients is evaluated. Nitrogen (N) is assumed to be provided through KNO₃; and Phosphorus (P) is provided through P₂O₅ (Razon and Tan, 2011). The CO_2 and solar energy needs are considered to be freely supplied, and thus their energy balance is not considered. In the biodiesel unit, the major energy input is from electricity and chemical consumables (methanol and NaOH catalyst). Algae harvesting and biogas production units require electricity and thermal energy inputs, while lipid extraction requires electricity input. And finally, the energy output of the product fuels are estimated through the volume produced and their energy density.

The LHV of chemical consumable and materials are

methanol, 20.09 MJ/kg (Boundy et al., 2011); and waste paper 17MJ/kg (BEC, 2013; Kofman, 2010).

The Net Calorific Value of dry wood is assumed for waste paper.

Lower heating values for product materials in the integrated system includes algae biomass, 30 MJ/kgDM (Schlagermann et al., 2012); algal oil, 38.2 MJ/kg (Schlagermann et al., 2012); algae oil extracted residue, 23 MJ/kgDM (Schlagermann et al., 2012); crude glycerol, 25.30MJ/kg (Trigo et al., 2013); Biodiesel , 3753MJ/kg (Boundy et al., 2011); and methane is 50 MJ/kg (Staffell, 2011).

In a separate analysis, energy inputs of nutrients and NaOH based on life cycle energy consumed for their production is evaluated; only to make comparisons with the main approach of LHV of the input materials. The life cycle energy required to produce a unit mass of the nutrients and NaOH are NaOH, 18.25MJ/kg NaOH (Pleanjai and Gheewala, 2009); KNO₃, 5.96 MJ/kg KNO₃ (Kongshaug, 1998); and P₂O₅, 15.80 MJ/kg (CROPGEN, 2004).

3. Results

The result herein represents the flow of material and energy, amount of biofuels produced, the energy performance, and CO_2 and nutrient recovered of the integrated process systems of algae cultivation and anaerobic digestion.

Algae Production

Algae production involves two major procedures: cultivation process and harvesting process. Based on the basic assumptions outlined in sections 1 and 2 of methodology, the model for the potential algae biomass production gave the results as obtainable in Table 5. The Table 5 results presented here includes the amount of algae biomass cultivated and associated nutrient demands, and amount of processed algae biomass at harvesting stage, where it is processed to an acceptable level for further processes to biofuels production.

| Table 5: Algae Biomass Pr | oduction and Nutrients |
|---------------------------|------------------------|
|---------------------------|------------------------|

| Parameter | | | τ | Jnit | |
|--|------------|------|------|------|------|
| 1. Algae Cultivation | | | | | |
| Production rate (kg/day) | 101.1 8 | | | | |
| Algae density (kg/m ³) | 0.125 | | | | |
| Volume of algae (m ³ /day) | 809.4 | | | | |
| water evaporation (m ³ /m ²) | 16.19 | | | | |
| Pond water leakage (m ³ /m ²) | 4.45 | | | | |
| Nutrient composition in the | C | Н | 0 | Ν | Р |
| Produced algae (kg) | 54.43 | 7.89 | 31.4 | 6.1 | 1.35 |
| CO2 Required (kg CO2/day) | 199.5 | | | | |
| 2. <u>Harvesting</u> | | | | | |
| Mass of algae not retained: | | | | | |
| Gravity Thickener(kg) | 4.55 | | | | |
| Centrifugation (kg) | 4.33 | | | | |
| Algae to biofuel (kg/day) | 82.18 | | | | |

Composition from Pond.

Anaerobic Digestion (AD)

In the anaerobic digestion system, biogas is produced, and CO₂ and nutrients are recovered and recycled, and methane is taken to CHP system for heat and electricity generation. Substrates to AD are sourced from the harvested algae biomass, algae oil extracted residues, glycerol (by-product in biodiesel production), and waste paper. The summary of result in AD system follows the basic assumptions outlined in sections 3 to 8 of methodology. The result presented under this section is divided into two categories: the process material flow, and the process energy flow. Table 6 shows the process material flow, while Figures 7, 8, 9 and 10 graphically represent the process energy performance in the integrated system. The biofuels produced, nutrient recovered and waste paper demand are indicated in Table 6

| Frac | ctions of | of Alg | ae Bio | mass t | o AD | - |
|------------------------------|-----------|----------|----------|---------|-----------|--------|
| | | Fraction | of Algae | Biomass | to AD (%) |) |
| | Base | 0 | 20 | 50 | 80 | 100 |
| <u>Anaerobic</u> | | | | | | |
| Digestion | | | | | | |
| CH_4 | 0 | 30.80 | 32.98 | 36.25 | 39.53 | 41.71 |
| Production (m ³) | | | | | | |
| Waste paper | 0 | 22.60 | 21.75 | 20.47 | 19.21 | 18.36 |
| required (kg) | | | | | | |
| <u>Lipid</u> | | | | | | |
| Extraction Unit | | | | | | |
| Lipid | 22.25 | 22.25 | 17.80 | 11.13 | 4.45 | 0 |
| extracted (kg) | | | | | | |
| Algae residue | 54.65 | 54.65 | 43.72 | 27.33 | 10.93 | 0 |
| (kg) | | | | | | |
| <u>Biodiesel Unit</u> | | | | | | |
| Biodiesel | 25.30 | 25.30 | 20.24 | 12.65 | 5.06 | 0 |
| production (L) | | | | | | |
| Glycerol | 7.62 | 7.62 | 6.10 | 3.81 | 1.52 | 0 |
| production (m ³) | | | | | | |
| Methanol | 7.96 | 7.96 | 6.37 | 3.98 | 1.59 | 0 |
| consumption | | | | | | |
| (m ³) | | | | | | |
| NaOH | 0.22 | 0.22 | 0.18 | 0.11 | 0.04 | 0 |
| catalyst used | | | | | | |
| (kg) | | | | | | |
| Nutrient and | | | | | | |
| <u>CO2</u> recovered | | | | | | |
| N (kg) | 0 | 4.12 | 4.12 | 4.12 | 4.12 | 4.12 |
| P (kg) | 0 | 0.64 | 0.64 | 0.64 | 0.64 | 0.64 |
| $CO_{2}(kg)$ | 0 | 82.05 | 87.86 | 96 58 | 105 28 | 111.00 |

Table 6: Process Material Flow on Varying











Figure 9: Comparison of the Overall Energy Input and Output in the Integrated System



Figure 10: On-site Electricity and Heat Demand and Supply

Waste Paper Input to Anaerobic Digestion

In AD, optimum biogas yield was reported to occur when C/N ratio is between 15 - 30 (see methodology, section 5). The analysis in this study is based on C/N ratio 15, but it tries to increase the ratio to 25 to see its implications on the total process energy, nutrient and CO₂ recovery. Increase in C/N ratio suggests more input of waste paper, as a source used to boost the carbon content in AD. The outcome of this is summarised in Table 7, while Figure 11 compares the on-site energy demand and supply of the two ratios, with 50% algae biomass fraction to AD.

Table 7: Total Energy Flow, Waste Paper Requirement, and Nutrient and CO_2 Recovery with 50% Algae Biomass to AD at C/N: 15 and C/N: 25

| | AD C/N Ratio | | | |
|-------------------------------|--------------|----------|--|--|
| - | C/N = 15 | C/N = 25 | | |
| Total Energy input (MJ) | 932.20 | 1460.23 | | |
| Total Energy output (MJ) | 1606.64 | 1913.60 | | |
| Waste paper required (kg) | 20.48 | 46.80 | | |
| Nitrogen recovered (%) | 64.8 | 64.8 | | |
| Phosphorus recovered (%) | 45 | 45 | | |
| CO ₂ recovered (%) | 48.39 | 60.81 | | |



Figure 11: Comparison of Electricity – Heat Demand and Supply for On-site Use for AD C/N ratio 15 and 25 at 50% Algae Biomass to AD

Sensitivity Analysis

Table 8 presents a summary of result of the

production output by changing oil content

parameter of the algae biomass.

| Table 8: Production Output at Vary | /ing |
|------------------------------------|------|
| Percentage Lipid Content | |

| | Algae Lipid Content | | | | |
|--------------------|---------------------|---------|---------|--|--|
| - | 20% | 30% | 40% | | |
| Methane production | 36.50 | 36.25 | 36.01 | | |
| (m ³) | | | | | |
| Biodiesel | 8.43 | 12.65 | 16.87 | | |
| production (L) | | | | | |
| Energy input (MJ) | 883.15 | 932.20 | 981.26 | | |
| Energy output (MJ) | 1477.98 | 1606.64 | 1735.30 | | |
| CO2 recovered (kg) | 97.22 | 96.58 | 95.92 | | |

Energy from Process Input Materials

The process input materials into the integrated process system includes consumables such as methanol, NaOH, KNO₃ (for nitrogen input), and P_2O_5 (for phosphorus input). Basically in this study, the energy analysis of these materials has been based on consideration of their energy

content (LHV), however, it also seeks to investigate the energy input of these materials (that do not have LHV data) based on the life cycle energy consumption for their production. The materials that with no LHV includes: NaOH, KNO₃ and P₂O₅. Figure 12 shows the energy inputs of the materials, comparing the two approaches when 50% of algae biomass is sent to AD.



Figure 12: The Integrated System Energy Demand Based on the Energy Content of Input Material and Life Cycle Energy Consumption for their Production

4. Discussions of Results

In the process, a basic scale was used for the assessment; that is algae production on the basis of 1 acre open pond per day.

Algae Production

The starting point is the cultivation and harvesting of algae. The output from this point is represented in Table 5. The algae production per day is 101.18kg/day. Not all of this production is sent to biofuel production as some are lost in the

process of harvesting, particularly bioflocculation. Although 4.55kg algae and 4.33kg algae are losses of algae in gravity thickener and centrifugation harvesting stages respectively but are recovered to be processed to biofuels. The bulk output of dewatered algae biomass with 20 wt% total solid from the centrifugation stage is 82.18kg, is sent wholly or in fractions to anaerobic digestion to produce biogas while some fractions is sent to lipid extraction unit to further process to biodiesel production.

Water keeps escaping from the pond through evaporation and pond leaks, $16.19m^3/m^2$ and $4.45m^3/m^2$ respectively, and needs to be replaced by same volume to maintain the volume of water in the pond daily.

The nutrient required for the quantity of algae cultivated are 54.43kgC, 7.89kgH, 31.40kgO, 6.11kgN, and 1.35kgP representing Carbon, Hydrogen, Oxygen, Nitrogen and Phosphorus respectively. CO_2 being the only source to meeting the carbon need has its demand put at 199.56kg CO_2 .

Anaerobic Digestion (AD)

The substrates to AD are sourced from the harvested algae biomass, algae oil extracted residues, glycerol (by-product in biodiesel production), and waste paper. The assessment considers some percentage of harvested algae biomass into the AD while the remainder goes to oil extraction to biodiesel production. Table 6 represents the material flow in the process of transforming algae into biofuels, and feedstocks feed to the AD and the nutrient recovery. The 'base case' here means biodiesel production only, without integration with AD. In this case, there is no nutrient and CO_2 recovery as the system is not integrated with AD through which the nutrients and CO_2 are sourced.

Distribution of harvested algae biomass to AD is varied in the order of 0%, 20%, 50%, 80% and 100% of the harvested algae from centrifugation dewatering system. The most important issue in the model is the amount of biodiesel produced from the remainder of the algae biomass going to lipid extraction. When algae to AD is 0% it means that the entire harvested 82.18kg algae goes into biodiesel production, which yields 22.25L (21.86kg biodiesel). This keeps decreasing as the algae biomass ratio to extraction reduces, while the methane yield increases to the highest of 41.71m³(27.53kgCH₄) when 100% of algae biomass is fed to AD. This trend is further illustrated in Figure 13.



Figure 13: Methane and Biodiesel Yield in the Integrated System

The waste paper required to boost the carbon content in the AD keeps decreasing with algae biomass increment to AD. This is expected of it since more carbon move into AD with the algae biomass, and small amount of carbon is given to biodiesel production (from the amount of algae biomass sent to oil extraction). Nutrient recovered, 4.12kgN and 0.64kgP, remains unchanged irrespective of algae biomass fed to AD. Of course, this is expected to be so because it has earlier been assumed that Nitrogen and Phosphorus are not part of the constituents of biodiesel. However, it is observed that more CO_2 is recovered when more CH₄ is produced, since CO₂ is produced along with CH₄ as biogas from AD and from combustion of CH₄ in CHP system.

Figure 7 represents the energy input in the integrated system for different processing units. In the overall, the energy input in the option of 0% algae to AD requires the most energy input, owing to the fact that the entire biomass is processed to biodiesel; the higher the raw material to process, the more the energy requirement. Drying is a form of pre-treatment given to algae biomass to aid in lipid extraction (Williams and Laurens, 2010), consequently, this makes harvesting usually an energy intensive drying process contributes enormous energy to energy requirements (Lardon et al., 2009), but in this study the wet extraction was adopted which avoids drying process after centrifugation and

thus reduces the net energy input grately. Energy requirement for lipid extraction and subsequent biodiesel production also varies with the amount of algae biomass feed to extraction unit. Cell disruption and heating are another form of algae pre-treatment which consumes quite a lot of energy, but this is helpful as it aids lipid extraction as well (Andersson, 2011; Lardon et al., 2009).

Looking at the whole processing units, the highest energy demand in the entire integrated system comes from AD unit. The reason is the $(50^{\circ}C \text{ to})$ 55°C) regimes thermophilic of bioconversion assumed in the digester for biogas production (Vindis et al., 2009), and the energy input from the waste paper. Waste paper energy input appears to be a major challenge in this integrated system and alarming (37% of total energy input); 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.

However, the net energy input to the system from cultivation and harvesting does not change with varying algae biomass input to AD.

Figure 8 represents the energy output through production of methane and biodiesel. The energy

content of product and its quantity determines the amount of energy output, so, the amount of biodiesel and methane produced in Table 6 is proportional to energy output. However, the methane produced is directed to CHP for heat and power generation. The Co-production of biodiesel and methane yield a higher net energy than when the algae biomass is to produce only either biodiesel or biogas. This finding agrees with Harun et al. (2011) where energy output of various types of biofuels from a specie of microalgae reveals: the energy output for combined production of biogas and biodiesel (16.4MJ/kgAlgae) is higher than energy output for producing either methane (14.04MJ/kgAlgae) or biodiesel (6.6MJ/kgAlgae. Although it was not investigated further by Harun et al. to determine the ratios of algae biomass feeds to anaerobic digestion and biodiesel production and a more analysis into the energy burdens associated with these production outputs, which this work has achieved.

Figure 9 shows the overall energy input and output already discussed in Figure 7 and 8 above.

In Figure 10, the energy demand and supply for on-site use is illustrated. Base case has no integration with AD, and so, methane is not produced to meet its energy demand. In the entire integrated system of various options (algae fractions to AD) the heat energy requirement is met by the methane produced on site. For electricity, there is deficit in options 0% and 20% algae biomass to AD, while surplus in options 50%, 80% and 100% algae biomass to AD.

Waste Paper Input to AD

Table 7 presents the integrated system performance in terms of total energy and nutrient and CO₂ recovery as comparison between AD C/N ratios of 15 and 25 at 50% algae biomass fraction to AD. As explained earlier in section 4.2.1 of Chapter 4, the analysis in this study is based on C/N ratio 15. Optimum ratio is between 15 to 30. Waste paper is used to increase the carbon content of substrates in AD; therefore, increasing AD C/N ratio to 25 means increase in waste paper input to AD as well. From Table 7, the total energy input increases to 14.60.23MJ, which is 56.64% increment, while the total energy output increases to 1913.60MJ, which is 19.0% increment. Waste paper also increases to 46.80kg which is 128.52% increment. Similarly, CO₂ recovered increases from 48.39% to 60.81% but, Nitrogen and Phosphorus are not affected by variations of C/N ratio or amount of waste paper and algae biomass to AD as they do not form part of the products of energy, however though, in any case, 64.8% of N and 45% of P are recovered for utilization in the pond. It is noted that biogas yield increases with waste paper input to AD. Using AD C/N ratio of 25 places great energy burden on the system, and low energy output. Therefore, it is observed here that waste paper with high carbon content may not necessarily suggest a better methane output that will enhance CO₂ 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.

Figure 11 shows the electricity – heat demand and supply for on- site use for AD C/N ratios 15 and 25 at 50% algae biomass to AD. For each scenario (C/N 15 and 25) heat demand is adequately supplied for on-site use. Electricity demand on-site is satisfied with surplus for both operations at C/N 15 and C/N 25 standing at 3.50MJ and 49.49MJ respectively.

Sensitivity Analysis

Table 8 shows the output of the sensitivity analysis conducted by varying the lipid composition of the microalgae at 50% of algae biomass fed to AD. It is observed that lipid composition does not affect significantly the general energy performance and product, except for biodiesel which changes by 50%. The deficit in CO_2 encountered is not resolved even at higher algal lipid contents.

Energy from Process Input Materials

In Figure 12, the system energy input computation from the input materials is compared between two methods: energy content of input materials, and life cycle energy requirement for production of the input materials. The life cycle approach has a higher energy input, especially in cultivation (from KNO₃ and P_3O_5 input) and biodiesel production (from NaOH input). The life cycle energy energy input for the unit mass production of KNO₃, P_3O_5 and NaOH are 262.30MJ, 49.14MJ and 2.03MJ respectively for 50% algae biomass sent to AD.

In the long run, from the results obtained from this assessment, it can be summarised that energy is generated which can be used on-site for algae cultivation. harvesting, lipid extraction, transesterification process and AD system, and the excess sold to grid - (electricity excess in the range of 1.65% to 35.90%, pending on the amount of algae biomass feeds to AD). The CO₂ is in deficit which needs to be supplied through an alternative means within the system or externally; 41.08% - 55.67% CO₂ can be recovered in the integrated system. Nutrients recovered are 64.8% N and 45%P (nutrient balance shown in Figure 15) from anaerobic digestion effluents, and it is not enough to provide the cultivation requirement, thus, cultivation with waste water is suggested. Waste paper used to raise the C/N ratio of substrates in AD comes with huge energy burden which is responsible for 37% of total energy input. Using the whole harvested algae biomass to produce either biodiesel or methane is not encouraging in terms of energy output, particularly biodiesel, which is quite lower than methane. Rather, combined biodiesel and methane production yields higher energy output. However, it is found that the highest energy output from combined production comes from 100% harvested algae biomass be used for biodiesel production, while the oil extracted algae residue and glycerol are channelled as a feed to AD, with addition of waste paper to meet the C/N ratio requirement in

AD (process flow illustrated in Figure 14). On the other way, methane production only, without biodiesel, is favourably disposed to in terms of electricity and CO_2 savings. Lastly, it is found out from this study that the feasible technological path of integrated anaerobic digestion and algae cultivation for biofuel production is in the simultaneous combined production of methane and biodiesel and electricity; and this promises viable biorefinery algae biofuels production.



Figure 14: Process Flow Diagram for 0% Algae Biomass Fraction to AD Indicating the Material Mass Flows and their Energy Content



5. Conclusions

A study of an assessment of systems integrating anaerobic digestion (AD) and algae cultivation using AD effluents has been carried out. The possible alternative 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 integrated system by varying input parameters.

In the assessment, the effluents from AD still contain some vital nutrients which are recovered to be fed to algae cultivation pond (raceway). However, not all are recovered as some are lost to the solid effluent of AD. Therefore, cultivating the algae using waste water could supply the needed nutrients.

The algae biomass cultivated was meant for different biofuels processing paths: production of methane from AD and electricity generation, biodiesel production and electricity generation, and combined production of methane and biodiesel and electricity production. The energy generated is in surplus after supply for on-site use in algae cultivation, harvesting, lipid extraction, transesterification process and AD system. The surplus electricity is an asset to the biorefinery; it can be sold to national grid.

It is found from this study that the highest net energy output is achieved when the whole harvested algae biomass is taken to extraction unit to produce biodiesel while the algae oil extracted residues and glycerol are feeds to AD to produce methane. Although, in this case, high carbon content material such as waste paper added to AD to boost the C/N ratio. Addition of waste paper comes with great challenge of huge amount of energy input. Therefore there is need for Research and Development in algae biofuels to investigate a suitable material of low energy input for co-digestion while optimum C/N ratio is sustained.

 CO_2 recovered from AD and CHP is not sufficient for algae cultivation; there is need for supply through external means or employing larger volume of waste papers in the digester, but the C/N limit must not be exceeded.

Finally, it can be stated here that the integrated system of processing path of algae cultivation, combined production of methane and biodiesel, and electricity production promises a viable biorefinery algae biofuels production. But in this case the 100% algae biomass is directed to biodiesel production while the by-products from biodiesel production processes are directed to biogas production.

6. Possible Future Work

The suggested possible future work in relation to this study would focus on the following:

 A thorough investigation on a better material to be used for co-digestion; a material with high specific methane yield and low nitrogen content, so as to increase the methane output which would neutralize the deficit of CO₂.

- 2. 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. The biomass includes algae cultivation for feed to biogas and biodiesel production, and wood cultivation for use as co-digestion in AD.
- 3. Although researches have approved cultivation of algae in waste water for nutrient utilization, there is also need to further reduce the energy consumption in the cultivation and harvesting stages, so that algal biodiesel production will be competitive with other oil sourced biodiesel.
- 3. A detailed economic analysis for the technological route recommended in this study should be carried out.

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